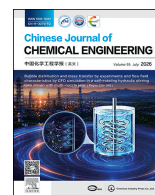




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Full Length Article

MnO nanoflower network anchored on lamellar carbon: A high-performance cathode for aqueous zinc-ion batteries

Menghua Li^{1,*}, Xinzheng Liu¹, Changhui Sun¹, Xiaorong Cao¹, Qiqi Han¹, Yiye Kong¹, Caixia Xu²¹ Department of Chemistry, Qilu Normal University, Jinan 250011, China² Institute for Advanced Interdisciplinary Research, University of Jinan, Jinan 250022, China

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ABSTRACT

Aqueous zinc-ion batteries (AZIBs) have emerged as a promising alternative in the field of energy storage due to their lower cost, enhanced safety, and environmental friendliness. However, the development of efficient and stable cathode materials remains a significant challenge. In this work, the MnO nanoflower network anchored on a two-dimensional lamellar carbon (MnO NN/LC) was synthesized via metal-organic framework-derived method. The lamellar carbon serving as the 2D conductive matrix facilitates faster ion diffusion and electron transfer, resulting in superior zinc storage performance. MnO NN/LC displays larger reversible capacity, superior rate capability, and much higher cycling stability compared to traditional bulky MnO/C (B-MnO/C) material. Especially, the MnO NN/LC demonstrates long-term cycling stability with the retained capacity as high as $104.2 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ after 1400 cycles at $1 \text{ A} \cdot \text{g}^{-1}$, presenting substantial enhancement over the capacity of $75.7 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ for B-MnO/C. Ex-situ experiments indicate that MnO during the zinc ion storage is electrochemically oxidized into MnO_2 species, and actually facilitates the intercalation/deintercalation of H^+ and Zn^{2+} . These findings underscore the potential of the MnO NN/LC composite as a promising cathode material for AZIBs.

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1. Introduction

The growing scarcity and overconsumption of traditional fossil fuels have accelerated the development of alternative energy technologies, particularly the battery systems for energy storage [1–4]. Batteries play a crucial role in enhancing the reliability and efficiency of renewable energy sources, such as solar and wind power, by storing excess energy and releasing it as demand fluctuates [5]. Ongoing innovations in battery technology have been focusing on improvements in capacity, durability, and cost-effectiveness [6]. Lithium-ion batteries as the currently most popular device still face significant challenges, including resource scarcity, flammability, and environmental pollution [7–9]. Consequently, it is important to develop novel battery technologies that address security and economic concerns [10].

Aqueous zinc-ion batteries (AZIBs) have emerged as a viable alternative, offering a superior safety profile due to their use of a

water-based, non-flammable electrolyte. AZIBs also have extra advantages with high theoretical capacity of zinc metal (approximately $820 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$), low anode potential, as well as the abundance of zinc and the cost-effectiveness [11–14]. The development of high-performance cathode materials is paramount for advancing AZIBs, as these materials largely determine the capacity, operating voltage, and cycling stability by facilitating the reversible insertion and extraction of Zn^{2+} ions [15,16]. A variety of cathode materials have been explored for AIBs, in which manganese-based oxides, such as MnO, Mn_3O_4 , Mn_2O_3 , and MnO_2 , have gained particular attention due to their high operating voltage, substantial capacity, low cost, and environmental friendliness [17–23]. Recent studies indicate that MnO possesses favorable performance in zinc storage through *in-situ* reversible electrochemical oxidation and reduction process [20,21]. However, some issues need resolved, such as significant volume expansion during the repeated intercalation and deintercalation of Zn^{2+} , manganese dissolution during prolonged cycling, and sluggish kinetics owing to low conductivity.

At present, considerable research efforts have focused on mitigating these challenges through various strategies, including

* Corresponding author.

E-mail address: limenghua668@126.com (M. Li).

nanostructure tailoring, composites construction with conductive materials, and interlayer engineering [19–23]. For instance, Zhu *et al.* [15] employed an *in-situ* electrochemical method to activate MnO, generating Mn defects during the charging process to create a highly electrochemically active cathode for AZIBs. Similarly, Yu *et al.* [22] reported the preparation of a nitrogen-doped MnO cathode with abundant oxygen vacancies, which demonstrated exceptional rate performance, cycling durability, and high energy density for zinc ion storage. These advances have stimulated further exploration of MnO-based cathodes by engineering their structure and composition. Notably, the introduction of a two-dimensional (2D) structure can offer unique advantages for facilitating efficient charge transfer and significantly shortening the ion diffusion pathways within the solid electrode material, ultimately leading to rapid ionic transport and enhanced kinetics [24,25]. Therefore, integrating manganese oxide materials into a 2D structure represents a promising strategy for achieving high performance for AZIBs. For example, Zhu *et al.* [25] synthesized 2D MnO supported on carbon composite that effectively promoted reaction dynamics and alleviated volume expansion during long-term cycling, achieving large capacity retention after long term cycles at $1.0 \text{ A} \cdot \text{g}^{-1}$.

Inspired by these advancements, we aim to design a MnO nanoflower network anchored on a 2D lamellar carbon through a metal-organic framework (MOF)-derived method [25,26]. The resulting MnO NN/LC composite exhibits unique zinc ion storage performance characterized by a larger reversible capacity, enhanced cycling stability, and superior rate capability when compared to the bulky MnO/C (B-MnO/C) composite. The 2D lamellar carbon serves as a highly conductive matrix, while the MnO flower-like network provides a robust framework that facilitates the diffusion of Zn^{2+} ions and charge transfer. Ex-situ measurements disclose that MnO is electrochemically oxidized into MnO_2 species during the charge and discharge process, which actually facilitates the intercalation/deintercalation of H^+ and Zn^{2+} . The as-made MnO NN/LC composite demonstrates excellent zinc storage properties, showcasing remarkable rate capability, cycling stability, and improved electrochemical dynamics.

2. Experimental

2.1. Preparation of MnO NN/LC and B-MnO/C materials

All reagents were procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai) and utilized without further purification. Initially, 5.5 mmol of sodium benzoate and 7.8 mmol of manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were added to a 100 ml beaker containing 60 ml of *N,N*-dimethylformamide (DMF, 99.8%). The resulting mixture was subjected to continuous stirring in a water bath maintained at 26°C for a duration of 12 h. Subsequently, 11 mmol of benzoic acid was introduced into the system, and stirring was continued for an additional hour. Following this, the mixture was transferred to a 100 ml Teflon-lined reactor and placed in an oven set to 180°C for 10 h. After cooling to room temperature, the resultant white product was collected via centrifugation and thoroughly washed three times with DMF and absolute alcohol. The collected white precursor was then dried for 12 h in a vacuum oven at 80°C .

In the subsequent step, the products were transferred to a porcelain boat and subjected to heating from room temperature to 600°C at a rate of $2^\circ\text{C} \cdot \text{min}^{-1}$ in a tube furnace under a nitrogen atmosphere for 2 h. The resulting black product was again washed three times with DMF and absolute alcohol, followed by drying at 80°C for 12 h. The B-MnO/C sample was prepared as a control

using the same procedure, with the exception that sodium benzoate was omitted from the reaction mixture.

2.2. Materials characterization

The phase structure and composition of the samples were investigated using powder X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer, employing Cu-K_α radiation ($\lambda = 0.15481 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific ESCALAB 250Xi instrument with an Al K_α source, utilizing the C 1s peak at 284.6 eV as a reference for analyzing the surface elemental states. Additionally, laser confocal Raman spectroscopy was conducted using a Horiba Scientific LabRAM HR Evolution system with 532 nm excitation to assess the vibrational modes of the materials. The detailed microstructures of the samples were characterized using scanning electron microscopy (SEM) on a JEOL JSM-6700 and transmission electron microscopy (TEM) using a JEOL JEM-2100. The surface area and pore size of all materials were measured using the Brunauere-Emmette-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods by adsorption/desorption under nitrogen at 200°C with a high-performance adsorption analyzer (Micromeritics 3 Flex, Micromeritics Instrument Corporation, United States).

2.3. Electrochemical tests

The electrochemical performance of the samples was evaluated using 2032 coin-type cells, with zinc foil serving as the anode. The working electrode was constructed by dispersing a homogeneous mixture comprising 70% (mass) active material, 20% (mass) conductive carbon (Super P), and 10% (mass) polyvinylidene fluoride (PVDF) into *N*-methylpyrrolidone (NMP). Each electrode mass is almost the same with approximately $1.8 \text{ mg} \cdot \text{cm}^{-2}$. This slurry was subsequently coated onto titanium foil and dried at 60°C to form the electrode.

