

Document Version

Final published version

Licence

CC BY

Citation (APA)

Chandran, B., Babu, R. S., Nair, D. S., Padmaraj, O., Gonugunta, P., Panneerselvam, T., Murugan, R., Babu, G. R., Hendrikx, R., Taheri, P., Mol, A., Satyanarayana, N., & Anusuyadevi, P. R. (2026). Interfacial engineering of ZnMn_2O_4 via N-doped rGO wrapping for improved electrochemical kinetics and stable lithium storage. *Materials Chemistry and Physics*, 370, Article 133161. <https://doi.org/10.1016/j.matchemphys.2026.133161>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

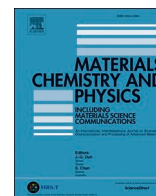
In case the licence states "Dutch Copyright Act (Article 25fa)", this publication was made available Green Open Access via the TU Delft Institutional Repository pursuant to Dutch Copyright Act (Article 25fa, the Taverne amendment). This provision does not affect copyright ownership.
Unless copyright is transferred by contract or statute, it remains with the copyright holder.

Sharing and reuse

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.



Interfacial engineering of ZnMn_2O_4 via N-doped rGO wrapping for improved electrochemical kinetics and stable lithium storage

Bharath Chandran^a, Reshma S. Babu^a, Durga S. Nair^c, O. Padmaraj^d, Prasad Gonugunta^b,
Thamayanthi Panneerselvam^a, R. Murugan^a, Gangineni Ramesh Babu^a, Ruud Hendrikx^b,
Peyman Taheri^b, Arjan Mol^b, N. Satyanarayana^{a,*}, Prasaanth Ravi Anusuyadevi^{b,**}

^a Department of Physics, Pondicherry University, Puducherry, 605014, India

^b Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, the Netherlands

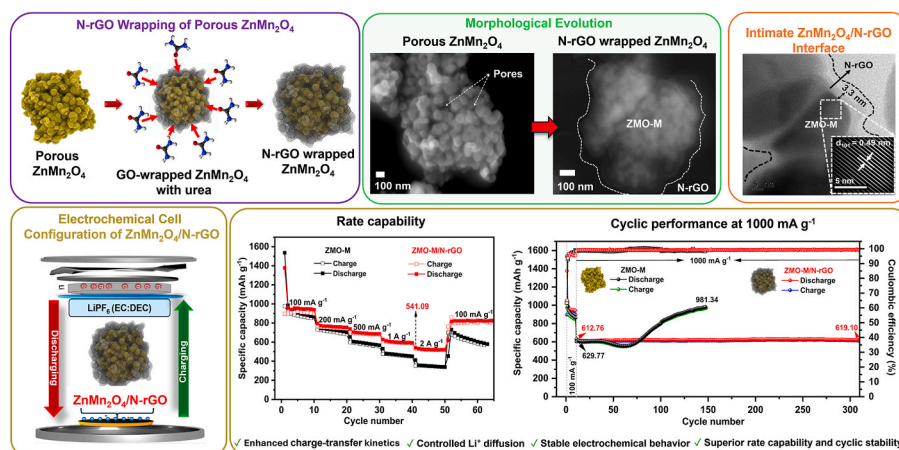
^c Department of Physics, Sree Narayana College, Chengannur, Alappuzha, Kerala, 689126, India

^d Department of Physics, Puducherry Technological University, Pondicherry, 605014, India

HIGHLIGHTS

- Microwave-assisted synthesis enabled $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposite formation.
- APTMS-assisted assembly promoted intimate $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ interfaces.
- N-rGO wrapping enhanced charge-transfer kinetics of ZnMn_2O_4 electrodes.
- Stable lithium-storage behavior was achieved for over 300 cycles at 1 A g^{-1} .
- EIS revealed controlled Li^+ diffusion and lower interfacial resistance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

ZnMn_2O_4
N-doped reduced graphene oxide (N-rGO)
Interfacial engineering
Lithium-ion batteries
Electrochemical kinetics
Rate capability

ABSTRACT

Spinel ZnMn_2O_4 is a promising anode material for lithium-ion batteries owing to its high theoretical capacity, low cost, and environmental compatibility. However, its practical utilization is limited by poor electrical conductivity, sluggish reaction kinetics, and structural instability during repeated lithiation and delithiation. These limitations motivate the development of an interfacial strategy that can simultaneously improve charge transport and mitigate the structural degradation associated with conversion-type lithium storage. In this work, N-doped reduced graphene oxide (N-rGO) is intimately wrapped around porous ZnMn_2O_4 nanoparticles to construct an interconnected oxide-graphene interface. The N-rGO framework provides continuous electronic pathways and

* Corresponding author.