For the electrolyte, a mixed aqueous solution of $2 \text{ mol} \cdot \text{L}^{-1} \text{ ZnSO}_4$ and $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ MnSO}_4$ was employed. Galvanostatic charge/discharge (GCD) tests were conducted using a Neware battery testing system, with the voltage range set between 0.8 and 1.8 V. Additionally, cyclic voltammetry (CV) measurements were performed on a CHI 760E electrochemical workstation, employing a scanning rate varying from 0.1 to $2.0 \text{ mV} \cdot \text{s}^{-1}$. Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 10^5 to 10^{-2} Hz , providing insights into the charge transfer resistance and overall electrochemical dynamics of the assembled cells.

3. Results and Discussions

The MnO NN/LC composite was synthesized through a two-step process. Initially, sodium benzoate was incorporated during the preparation to regulate the formation of the 2D lamellar structure of the Mn-MOF precursor. Such the structure was well preserved upon calcination in a nitrogen atmosphere, resulting in MnO interconnected nanoflowers network anchored on carbon layers. For comparison, the B-MnO/C composite was synthesized without the addition of sodium benzoate to elucidate the impact of microstructure on zinc storage performance.

The crystal phases of both products were characterized using XRD technique. As illustrated in Fig. 1(a), both samples exhibit similar diffraction peaks. The broad peak at approximately 25° corresponds to carbon species, while the distinct diffraction peaks at 34.9° , 40.5° , 58.7° , 70.2° , 73.8° , and 87.8° can be attributed to the MnO phase (JCPDS No. 07-0230) [27]. This observation confirms the formation of the MnO/C composite. XPS was further employed to analyze the surface chemical valence states of the MnO NN/LC

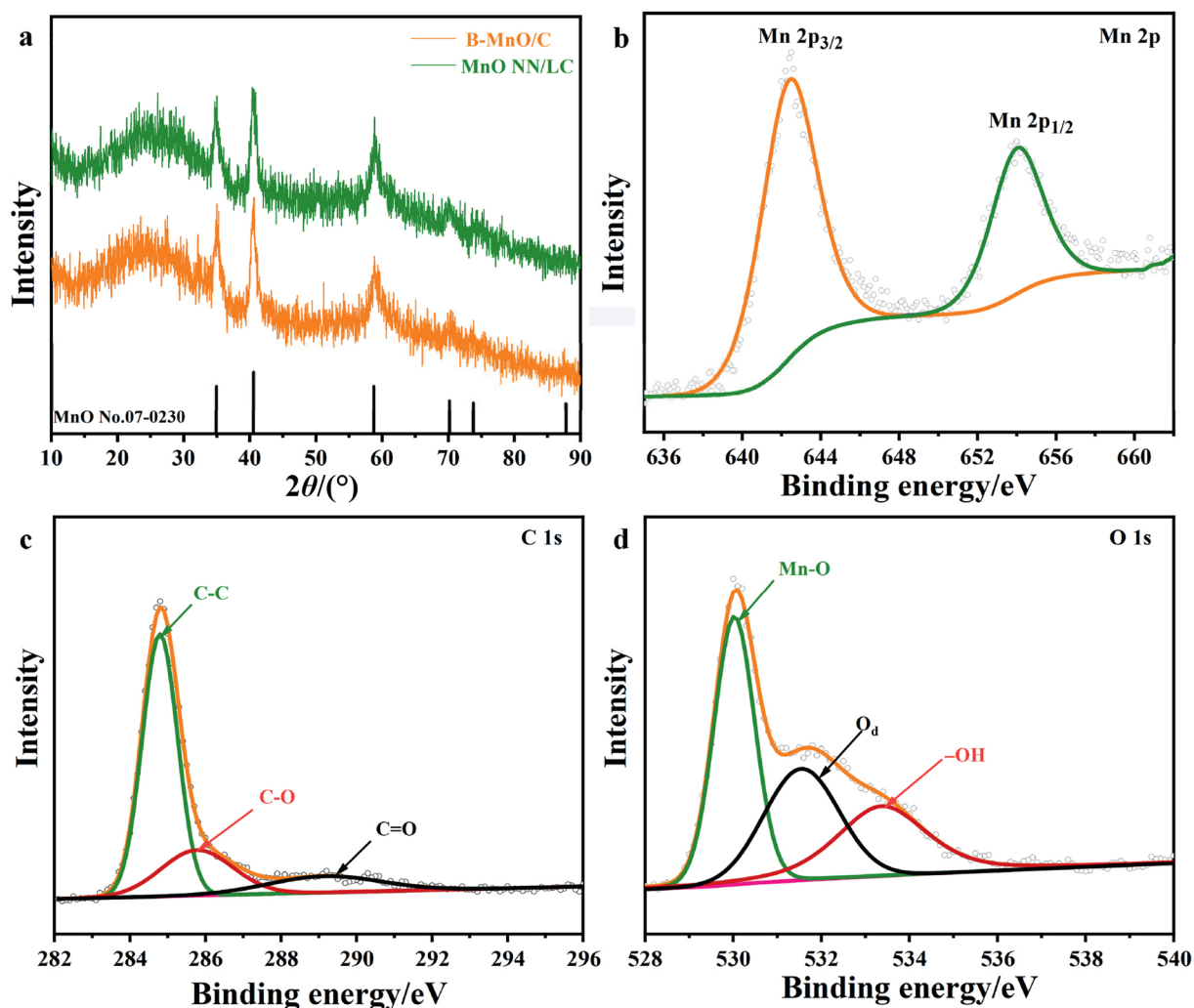


Fig. 1. (a) XRD pattern of MnO NN/LC and B-MnO/C materials, XPS data of (b) Mn 2p, (c) C 1s, and (d) O 1s for the MnO NN/LC.

composite. The Mn 2p spectra Fig. 1(b) reveal two peaks at 642.5 and 654.2 eV, corresponding to the 2p_{3/2} and 2p_{1/2} Mn²⁺ states in MnO [24], respectively. In the high-resolution C 1s spectrum Fig. 1(c), three peaks at 284.8, 285.8, and 289.3 eV are assigned to C—C, C—O, and C=O bonding coming from the carbon support [28], respectively. Additionally, the O 1s spectrum Fig. 1(d) is divided into three peaks, which correspond to anhydrous manganese oxides (Mn—O—Mn bond), defective oxygen, and hydroxyl group sites (H—O—H bond) [29]. Collectively, these results affirm the scalable fabrication of the MnO/C composite utilizing a MOF-based approach.

SEM was employed to observe the morphological formation and evolution for both the MnO NN/LC and B-MnO/C composites. Fig. 2(a) depicts the microstructure of the bulky Mn-MOF precursor (B-Mn-MOF), characterized by a particle size primarily ranging from 15 to 30 μm . This diamond cubic morphology was well retained after calcinating the precursor Fig. 2(b). In contrast, the introduction of sodium benzoate facilitated the formation of a stacked lamellar structure in the L-Mn-MOF precursor Fig. 2(c). The resulting MnO NN/LC composite, obtained after calcination, also preserved the layered structure as shown in Fig. 2(d). By careful observations, it can be found that a thin layer of a MnO network with an interconnected porous structure anchored on the carbon support. By comparison, sodium benzoate plays important role for the formation of the 2D layered MOF precursor through

the synergistic effects of coordination competition and steric hindrance. The benzoate ions dissociated from sodium benzoate can compete with terephthalic acid for coordination sites with manganese ions [30]. Meanwhile, the phenyl groups in the benzoate ions introduce steric hindrance, inhibiting the axial growth of MOF crystal nuclei and inducing preferential lateral growth of the crystals, thereby promoting the formation of a 2D layered structure [30].