** Corresponding author.

E-mail addresses: nallanis2011@gmail.com (N. Satyanarayana), P.RaviAnusuyadevi@tudelft.nl, ranu.prasaanth@gmail.com (P.R. Anusuyadevi).

stable interfacial transport channels, while its flexible network helps accommodate volume variations and maintain electrical connectivity during cycling. The resulting ZMO-M/N-rGO nanocomposite exhibits improved electrochemical kinetics and high-rate capability compared with pristine ZMO-M, delivering a reversible discharge capacity of $541.09 \text{ mA h g}^{-1}$ at a current density of 2 A g^{-1} . Following an initial 10-cycle activation period, the nanocomposite maintains a stable electrochemical response for 300 cycles at 1 A g^{-1} , retaining a discharge capacity of $619.10 \text{ mA h g}^{-1}$, whereas pristine ZMO-M exhibits pronounced capacity fluctuations. Electrochemical impedance analysis further reveals lower interfacial resistance and a more gradual, controlled evolution of Li^+ transport behavior in the nanocomposite. These results demonstrate that N-rGO interfacial wrapping is an effective approach for improving charge-transfer kinetics, maintaining stable transport pathways, and enhancing the long-term electrochemical stability of ZnMn_2O_4 -based anodes.

1. Introduction

The increasing demand for portable electronic devices, electric vehicles (EVs), and large-scale energy storage systems has intensified research on advanced electrochemical energy storage technologies. Among the various energy storage systems currently available, lithium-ion batteries (LIBs) are still the dominant technology owing to their high energy density, long cycle life, low self-discharge rate, and mature manufacturing infrastructure [1,2]. Consequently, LIBs are widely employed in consumer electronics and are expected to play a crucial role in future sustainable energy applications [1,2]. The performance of LIBs strongly depends on the properties of their electrode materials. Graphite is currently the most commonly used commercial anode material because of its excellent cycling stability and low operating potential. However, its relatively low theoretical capacity of 372 mA h g^{-1} limits the achievable energy density of next-generation LIBs [3–5]. Therefore, considerable effort has been devoted to developing alternative anode materials with higher lithium-storage capacities while maintaining good cycling stability and rate performance [3–5].

Among the various candidates investigated, transition-metal oxides (TMOs) have attracted significant attention due to their high theoretical capacities arising from conversion-type lithium storage reactions [6,7]. However, they suffer from poor intrinsic electrical conductivity and severe volume changes during repeated lithiation and delithiation, leading to electrode pulverization, unstable solid-electrolyte interphase (SEI) formation, and rapid capacity fading [6,7]. Among TMOs, mixed transition-metal oxides (MTMOs) with spinel AB_2O_4 structure where $\text{A} = \text{Zn, Co, Ni, etc.}$, and $\text{B} = \text{Mn, Fe, Co, etc.}$, have been extensively explored. The coexistence of two metal cations provides multiple redox centers and enhanced electronic conductivity compared with single transition metal oxides [8–10].

Among the reported MTMOs, ZnMn_2O_4 has emerged as a promising anode material because of its high theoretical capacity ($\sim 1008 \text{ mA h g}^{-1}$), low cost, natural abundance, environmental compatibility, and suitable operating potential [11,12]. Nevertheless, ZnMn_2O_4 suffers from poor electrical conductivity and large volume changes during cycling, leading to structural degradation and gradual capacity loss [12]. To address the limitations of ZnMn_2O_4 , various structural engineering strategies, including nano and microstructures such as loaf-like nanorods [13], nanofibers [14], mesoporous nano-peanuts [15], ball-in-ball microspheres [16], porous microspheres [17–19], hollow porous panpipes [20] and porous hollow microrods [21], have been explored. Among these approaches, porous architectures have attracted considerable interest because their interconnected pore networks provide enhanced electrolyte accessibility, abundant electrochemically active sites, and shortened lithium-ion diffusion pathways, thereby improving electrochemical performance [17]. However, despite these advantages, the electrochemical performance of pristine porous ZnMn_2O_4 materials remains significantly below their theoretical capacity, particularly during prolonged cycling and at high current densities [12]. Furthermore, the intrinsically low electronic conductivity of ZnMn_2O_4 continues to hinder rapid charge transport. To overcome these limitations, several researchers have employed 3-aminopropyltrimethoxysilane (APTMS)-assisted reduced graphene oxide (rGO) wrapping

strategies, in which APTMS serves as a surface functionalization agent that promotes electrostatic interactions between the prepared ZnMn_2O_4 particles and negatively charged graphene oxide sheets. Using this approach, Zheng et al. [22], Cai et al. [12], and Zhang et al. [23] reported rGO-wrapped ZnMn_2O_4 nanorods, nanospheres, and microspheres, respectively. The incorporation of rGO established a conductive interfacial network that facilitated electron transport and lithium-ion migration, thereby enhancing electrochemical stability and rate capability [12,23].

More recently, Chandran et al. [24] demonstrated the feasibility of incorporating N-rGO into ZnMn_2O_4 to improve its electrochemical performance. This further highlights the potential of N-rGO as a conductive and interfacial component for ZnMn_2O_4 -based anodes. Although APTMS/APS-assisted graphene wrapping has been demonstrated as an effective strategy for improving the electrochemical performance of ZnMn_2O_4 , many reported composites employ undoped reduced graphene oxide (rGO) as the conductive component. Compared with undoped rGO, nitrogen-doped reduced graphene oxide (N-rGO) possesses several advantageous characteristics for electrochemical energy storage. The incorporation of nitrogen atoms into the graphene lattice can modify its electronic structure, enhance electrical conductivity, and generate additional electrochemically active defect sites that facilitate lithium-ion adsorption and charge transfer [25–27]. Furthermore, nitrogen-containing functional groups can strengthen the interfacial interaction between graphene and metal oxide nanoparticles through electronic coupling and charge redistribution effects, thereby promoting more efficient charge transport across the oxide-carbon interface [28]. As a consequence of all these, N-rGO has emerged as an attractive conductive framework for improving the electrochemical performance of metal-oxide-based anodes [25–27]. In parallel, the development of rapid and efficient synthesis strategies is equally important for the practical fabrication of advanced electrode materials. Compared with conventional hydrothermal approaches, microwave-assisted hydrothermal processing provides rapid and uniform volumetric heating, resulting in shorter reaction times, improved reaction efficiency, and controlled formation of nanostructured materials [11]. Therefore, the integration of porous ZnMn_2O_4 , N-rGO interfacial engineering, and microwave-assisted synthesis represents a promising strategy for achieving enhanced lithium-storage performance and improved electrochemical stability.

Motivated by these considerations, porous ZnMn_2O_4 was synthesized via a microwave-assisted hydrothermal route followed by controlled calcination to obtain a porous framework with enhanced electrolyte accessibility. Subsequently, APTMS-assisted interfacial assembly and a second time microwave-assisted hydrothermal treatment in the presence of graphene oxide and urea were employed to achieve intimate interfacial wrapping of nitrogen-doped reduced graphene oxide (N-rGO) around the porous ZnMn_2O_4 nanoparticles. The synergistic combination of the porous architecture, conductive N-rGO network, and strong oxide-carbon interfacial contact is expected to facilitate electron transport, improve lithium-ion diffusion, and enhance structural stability during repeated lithiation-delithiation processes. The lithium-storage performance and electrochemical behavior of the resulting ZnMn_2O_4 /N-rGO nanocomposite were systematically evaluated and compared with those

of pristine porous ZnMn_2O_4 .

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade and used without further purification. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$], manganese acetate tetrahydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$], ammonium hydrogen carbonate [NH_4HCO_3], ethanol [$\text{C}_2\text{H}_5\text{OH}$], 3-aminopropyltrimethoxysilane [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$], urea [$\text{CO}(\text{NH}_2)_2$]. Graphene oxide [GO] used was prepared by the modified Hummers' method as described in the supplementary information. Deionized (DI) water was used throughout the experiments.

2.2. Synthesis of pristine porous ZnMn_2O_4 (ZMO-M)

Fig. 1 illustrates the schematic illustration for the synthesis of porous ZnMn_2O_4 (ZMO-M). Initially, 3 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 6 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 mL of deionized (DI) water. In a separate beaker, 30 mmol of NH_4HCO_3 was dissolved in 30 mL of DI water. Both solutions were ultrasonicated for 0.5 h, then mixed and continuously stirred for 1 h. The resulting mixture was transferred into a 100 mL Teflon-lined autoclave and subjected to microwave-assisted hydrothermal treatment using a CEM MARS 5 system at 160°C , with a ramp time of 0.5 h and an output power of 800 W for 15 min. After naturally cooling to room temperature, the precipitate was collected by centrifugation and washed repeatedly with a 1:1 ratio of ethanol-DI water mixture until a neutral pH was achieved. The obtained product was then dried at 60°C for 12 h and ground into a fine powder. The obtained white intermediate powder is denoted ZMO-I. Subsequently, ZMO-I was calcined at 600°C for 2 h (heating rate: 2°C min^{-1}) to obtain a dark-yellow porous ZnMn_2O_4 powder, referred to as ZMO-M, which was used for further characterization and composite preparation.