TEM was conducted to investigate the detailed structure of the MnO NN/LC composite. As shown in Fig. 3(a) & (b), the transparent framework implied the formation of one thin carbon sheet, where a layer of flower-like network structures covered on the carbon surface. From Fig. 3(b), it can be clearly found that there are some scattered nanoflowers over the marginal region. From high-resolution TEM (HRTEM) image Fig. 3(c), many ordered fringes distinguished with a lattice spacing calculating to be 0.222 nm, which aligns well with the (200) plane of MnO species [29]. EDS analysis confirms the composition of the freshly synthesized MnO NN/LC product, revealing an atomic ratio of Mn to O close to 1:1, with a carbon content of 53.62% Fig. 3(d). Notably, the edge region reveals that the 2D carbon support is not entirely smooth as displayed in Fig. 3(e), which exhibited large pits on the surface alongside numerous scattered particles and several nanoflowers. Element distribution mapping Fig. 3(f)–(i) indicates Mn and O elements distributed through the whole surface particles, while

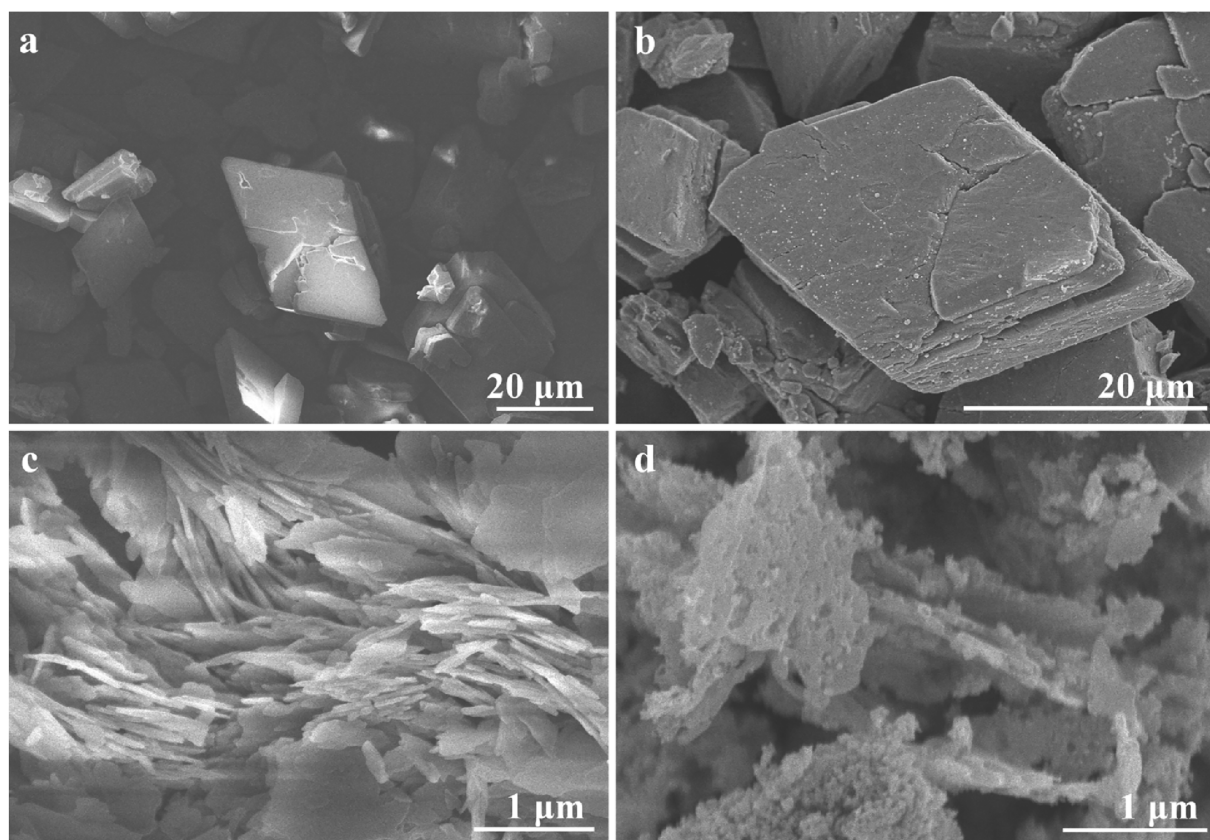


Fig. 2. SEM images of the precursor (a) and corresponding B-MnO/C composite (b), the precursor (c) and corresponding MnO NN/LC composite (d).

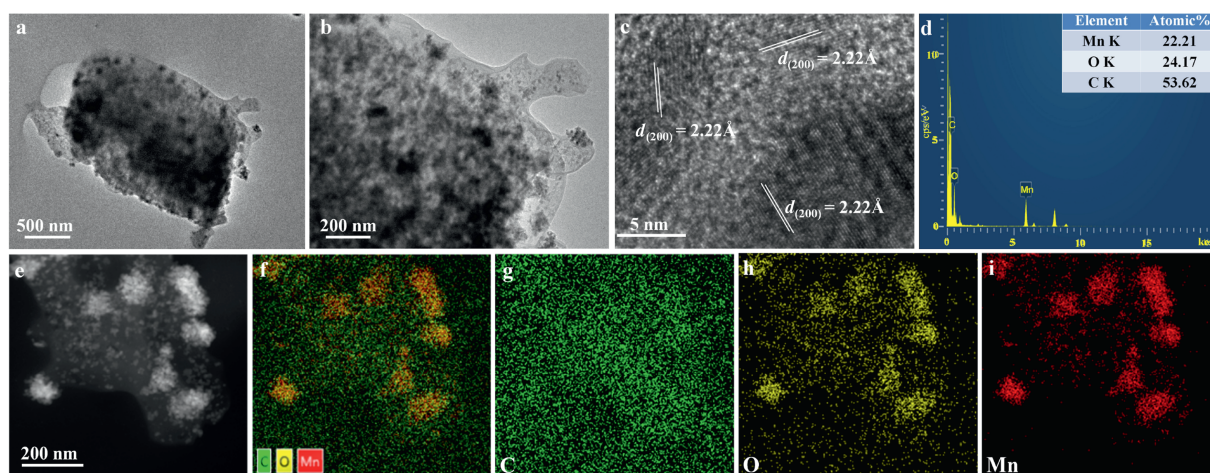


Fig. 3. (a, b) TEM images, (c) HRTEM image, (d) EDS analysis, (e)–(i) element mapping images for MnO NN/LC composite.

the C element mainly existed in the bottom support. The surface area and porous structure for both samples was characterized by BET method. As shown in Fig. S1(a) & (b), both B-MnO/C and MnO NN/LC exhibit typical type IV isotherms with H3 hysteresis loops [31], indicating the presence of mesoporous structures within the samples. BET results show that the specific surface area of MnO NN/LC reaches $44.08 \text{ m}^2 \cdot \text{g}^{-1}$, which is dramatically higher than that of B-MnO/C. The corresponding pore size distribution curves as given in Fig. S1 (c) & (d) further reveal that MnO NN/LC possesses the pores mainly distributed in the range of 3–15 nm, demonstrating a higher porosity compared to B-MnO/C. The high

specific surface area and rich mesopores of MnO NN/LC not only facilitate electrolyte penetration within the electrode but also provide rich active sites for redox reactions and enhance ion diffusion kinetics, ultimately contributing to improved electrochemical performance [32].

This 2D nanosheet structure is expected to significantly enhance the electron transfer, shorten the ion diffusion pathway, and improve the electrochemical dynamics of the electrode material. To evaluate the zinc storage properties of the two synthesized cathode materials, the first cyclic voltammetry (CV) curves of both electrodes at a scanning rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ are presented in

Fig. 4(a). The two CV curves exhibit similar shapes, indicating that both the bulky and flower-like network MnO/C composites possess analogous electrochemical behaviors concerning zinc ion storage. However, the peak area and peak current intensity of the MnO NN/LC composite are significantly greater than those of the B-MnO/C composite, signifying its superior capacity and enhanced electrochemical storage capability [33]. Fig. 4(b) illustrates the first five CV cycles for the MnO NN/LC electrode at a scanning rate of $0.2 \text{ mV} \cdot \text{s}^{-1}$, where two distinct reduction peaks at approximately 1.24 and 1.39 V are observed, corresponding to the insertion of Zn^{2+} and H^{+} during the discharge process [34]. The oxidation peaks at 1.58 and 1.60 V are attributed to the ion release during the charging process, consistent with the CV characteristics typically observed in manganese-based oxides [25]. Moreover, the peak area and current intensity of the CV curve for the first five cycles progressively increases, reflecting the gradual activation of the charge storage activity for the electrode materials, akin to previous reports [25].

Fig. 5(a) displays the first constant current charging-discharge curves of the two synthesized electrodes at a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$. It is evident that the potential gap of the MnO NN/LC electrode is narrower than that of the B-MnO/C electrode, suggesting that the lamellar 2D carbon support effectively enhanced the cycling reversibility and accelerated reaction kinetics, thus alleviating the polarization [28]. To further investigate the advantages of the 2D electrode structure, the rate performance of both electrodes was assessed, as depicted in Fig. 5(b). At a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$, the capacity of the MnO NN/LC electrode increased from an initial value of $177.3 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ to $256.6 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, attributed to the gradual activation of the electrode material. As the current density was incrementally increased to 0.4, 0.6, 0.8, and $1.5 \text{ A} \cdot \text{g}^{-1}$, the corresponding capacities at the last cycle of each current density were 224.5, 171.6, 124.7, and $64.2 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, respectively. Upon restoring the current density to $0.2 \text{ A} \cdot \text{g}^{-1}$, the MnO NN/LC electrode was able to regain a capacity nearly equivalent to that observed at the initial current density. In contrast, the capacities of the B-MnO/C electrode were significantly lower, registering 162.6, 115.1, 59.1, 31.0, and $15.4 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at the 10th, 20th, 30th, 40th, and 50th cycles, respectively. These results underscore the structural advantages of the porous network MnO architecture anchored on 2D lamellar carbon support, which provides a large specific surface area to ensure full contact with the electrolyte as well as the fluent pathway for mass transfer, thereby enhancing the electrochemical activity and facilitating rapid and efficient insertion/desertion of Zn^{2+} ions.