2.3. Synthesis of $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ (ZMO-M/N-rGO) nanocomposite

Initially, 140 mg of ZMO-M powder was dispersed in 100 mL of ethanol, stirred for 1 h, and ultrasonicated for 1 h to ensure uniform

dispersion. Subsequently, 1 mL of 3-aminopropyltrimethoxysilane (APTMS) was added, and the mixture was stirred continuously for 3 h to achieve surface functionalization, following a method similar to that reported by Cai et al. [12]. The APTMS-functionalized product was collected by centrifugation, washed several times with ethanol, and dried at 60°C in a hot air oven for 12 h. The dried powder was then redispersed in 60 mL of DI water, stirred for 1 h, and ultrasonicated for 30 min to obtain a homogeneous dispersion (Solution A). In a separate beaker, 60 mg of graphene oxide (GO) was dispersed in 60 mL of DI water and ultrasonicated for 30 min to obtain Solution B. Considering the initial amounts of ZMO-M (140 mg) and GO (60 mg), the nominal ZMO-M: GO mass ratio was 70:30 (w/w). Solution B was then added dropwise to Solution A under continuous stirring, and the mixture was stirred for an additional 3 h to form a uniform suspension (Solution C). Subsequently, 1.8 g of urea was added to Solution C, and the mixture was stirred for 1 h. The resulting mixture was transferred into two 100 mL Teflon-lined autoclaves and subjected to microwave-assisted hydrothermal treatment using a CEM MARS 5 system at 160°C , with a ramp time of 0.5 h and an output power of 800 W for 30 min. The obtained black precipitate was collected, washed thoroughly, and dried to yield the ZMO-M/N-rGO nanocomposite, which was used for structural, morphological, and electrochemical characterizations. The overall synthesis process of the ZMO-M/N-rGO nanocomposite is schematically illustrated in Fig. 2.

As illustrated in Fig. 2, the electrostatic assembly between ZnMn_2O_4 (ZMO-M) and graphene oxide is facilitated by surface functionalization using APTMS, which introduces positively charged amine ($-\text{NH}_2/-\text{NH}_3^+$) groups onto the ZMO surface. This modification enables a strong electrostatic attraction with the negatively charged oxygen-containing functional groups present on graphene oxide sheets [12,29]. Consequently, GO sheets anchor and wrap around the ZMO-M particles. During the second time microwave-hydrothermal treatment, urea plays a dual role by promoting the reduction of GO to N-rGO and simultaneously introducing nitrogen functionalities, thereby further enhancing electronic conductivity and interfacial interactions. This synergistic electrostatic interaction and in situ nitrogen doping result in the formation of a well-integrated ZMO-M/N-rGO nanocomposite with improved structural stability and charge transport properties.

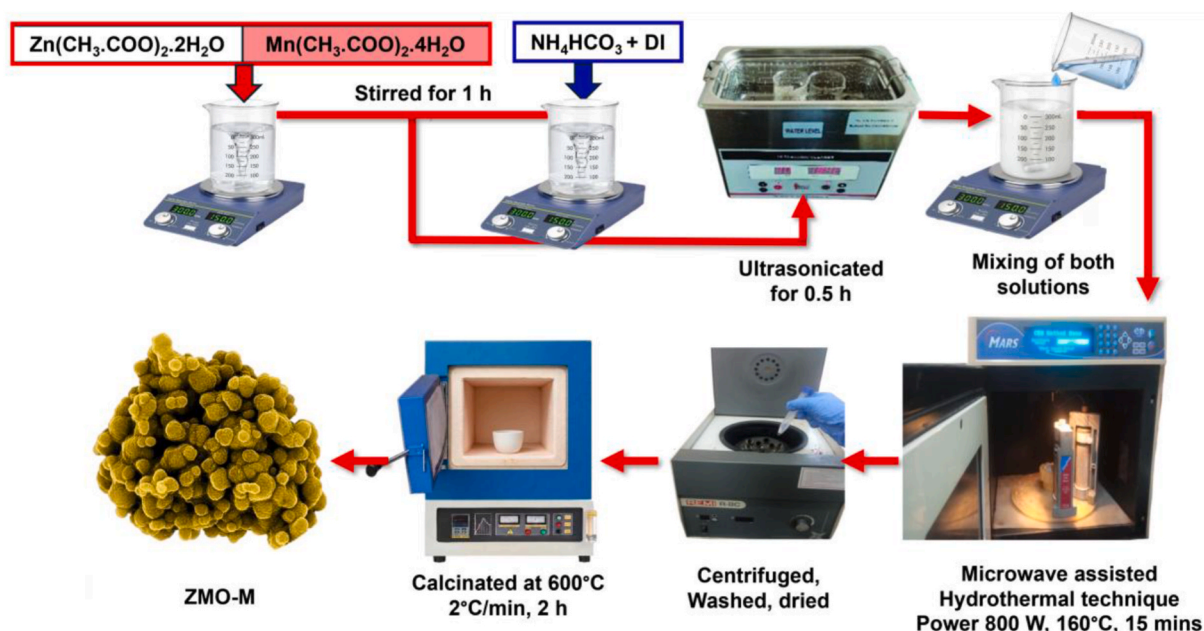


Fig. 1. Schematic illustration for the synthesis of porous ZnMn_2O_4 (ZMO-M).