The cycling stability of both electrodes was further assessed at $1.0 \text{ A} \cdot \text{g}^{-1}$ over an extended period. As illustrated in Fig. 5(c), the initial capacity of the MnO NN/LC electrode was $72.0 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, which gradually increased to a peak value of $141.7 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ by the 13th cycle, attributed to the activation process of the electrode. In contrast, it required 96 cycles for the B-MnO/C electrode to achieve its highest capacity of $91.2 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. Subsequently, both electrodes exhibited a decline in capacity. After the 1400th cycle, the remaining capacities were $104.2 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ for the MnO NN/LC electrode and $75.7 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ for the B-MnO/C electrode. As shown in Fig. 5(c), the capacity evolution of the MnO NN/LC electrode exhibits a typical three stage activation process, which involves a rapid capacity increase followed by the slight decrease, and then gradually increasing and stabilizing process. This phenomenon corresponds to three consecutive kinetic stages. The initial capacity rise is primarily attributed to the thorough wetting of the electrode along with the increase in active surface area [35,36]. The subsequent rapid decay is closely related to the dissolution of active Mn^{2+} and side reactions at the unstable electrode/electrolyte interface [37]. The following slow recovery signifies the system entering a dynamic rebalancing process. On one hand, a dense and stable interfacial film gradually forms on the surface, effectively suppressing the ongoing Mn dissolution and side reactions. On the other hand, the repeated $\text{Zn}^{2+}/\text{H}^{+}$ insertion/extraction induces minor adaptive changes in the crystal structure, facilitating ion transport kinetics [18]. Ultimately, after undergoing the aforementioned dynamic adjustments, the electrode enters a stable long-term cycling plateau. This process clearly reveals the interfacial stabilization and electrochemical self-adaptive capabilities resulting from the flexible 2D carbon layer support.

The TEM image of MnO NN/LC after long term cycles is given in Fig. S2, which clearly shows that the nanoflower-like network anchored on carbon sheets well preserved, demonstrates the highly reversible dynamic phase transition during the repeated Zn ion storage. Table S1 provides one comparison of the cycling stability for some MnO-based cathodes as reported previously [15,22,27,33,38–40], from which it is evident that the as-made MnO NN/LC shows superior cycling stability. The superior capacity retention, the robust architecture, and accelerated activation process of the MnO NN/LC demonstrate its enhanced electrochemical storage ability in terms of excellent rate performance and prolonged cycle life, implying the potential application as one cathode in AZIBs.

To systematically elucidate the electrochemical dynamics of the MnO NN/LC electrode, CV tests were conducted at varying

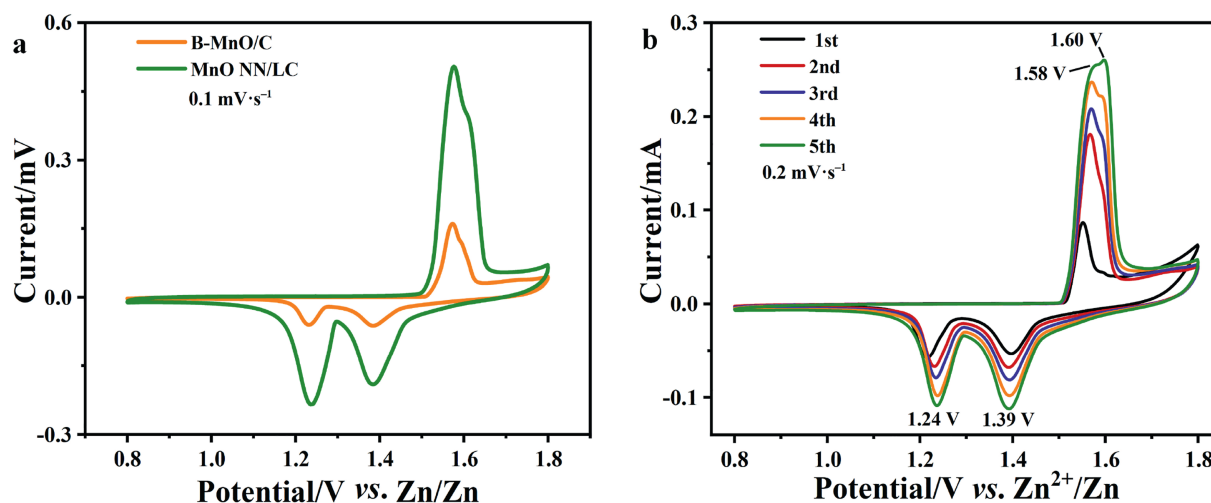


Fig. 4. (a) The first CV curves of MnO NN/LC and B-MnO/C electrodes at a scanning rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$, (b) the first five cycles for CV curves of MnO NN/LC electrode.

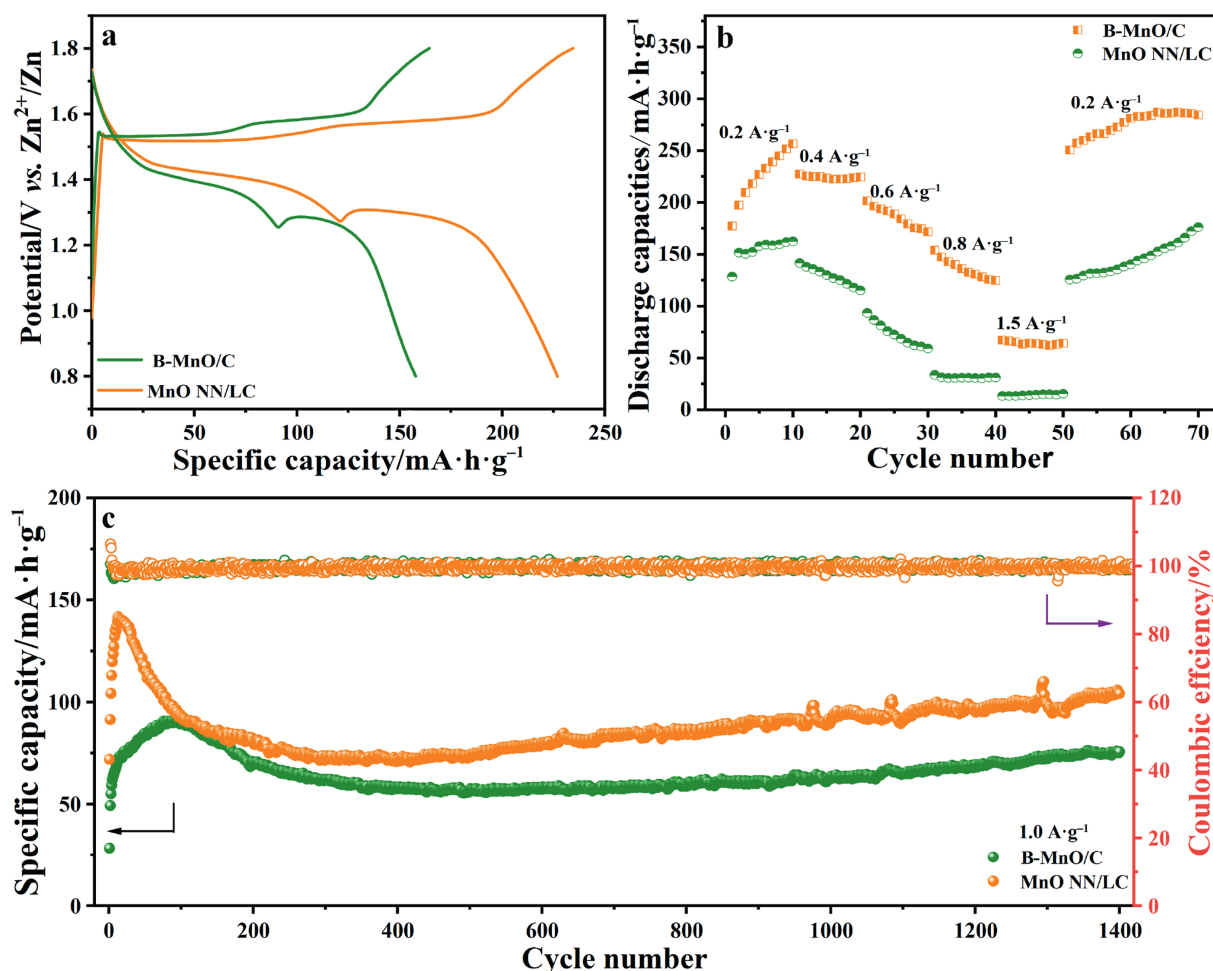


Fig. 5. (a) The first constant current charging-discharging curves at 0.2 A·g⁻¹, (b) Rate performances, (c) cycling performances of MnO NN/LC and B-MnO/C electrodes.

scanning rates. As shown in Fig. 6(a), the CV curves maintained similar shapes with increasing scan rates, while both cathodic and anodic peaks exhibited broadening and shifts toward lower and higher potential values, respectively. The relationship between peak current (i) and scanning rate (v) can be described by Eq. (1) [41].

$$i = a v^b \quad (1)$$

Here, a and b are adjustable parameters associated with the scanning rates. The boundary values of parameter b range from 1.0 to 0.5. A b value of 0.5 indicates that the electrochemical reaction is primarily governed by ion diffusion behavior, while a value of 1 points to reaction control by pseudo-capacitive behavior. The b value is determined according to Eq. (2) [42]:

$$\lg(i) = \lg(a) + b \lg(v) \quad (2)$$

The correlation between $\lg(i)$ and $\lg(v)$ is presented in Fig. 6(b). The b values for peak I, II, and III are 0.51, 0.51, and 0.69, respectively. It can be conclusive that the electrochemical charge/discharge reactions in MnO NN/LC are mainly controlled by diffusion behaviors. And the diffusion contribution ratio is evaluated based on Eq. (3) [43].

$$i(v) = k_1 v + k_2 v^{1/2} \quad (3)$$

Herein, $k_1 v$ represents capacitive contribution, and $k_2 v^{1/2}$ represents diffusion contribution. The analysis for quantitative kinetic

data based on CV fitting has been provided as shown in Fig. 6(c). It is clearly found that the specific peak currents of each redox process at various scan rates exhibit a good linear relationship with the square root of the scan rate ($v^{1/2}$). This directly demonstrates that the redox reactions are primarily diffusion-controlled, in line with the diffusion-dominated kinetic mechanism described by the Randles-Sevcik equation. Specifically, specific peak current shows a linear increase in the anodic oxidation process ($\sigma_a = 1.28$) with increasing $v^{1/2}$, reflecting the diffusion-controlled nature of the conversion from low to high valence Mn species (e.g. $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}/\text{Mn}^{4+}$) [18]. The two cathodic reduction processes exhibit the slopes of $\sigma_b = -0.47$ and $\sigma_b = -1.07$, respectively, indicating that the reduction from high to low valence Mn is also diffusion-controlled, with peak currents varying linearly with $v^{1/2}$ [44]. It is conclusive that the redox reaction rates for MnO NN/LC material within the tested potential range are predominantly governed by the diffusion of ions at the electrode/electrolyte interface. The differing slopes between the oxidation and reduction processes further reveal an asymmetry in the kinetic behavior during the electrochemical reactions.

It can be seen from Fig. 6(d) that the capacitive contribution ratio increases from 34.35% to 51.75% with the increment of the scanning rate from 0.4 to 2.0 $\text{mV} \cdot \text{s}^{-1}$. The b values further disclose that the electrochemical charge/discharge reactions are primarily influenced by diffusion behaviors. The increasing capacitive contribution ratio with scan rate suggests an enhancement in electrochemical storage performance at elevated rates.

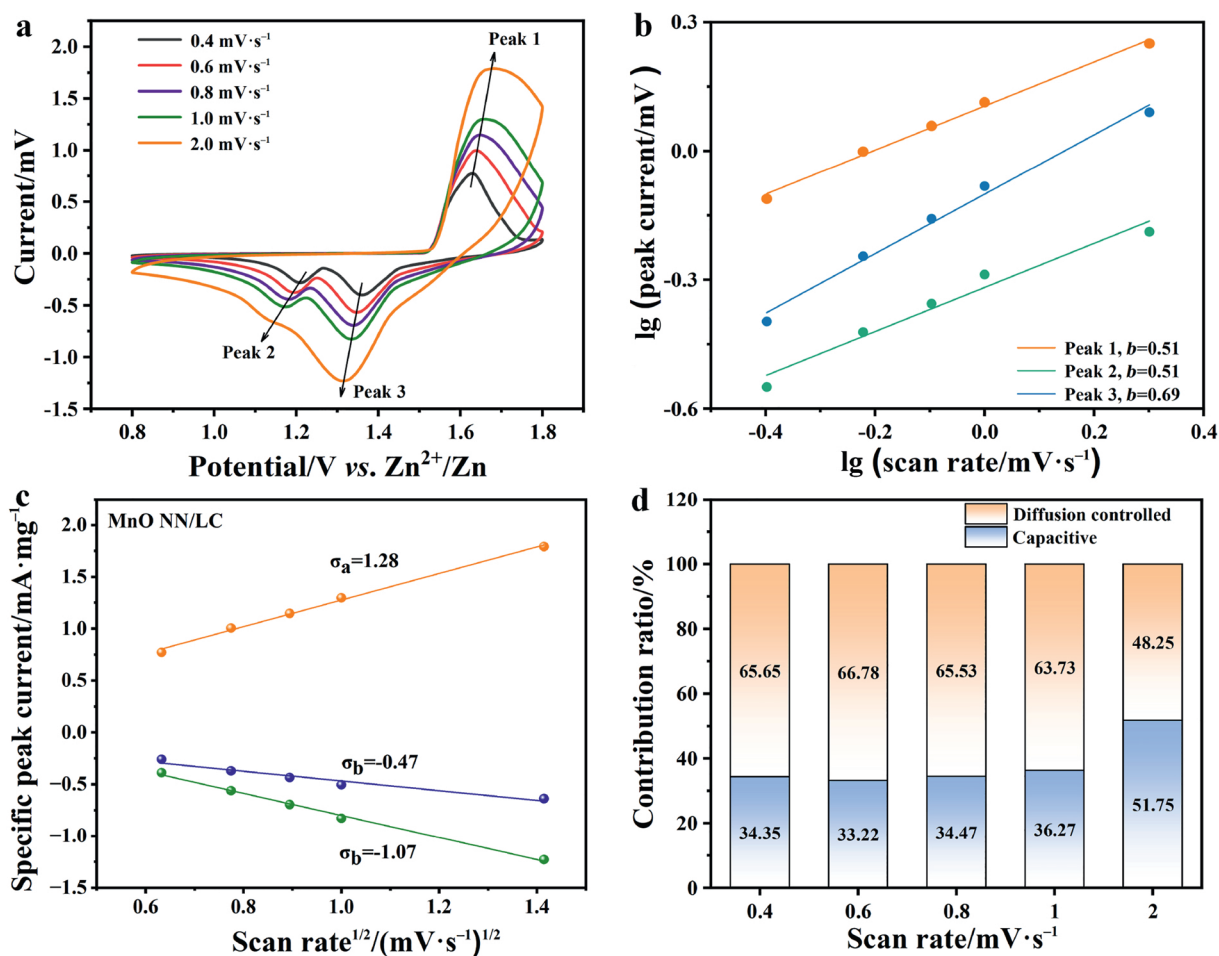


Fig. 6. (a) CV curves, (b) Simulation results of $\lg i$ vs. $\lg v$, (c) linear-fitting curves of the major peak currents versus scanning rates, (d) capacitive contribution ratio of MnO NN/LC at different scan rates.

Electrochemical impedance spectroscopy (EIS) measurements were conducted for both the MnO NN/LC and B-MnO/C electrodes, with the corresponding Nyquist diagram presented in Fig. 7. As observed in Fig. 7(a), the charge transfer resistance (R_{ct}) of the MnO NN/LC electrode (271.6Ω) is significantly lower than that of the B-MnO/C electrode (428.6Ω). This pronounced reduction in charge transfer resistance for the MnO NN/LC composite indicates faster charge transfer rates [45]. The enhanced charge transfer rate can be attributed to the diminished structural dimensions and the advantages of the 2D layered support with the network MnO architecture. Fig. 7(b) reveals that the fitting curve for the MnO NN/LC electrode exhibits a smaller slope, indicative of superior ion diffusion capability. Thus, the construction of a 2D conductive matrix effectively accelerates charge transfer and ion diffusion within the composite material [24].