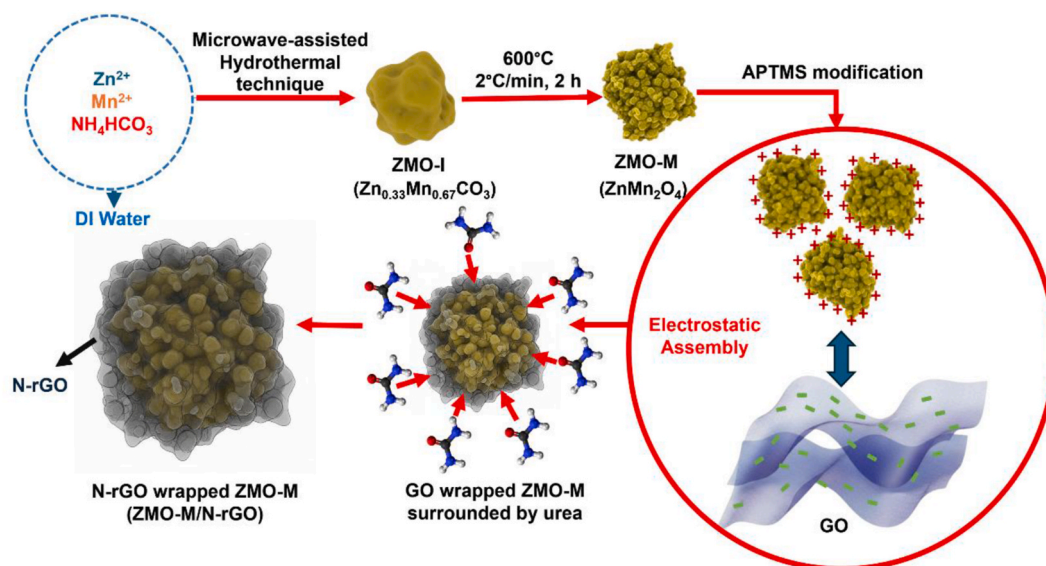


Fig. 2. Schematic illustration of the synthesis of the ZMO-M/N-rGO nanocomposite.

2.4. Material characterization

The phase composition, morphology, microstructure, and surface chemical properties of pristine porous ZnMn_2O_4 (ZMO-M) and the ZnMn_2O_4 /N-rGO nanocomposite (ZMO-M/N-rGO) were systematically investigated using a combination of structural, spectroscopic, microscopic, and surface characterization techniques.

Crystallographic phase analysis was performed by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating in Bragg–Brentano geometry. Diffraction patterns of the intermediate precursor (ZMO-I), pristine porous ZnMn_2O_4 (ZMO-M), and the ZnMn_2O_4 /N-rGO nanocomposite (ZMO-M/N-rGO) were recorded over a 2θ range of $10\text{--}80^\circ$ using a LynxEye position-sensitive detector to investigate phase evolution during synthesis and confirm the formation of the target ZnMn_2O_4 phase.

Raman spectroscopy was employed to investigate the structural characteristics and defect features of N-rGO in the nanocomposite. Raman spectra were collected using a laser confocal Raman spectrometer equipped with a 514 nm excitation source. Fourier-transform infrared (FTIR) spectroscopy was used to examine chemical bonding and surface functional groups, and the spectra were recorded on a Thermo Nicolet 6700 spectrometer in transmittance mode using KBr pellets.

The surface morphology and particle distribution were examined using field-emission scanning electron microscopy (FESEM, JEOL JSM-6500F) operated at accelerating voltages of 10 and 20 kV, with a working distance of approximately 10–12 mm, depending on the measurement. Elemental composition and spatial elemental distribution were analyzed by energy-dispersive X-ray spectroscopy (EDS) attached to the FESEM system. The microstructure and interfacial characteristics of the ZMO-M/N-rGO nanocomposite were further investigated by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) operated at 200 kV. Selected-area electron diffraction (SAED) patterns were recorded to assess crystallinity and phase structure. The microscope provides a point resolution of 0.23 nm and a lattice resolution of 0.14 nm.

The surface chemical states and elemental bonding environments were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 5400 ESCA system equipped with a non-monochromatic $\text{Al K}\alpha$ radiation source ($h\nu = 1486.7 \text{ eV}$). Measurements were performed under ultra-high vacuum conditions ($\sim 10^{-9}$ mbar), with the X-ray source operated at 200 W and an accelerating voltage of 13.5 kV. Survey spectra

were recorded at a pass energy of 89.45 eV, whereas high-resolution spectra were acquired at 71.55 eV. The obtained XPS data were processed using MultiPak v8.0 software.

2.5. Electrode preparation

Working electrodes were prepared by mixing the active material, Super P conductive carbon, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 using N-methyl-2-pyrrolidone (NMP) as the solvent. The resulting slurry was thoroughly homogenized and coated onto copper foil using the doctor-blade technique, followed by drying at 80°C for 12 h to remove residual solvent. Circular electrodes with a diameter of 8 mm were then punched from the dried coated foil. The active material loading was approximately 1.25 mg cm^{-2} for the pristine porous ZnMn_2O_4 (ZMO-M) electrode and 0.78 mg cm^{-2} for the ZnMn_2O_4 /N-rGO (ZMO-M/N-rGO) electrode employed in the cycling performance studies.

2.6. Lithium-ion half-cell fabrication and electrochemical measurements

CR2032-type coin half-cells were assembled in a high-purity argon-filled glovebox (Vigour SciLab, $\text{O}_2 < 1 \text{ ppm}$, $\text{H}_2\text{O} \sim 0.01 \text{ ppm}$), using lithium metal (10 mm diameter) as both the counter and reference electrode. The prepared ZMO-M and ZMO-M/N-rGO electrodes served as the working electrodes. A Whatman glass microfiber filter (16 mm diameter) was employed as the separator, while 1 M LiPF_6 dissolved in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte.

Electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS), were carried out using a Biologic BCS 810 battery testing system. CV measurements were recorded over a potential window of 0.01–3.0 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1} . GCD tests were performed within the same voltage range at various current densities to evaluate cycling stability and rate capability. EIS measurements were conducted over a frequency range of 10 kHz to 1 Hz with an AC perturbation amplitude of 10 mV before and after cycling. All electrochemical measurements were performed at room temperature.

3. Results and discussions

3.1. Structural and morphological analysis

3.1.1. XRD

Fig. 3 shows the XRD patterns obtained for the intermediate product ZMO-I, the calcined sample ZMO-M, and the ZMO-M/N-rGO nanocomposite along with the standard diffraction data of ZnMn_2O_4 (PDF#24-1133) and the intermediate carbonate precursors ZnCO_3 (PDF#08-0449) and MnCO_3 (PDF#44-1472).

The diffraction pattern of the intermediate sample, ZMO-I, exhibits peaks that match well with ZnCO_3 and MnCO_3 phases, confirming the formation of mixed metal carbonates during the microwave-assisted hydrothermal process [30,31]. The presence of these carbonate phases indicates that the ammonium hydrogen carbonate acted as a precipitating agent, leading to the co-precipitation of zinc and manganese carbonate intermediates prior to calcination. After calcination at 600 °C for 2 h with a heating rate of 2 °C min⁻¹, ZMO-M showed sharp and well-defined XRD peaks at 2θ values of 18.4°, 29.4°, 31.1°, 33.2°, 36.3°, 39.2°, 44.7°, 50.9°, 52.2°, 54.4°, 56.8°, 59.0°, 61.0°, 65.1°, and 75.0°. These XRD peak positions were compared with the standard diffraction data of ZnMn_2O_4 , PDF card No. 24-1133 and can be respectively indexed to the (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224), (400), and (413) crystallographic planes of

the tetragonal spinel ZnMn_2O_4 phase with space group $\text{I4}_1/\text{amd}$ [32,33]. The absence of any impurity peaks confirms that the carbonate precursor is fully converted to phase-pure ZnMn_2O_4 upon thermal treatment. Importantly, the XRD pattern of the ZMO-M/N-rGO composite obtained after the wrapping process exhibits diffraction peaks similar to those of pristine ZMO-M, indicating that the hydrothermal assembly and nitrogen-doping process did not alter the crystal structure of ZnMn_2O_4 . No distinct diffraction peak corresponding to graphene-based phases is observed, which can be attributed to their lower content with exfoliated nature, leading to an amorphous nature compared to the highly crystalline oxide framework.

Thus, the XRD results demonstrate that microwave-assisted hydrothermal synthesis proceeds via the formation of carbonate intermediate (ZMO-I), which is a mixture of ZnCO_3 and MnCO_3 phases, followed by calcination of this intermediate to yield crystalline spinel ZnMn_2O_4 , and subsequent N-rGO incorporation preserves the structural integrity of the metal oxide. Furthermore, the crystallite sizes of ZMO-M and ZMO-M/N-rGO were estimated using the Williamson–Hall (W–H) method based on the XRD peak broadening analysis. The corresponding W–H plots are provided in the Supplementary Information (Fig. S1). The average crystallite sizes obtained were approximately 25 nm for ZMO-M and 34 nm for ZMO-M/N-rGO. The increase in crystallite size observed for the ZMO-M/N-rGO nanocomposite can be attributed to the second-time hydrothermal treatment, which may have promoted crystallite growth and improved crystallinity. Nevertheless, the crystallite size remains within the nanoscale regime, which is beneficial, as smaller domains facilitate lithium-ion diffusion and enhance electrochemical performance when used as an anode material in lithium-ion batteries.