To elucidate the reaction mechanism of the B-MnO/C composite cathode during Zn^{2+} insertion/extraction, *ex-situ* Raman spectroscopy characterization was performed for the galvanostatic charge-discharge process. As shown in Fig. 7(c) & (d), the obtained Raman spectra provide clear evidence of dynamic phase transitions for the cathode material throughout the electrochemical cycling. Upon charging to 1.6 V (State A), a well-defined characteristic peak emerges at 644 cm^{-1} in the Raman spectrum corresponding to the symmetric stretching vibration of the Mn–O bonds in MnO_2 , which clearly confirms the formation of Mn^{4+} species from the MnO_2 phase [46]. As charging proceeds to 1.8 V

(State B), this characteristic peak exhibits a noticeable redshift to 634 cm^{-1} . This phenomenon reveals more profound structural evolution under high-voltage charging. Firstly, Zn^{2+} from the electrolyte pre-insert into the MnO_2 layered structure, leading to lattice expansion and increased interlayer spacing [47]. Secondly, the co-insertion of hydronium ions (H_3O^+) or water molecules from the aqueous electrolyte, promoting hydration with the $[\text{MnO}_6]$ framework and forming a hydrated phase (such as $\delta\text{-MnO}_2$) with enlarged interlayer spacing [48–50]. The synergistic effect of these two processes results in fine adjustments of the bond lengths and angles of the Mn–O bonds, which also causes the continuous redshift of the characteristic Raman peak-a and implies its structural instability under high voltage conditions. During the subsequent discharge process (from State B to D), the intensity of the MnO_2 characteristic peak at 634 cm^{-1} dramatically decreases, indicating the gradual reduction of Mn^{4+} species. Concurrently, a new broad feature appears around 347 cm^{-1} , corresponding to the characteristic vibration of rock-salt structured MnO [51,52]. As the discharge content increases (with continued extraction of Zn^{2+}), the MnO signal at 347 cm^{-1} showed monotonic enhancement.

Ex-XRD analysis has been performed to examine the phase evolution and valence changes of the electrodes before and after cycling. As shown in Fig. S3, upon charging the newly emerged diffraction peak of 37.8° can be ascribed to the formation of Zn_xMnO_2 , while the diffraction peaks around 38.07° and 39.8°

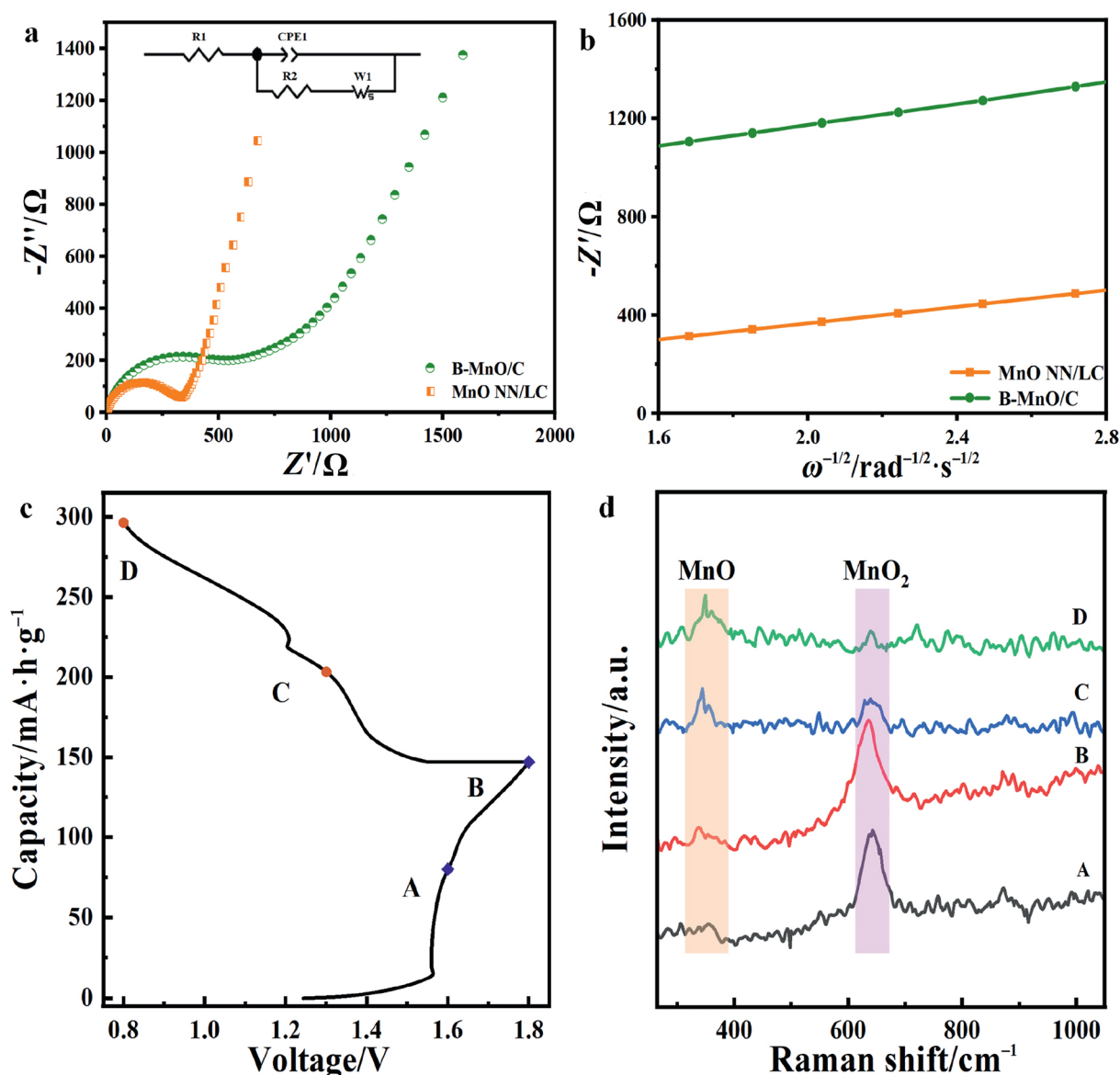


Fig. 7. (a) Nyquist diagram of MnO NN/LC and B-MnO/C electrodes, and (b) the relationship between $\omega^{-1/2}$ and $-Z''$, (c) The GCD curve at 4th cycle at $0.2 \text{ A} \cdot \text{g}^{-1}$, (d) *ex situ* Raman spectra at the different charging/discharging states of B-MnO/C anode.

with the shoulder peaks can be assigned to the production of MnO₂ coupled with different crystalline state [32]. This observation indicated the MnO was oxidized to high-valence $\text{Mn}^{3+}/\text{Mn}^{4+}$ during charging process [52]. After discharging (extraction of $\text{Zn}^{2+}/\text{H}^+$), the signal of Zn_xMnO_2 disappeared with only MnO₂ residues, disclosing that the formed MnO₂ has become the dominant active species toward Zn storage as the same as the previous report [52].

Given all that, the MnO NN/LC composite displays superior zinc ion storage performance, characterized by a large reversible capacity and high long-term cycling stability. The 2D carbon support can provide conductive in-plane matrix and thus facilitate unblocked electronic conductivity, enabling rapid electron movement through the percolating MnO network anchored on the lamellar architecture to the current collector. The synergistic effect of enhanced ionic diffusion perpendicular to the plane and efficient electronic conduction within the plane collectively reduces the overall internal impedance of the MnO electrode. This results in superior rate capability, high power density, and improved

cycling stability, establishing these materials as highly promising candidates for next-generation high-performance batteries.

4. Conclusions

The MnO nanoflower network on lamellar carbon composite, fabricated by a metal-organic framework-derived protocol, represents a significant advancement in cathode materials for aqueous zinc-ion batteries. Its unique 2D lamellar carbon support not only provides a highly conductive matrix but also stabilizes the MnO nanoflowers network, enabling enhanced zinc storage performance characterized by superior rate capability, extended cycling stability, and high reversible capacity. MnO underwent reversible electrochemical oxidation to MnO₂ species as well improved the Zn ion storage performance. This study underscores the scalable fabrication of the composite electrode incorporated with carbon layer and its potential to address challenges in energy storage technologies. Future research could explore the

optimization of synthesis techniques and the application of similar composite structures to other battery systems.