3.1.2. TG–DSC

Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was performed to investigate the thermal decomposition behavior of the intermediate carbonate precursor (ZMO-I) under flowing air at a heating rate of 20 °C min⁻¹. Fig. 4 shows the simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) curves recorded for the intermediate carbonate precursor (ZMO-I).

The TG curve reveals a multistep weight-loss process due to the removal of adsorbed species and the decomposition of mixed Zn–Mn carbonates. In the first stage, from 24.53 to 350.47 °C, a gradual weight loss of approximately 5.84% is observed, attributed to the desorption of physically adsorbed water and residual volatile species trapped within the porous precursor. This behavior is consistent with

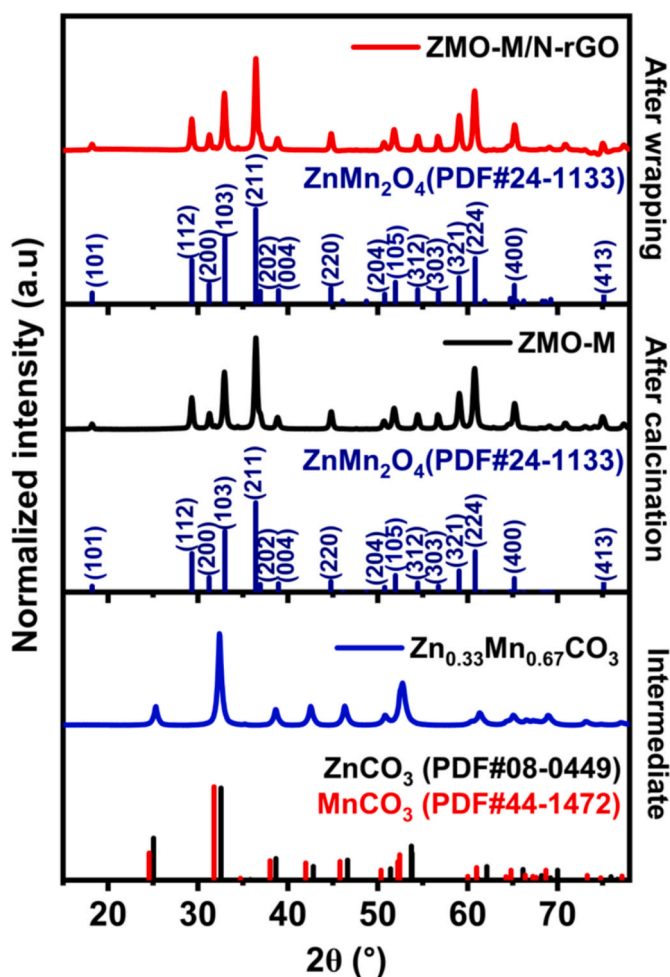


Fig. 3. XRD patterns of the intermediate carbonate precursor ZMO-I ($\text{Zn}_{0.33}\text{Mn}_{0.67}\text{CO}_3$) obtained after microwave-assisted hydrothermal treatment, the calcined sample ZMO-M, and the ZMO-M/N-rGO nanocomposite obtained after wrapping process, along with their corresponding JCPDS (PDF) reference patterns.

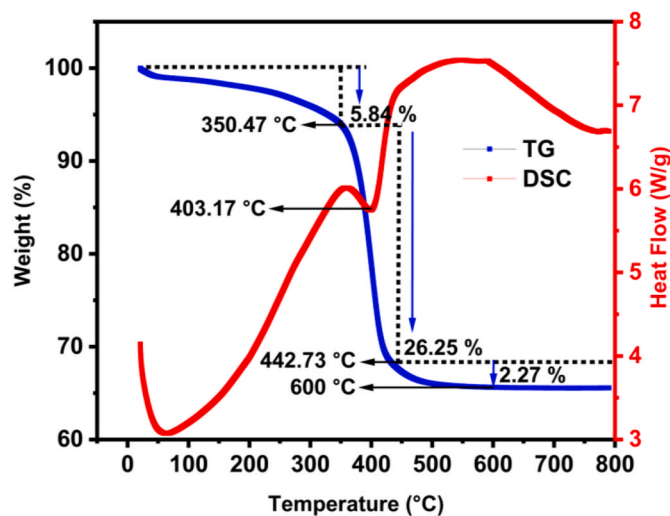


Fig. 4. Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of the intermediate carbonate precursor (ZMO-I).

previous reports on carbonate-based precursors [34].