CRediT Authorship Contribution Statement

Menghua Li: Writing – original draft, Resources, Methodology, Investigation, Formal analysis. Xinzhen Liu: Investigation, Funding acquisition. Changhui Sun: Software, Methodology. Xiaorong Cao: Funding acquisition, Formal analysis. Qiqi Han: Software, Resources. Yiye Kong: Software, Methodology. Caixia Xu: Writing – review & editing, Methodology, Investigation.

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.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2026.03.007>.

References

- [1] Q. Hao, Z.F. Ding, C.P. Li, F.X. Li, L. Li, R.M. Bai, J.Q. Wei, J.F. Dong, W.Q. Ma, C.X. Xu, R.Q. Zhang, Phosphorus doping for enhanced lithium storage performances over multiscale porous SiGeSnSbPd composite anode, *Trans. Tianjin Univ.* 31 (3) (2025) 306–319.
- [2] X.Y. Sun, D.R. Wang, H.C. Hu, X. Wei, L. Meng, Z.S. Ren, S.S. Li, Double-doped carbon-based electrodes with nitrogen and oxygen to boost the areal capacity of zinc–bromine flow batteries, *Trans. Tianjin Univ.* 30 (1) (2024) 74–89.
- [3] C. Li, R. Zhang, H.L. Cui, Y.B. Wang, G.J. Liang, C.Y. Zhi, Recent advances in aqueous Zn||MnO₂ batteries, *Trans. Tianjin Univ.* 30 (1) (2024) 27–39.
- [4] H.L. Li, Z.X. Liu, Y. Tang, S.Q. Liang, G.Z. Fang, Copper-based materials in anode electrode of aqueous zinc metal batteries, *cMat* 1 (2) (2024) e25.
- [5] Z. Wang, T. Long, J. Feng, Q. Sun, Application of SiC quantum dot sensitized g-C₃N₄ photoanode in photocatalytic fuel cells, *J. Liaocheng Univ. Nat. Sci.* 37 (4) (2024) 74–88.
- [6] Y. Zhou, W. Pan, L. Ma, T. Chen, Y. Sun, Application and challenges of coating technology in cathode materials of lithium-ion batteries, *China Powder Sci. Technol.* 31 (1) (2025) 74–86.
- [7] Z.R. Wang, Y.L. Zhang, R.Z. Zhang, W.W. Li, J. Song, S.L. Liu, The Road ahead for aqueous lithium-ion batteries, *cMat* 2 (2) (2025) e70010.
- [8] J. Ma, Research progress on crosstalk behavior in lithium batteries, *J. Liaocheng Univ. Nat. Sci. Ed.* 38 (1) (2025) 34–42.
- [9] J.W. Lu, T. Liu, Y.M. Chen, Y.X. Ma, J.L. Cao, K. Luo, W.W. Lei, D. Liu, Machine learning-based battery life detection and photoelectrode materials selection for lithium batteries, *Trans. Tianjin Univ.* 31 (3) (2025) 270–277.
- [10] H.H. Gao, N. Li, C.L. Li, X.X. Zhang, W.J. Liu, J. Sun, Q.X. Yu, J.W. Zhu, C.G. Wang, X.J. Xu, High-mass-loading NiCo-LDH hollow nanoflower for high-performance alkaline aqueous zinc batteries, *ChemPhysMater* 4 (4) (2025) 418–424.
- [11] X. Zhu, L. Tang, J. Wu, J. Gao, Z. Yuan, Research progress on three-dimensional zinc anodes in aqueous zinc-ion batteries, *China Powder Sci. Technol.* 32 (1) (2026) 44–52.
- [12] N. Li, C.G. Wang, X.X. Zhang, C.L. Li, G.M. Qu, X. Wang, X.J. Xu, High-performance alkaline aqueous zinc battery enabled by nickel-cobalt-tellurium materials, *ChemPhysMater* 3 (4) (2024) 415–421.
- [13] Y.J. Wang, Y.M. Fan, X.D. Chen, J.H. Liu, Y. Gao, X.H. Lin, Y. Huang, H.X. Jiang, C. C. Zhan, H. Zhang, X.H. Cao, Y. Xiao, Synergistic effects of structural and electronic dual engineering for ultra-stable aqueous zinc-ion batteries, *InfoMat* 7 (11) (2025) e70055.
- [14] J. Hou, Z. Xue, W. Ma, T. Jian, C. Xu, Research status and prospect of iodine positive electrode for zinc-iodine batteries, *J. Liaocheng Univ. Nat. Sci. Ed.* 37 (6) (2024) 1–9.
- [15] C.Y. Zhu, G.Z. Fang, S.Q. Liang, Z.X. Chen, Z.Q. Wang, J.Y. Ma, H. Wang, B.Y. Tang, X.S. Zheng, J. Zhou, Electrochemically induced cationic defect in MnO intercalation cathode for aqueous zinc-ion battery, *Energy Storage Mater.* 24 (2020) 394–401.
- [16] Y.T. Li, C.R. Zhao, Y.F. Xu, Z.Y. Liu, M. Li, Q. Huang, X. Wu, High capacity and temperature adaptive aqueous zinc ion batteries through Ca²⁺ intercalated into NH₄V₄O₁₀ cathode materials, *Nano Res. Energy* 4 (3) (2025) e9120173.
- [17] Z.C. Zhang, Y.B. Mu, L.J. Xiao, X.Y. Wei, M.S. Han, C. Yang, L.M. Zang, L. Zeng, J. H. Qiu, Advancements in manganese-based cathodes for aqueous zinc-ion batteries: challenges and optimization strategies, *cMat* 2 (1) (2025) e70000.
- [18] Y.Y. Chen, X.S. Hu, X.D. Chen, J.H. Liu, Y. Huang, D.P. Cao, Trimetallic-Organic Framework-Derived Ni-Doped MnO/PC as cathodes for High-Performance aqueous zinc-ion batteries, *Chem. Eng. J.* 478 (2023) 147411.
- [19] Y.J. Wu, K. Ding, P. Zhao, X.L. Wei, Z.H. Yang, J.X. Zhang, B.F. Wang, Metal-organic framework (MOF)-derived carbon coated hollow Mn₂O₃ microspheres enable highly reversible aqueous Zn-ion battery, *Tungsten* 8 (1) (2026) 106–117.
- [20] R.Y. Ge, Y. Yang, H. Li, S.W. Zhang, Y.F. Hu, Y.W. Shi, J.Z. Li, H. Fan, B.S. Yin, T.Y. Ma, Magnetic field-assisted synthesis of Co-doped Mn₃O₄/MnOOH multiphase manganese oxides for high-performance cathodes in aqueous rechargeable zinc-ion batteries, *J. Power Sources* 640 (2025) 236691.
- [21] Q.Q. Wu, Q. Fu, C.H. Mu, X.Q. Ao, Unveiling the energy storage mechanism in zinc-doped Mn₃O₄ cathode for high-performance AZIBs, *J. Alloys Compd.* 1014 (2025) 178843.
- [22] P.F. Yu, J.X. Zhou, M.T. Zheng, M.R. Li, H. Hu, Y. Xiao, Y.L. Liu, Y.R. Liang, Boosting zinc ion energy storage capability of inert MnO cathode by defect engineering, *J. Colloid Interface Sci.* 594 (2021) 540–549.
- [23] S.S. Bi, H.M. Wang, R. Wang, Z.Q. Niu, Two-dimensional materials for aqueous zinc-ion batteries, *2D Mater.* 9 (4) (2022) 042001.
- [24] Y.R. Wang, J. Yin, J. Zhu, Two-dimensional cathode materials for aqueous rechargeable zinc-ion batteries, *Chin. J. Chem.* 40 (8) (2022) 973–988.
- [25] Z.X. Zhu, Z.W. Lin, Z.W. Sun, P.X. Zhang, C.P. Li, R. Dong, H.W. Mi, Deciphering H⁺/Zn²⁺ co-intercalation mechanism of MOF-derived 2D MnO/C cathode for long cycle life aqueous zinc-ion batteries, *Rare Met.* 41 (11) (2022) 3729–3739.
- [26] G.L. Lu, D.D. Qin, H.H. Hu, Y.H. Feng, S.M. Qiu, W.J. Liu, X.J. Liu, Dual-function modulated MnO cathode for high-performance aqueous zinc-ion batteries, *J. Power Sources* 649 (2025) 237420.
- [27] X.M. Yan, H. Li, B.L. Zhang, B.H. Chen, W. Xiao, Constructing a high-performance cathode for aqueous zinc ion batteries via understanding the energy storage mechanism of MnO, *Rare Met.* 44 (1) (2025) 218–229.
- [28] J.R. Wang, Z.S. Hou, X. Liu, S.Y. Wang, S.Y. Yao, Y.B. Yao, D.W. Wang, X.Y. Gao, H.Y. Zhang, Z. Tang, Y.M. Liu, K.Q. Nie, J.Z. Xie, Z.Y. Yang, Y.M. Yan, Boosted sodium ion storage performance in MnO₂: understanding the bond angle-mediated orbital overlap in MnO₆ units for fast charge transfer, *J. Energy Chem.* 87 (2023) 295–303.
- [29] Z. Li, Y. Li, F. Xu, Z. Kuang, Z. Gan, H. Liu, S. Wang, J. Liu, Synthesis of nickel-doped MnCO₃ anode and its electrochemical performance, *J. Liaocheng Univ. Nat. Sci. Ed.* 39 (1) (2026) 44–53.
- [30] L.J. Kong, J. Zhu, W. Shuang, X.H. Bu, Nitrogen-doped wrinkled carbon foils derived from MOF nanosheets for superior sodium storage, *Adv. Energy Mater.* 8 (25) (2018) 1801515.
- [31] X.D. Chen, X.S. Chen, X.H. Lin, D.M. Qi, J.H. Liu, Y. Huang, C.C. Zhan, H. Zhang, Y. Gao, Y. Xiao, Suppressing Jahn-Teller distortion and accelerating ion kinetics via heterostructure engineering for stable aqueous zinc-ion batteries, *Chem. Eng. J.* 526 (2025) 170760.
- [32] Q. Chen, J.L. Jin, Z.K. Kou, C. Liao, Z.A. Liu, L. Zhou, J. Wang, L.Q. Mai, Zn(2+) pre-intercalation stabilizes the tunnel structure of MnO(2) nanowires and enables zinc-ion hybrid supercapacitor of battery-level energy density, *Small* 16 (14) (2020) e2000091.
- [33] X. Xiao, T.S. Wang, Y.X. Zhao, W.J. Gao, S.C. Wang, A design of MnO-CNT@C₃N₄ cathodes for high-performance aqueous zinc-ion batteries, *J. Colloid Interface Sci.* 642 (2023) 340–350.
- [34] H.F. Jia, Y.X. Li, U. Ali, B.Q. Liu, Z.S. Jin, L. Li, Y.N. Chen, L.Y. Zhang, T.T. Wang, C. G. Wang, High-entropy doping strategy towards reinforced Mn-O bond for durable aqueous zinc ion batteries, *Nano Energy* 122 (2024) 109348.
- [35] Q.P. Zeng, S.T. Zhou, N. Yu, J.C. Huo, C.F. Sun, K. Guo, In situ electrochemical activation enabling high-performance cathodes for aqueous zinc-ion batteries, *J. Mater. Chem. A* 13 (30) (2025) 24997–25007.
- [36] K. Guo, Y. Li, Y.J. Xiang, C.C. Yang, S.Q. Pan, Q.P. Zeng, Z.Y. Li, N. Yu, In-situ electrochemical activating VB for high-performance aqueous zinc-ion battery cathodes, *Electrochim. Acta* 538 (2025) 146979.
- [37] K. Guo, Y. Li, C.C. Yang, Y.J. Xiang, S.Q. Pan, Q.P. Zeng, Z.Y. Li, N. Yu, X.F. Wang, Metallic vanadium activated by an in situ dissolution–deposition process for a superior aqueous zinc ion battery cathode, *Chem. Commun.* 61 (11) (2025) 2329–2332.
- [38] J.J. Wang, J.G. Wang, H.Y. Liu, Z.Y. You, C.G. Wei, F.Y. Kang, Electrochemical activation of commercial MnO micro-sized particles for high-performance aqueous zinc-ion batteries, *J. Power Sources* 438 (2019) 226951.
- [39] T.T. Feng, H.L. Li, J. Tan, Y.F. Liang, W.Q. Zhu, S. Zhang, M.Q. Wu, Synthesis, characterization and electrochemical behavior of Zn-doped MnO/C sub-microspheres for lithium ion batteries, *J. Alloys Compd.* 897 (2022) 163153.
- [40] Q.G. Li, Y. Zhu, S.L. Wu, W.Z. Du, Y.Q. Wang, S.J. Feng, Co-coating strategy enables robust MnO cathode in aqueous zinc ion batteries, *J. Energy Storage* 141 (2026) 119358.
- [41] Z.H. Liu, Y.P. Liu, Y.N. Zhang, X.L. Liu, D. Yan, J.J. Huang, S.L. Peng, Selection of Cu²⁺ for intercalation from the electronegativity perspective: improving the

- cycle stability and rate performance of δ -MnO₂ cathode material for aqueous zinc-ion batteries, *Sci. China Mater.* 66 (2) (2023) 531–540.
- [42] Y.N. Zhang, Y.P. Liu, Z.H. Liu, X.G. Wu, Y.X. Wen, H.D. Chen, X. Ni, G.H. Liu, J.J. Huang, S.L. Peng, MnO₂ cathode materials with the improved stability via nitrogen doping for aqueous zinc-ion batteries, *J. Energy Chem.* 64 (2022) 23–32.
- [43] W.T. Dong, M. Du, F. Zhang, X.F. Zhang, Z.Y. Miao, H.Z. Li, Y.H. Sang, J.J. Wang, H. Liu, S.H. Wang, *In situ* electrochemical transformation reaction of ammonium-anchored heptavanadate cathode for long-life aqueous zinc-ion batteries, *ACS Appl. Mater. Interfaces* 13 (4) (2021) 5034–5043.
- [44] Y.Q. Feng, Q.Q. Lu, H. Liu, Defective MnO₂ functional separator coating as effective polysulfide mediators for lithium–sulfur batteries, *Tungsten* 6 (3) (2024) 536–543.
- [45] H.J. Zeng, J.T. Huang, Y.B. Chen, L. Chen, Z.H. Wu, H.Y. Yang, Z. Chen, Cu²⁺ pre-intercalated vanadium oxides as cathode materials for aqueous zinc-ion batteries, *Tungsten* 7 (3) (2025) 547–556.
- [46] Y.Q. Wang, H. Hong, Z.Q. Wei, D.D. Li, X.R. Yang, J.X. Zhu, P. Li, S.N. Wang, C.Y. Zhi, Cation-regulated MnO₂ reduction reaction enabling long-term stable zinc–manganese flow batteries with high energy density, *Energy Environ. Sci.* 18 (3) (2025) 1524–1532.
- [47] Y.X. Zhang, X.S. Cui, Y.P. Liu, S.T. Cheng, P. Cui, Y. Wu, Z.H. Sun, Z.P. Shao, J.C. Fu, E.Q. Xie, Aqueous Zn-MnO₂ battery: approaching the energy storage limit with deep Zn²⁺ pre-intercalation and revealing the ions insertion/extraction mechanisms, *J. Energy Chem.* 67 (2022) 225–232.
- [48] L.Y. Wu, Z.W. Li, Y.X. Xiang, W.D. Dong, X.D. Qi, Z.X. Ling, Y.H. Xu, H.Y. Wu, M. D. Levi, N. Shpigel, X.G. Zhang, Revisiting the charging mechanism of α -MnO₂ in mildly acidic aqueous zinc electrolytes, *Small* 20 (45) (2024) e2404583.
- [49] H.J. Kim, J. Ahn, N. Voronina, N. Yaqoob, M. Bokdam, J. Jeong, J.H. Park, K.Y. Chung, P. Kaghazchi, S.T. Myung, Impact of water on structure stabilization in layered manganese-oxide for high-voltage zinc storage in non-aqueous electrolyte: experimental and theoretical aspects, *Energy Storage Mater.* 63 (2023) 103028.
- [50] S. Xi, X. Cheng, X. Gao, H. Liu, Preparation and electrochemical properties of manganese dioxide flexible electrodes for zinc-ion batteries, *Chin. J. Eng.* 46 (11) (2024) 2036–2045.
- [51] B. Lee, H.R. Lee, H. Kim, K.Y. Chung, B.W. Cho, S.H. Oh, Elucidating the intercalation mechanism of zinc ions into α -MnO₂ for rechargeable zinc batteries, *Chem. Commun.* 51 (45) (2015) 9265–9268.
- [52] X.D. Chen, X.S. Hu, Y.Y. Chen, X.H. Cao, Y. Huang, H. Zhang, J.H. Liu, Y.W. Wang, S.L. Chou, D.P. Cao, Ultrastable hydrated vanadium dioxide cathodes for high-performance aqueous zinc ion batteries with H⁺/Zn²⁺ co-insertion mechanism, *J. Mater. Chem. A* 10 (41) (2022) 22194–22204.