In the second stage, from 350.47 to 442.73 °C, a major weight loss of about 26.25% occurs, which corresponds to the thermal decomposition of ZnCO_3 and MnCO_3 to spinel ZnMn_2O_4 , as reported for carbonate-derived systems [35]. The onset of this rapid decomposition begins near 359.92 °C, while the DSC curve shows a prominent thermal event centered at 403.17 °C, indicating the maximum rate of carbonate decomposition. The decomposition process undergoes its major weight loss between 350.47 and 442.73 °C, after which the rate of weight loss decreases substantially. However, the TG curve continues to show a gradual decrease in mass up to approximately 600 °C, above which it becomes essentially constant, indicating the attainment of a thermally stable state. Based on this thermal behavior, a calcination temperature of 600 °C for 2 h was selected to promote complete thermal conversion and adequate crystallization of the spinel ZnMn_2O_4 phase. The formation of the desired crystalline ZnMn_2O_4 phase under these conditions was subsequently confirmed by XRD.

3.1.3. Raman and FTIR

Fig. 5(a) shows the Raman spectra obtained for pristine ZnMn_2O_4 (ZMO-M) and the ZMO-M/N-rGO nanocomposite prepared through the second-time microwave-assisted hydrothermal wrapping process.

For the pristine ZMO-M sample, the Raman spectrum exhibits three characteristic vibrational modes located at approximately 320.91 cm^{-1} , 380.73 cm^{-1} , and 675.91 cm^{-1} , which correspond to the typical Raman-active modes of tetragonal spinel ZnMn_2O_4 . The bands at 320.91 cm^{-1} and 380.73 cm^{-1} can be assigned to the E_g -symmetric bending vibrations and T_{2g} stretching vibrations, respectively associated with Mn–O bonds in MnO_6 octahedral units. The sharp peak at 675.91 cm^{-1} corresponds to the A_{1g} symmetric stretching vibration of oxygen atoms in ZnO_4 tetrahedra. These Raman features are in good agreement with previously reported Raman studies on tetragonal ZnMn_2O_4 , confirming the successful formation of the spinel oxide phase after calcination [36–39].

After the microwave-assisted hydrothermal wrapping process with nitrogen-doped reduced graphene oxide, the Raman spectrum of the ZMO-M/N-rGO composite still exhibits the characteristic ZnMn_2O_4 vibrational modes at approximately 320.91 cm^{-1} , 380.73 cm^{-1} , and 665.10 cm^{-1} , indicating that the fundamental crystal structure of ZnMn_2O_4 remains preserved during the composite formation process. However, the A_{1g} mode becomes more prominent and exhibits a slight

shift toward lower wavenumbers compared to pristine ZMO-M, which may be attributed to subtle modifications in the local cation environment and metal-oxygen bond characteristics within the spinel lattice induced during the second-time hydrothermal treatment [38]. In addition to these oxide vibrational modes, the Raman spectrum of the ZMO-M/N-rGO composite exhibits two distinct graphitic bands located at 1357.28 cm^{-1} and 1601.18 cm^{-1} , corresponding to the D and G bands of graphene-based carbon materials, respectively. The D band arises from the A_{1g} breathing mode of disordered sp^2 carbon atoms and structural defects, whereas the G band corresponds to the E_{2g} in-plane stretching vibration of sp^2 -bonded carbon atoms in the graphene lattice [40]. The calculated I_D/I_G ratio for these bands for the ZMO-M/N-rGO composite is ~ 1.02 , which is higher than that of the pristine graphene oxide precursor used (0.85) as reported in the previous chapter, indicating the formation of defect-rich reduced graphene oxide during the second-time microwave heating [40,41]. These defect sites can enhance electrical conductivity and facilitate lithium-ion adsorption and diffusion within the electrode, thereby improving the electrochemical performance of lithium-ion batteries [42]. Overall, the Raman spectral analysis confirms that the characteristic vibrational modes of ZnMn_2O_4 are preserved after the nanocomposite formation, while the appearance of graphitic D and G bands verifies the successful integration of a conductive reduced graphene oxide (rGO) framework with the ZnMn_2O_4 structure.

Fig. 5(b) shows the FTIR spectra of pristine ZMO-M and the ZMO-M/N-rGO nanocomposite. The broad absorption band centered around 3419.17 cm^{-1} corresponds to the stretching vibration of surface –OH groups, which may arise from adsorbed moisture, residual hydroxyl groups on the metal oxide surface, or from the rGO surface [43]. The two weak bands observed at 2917.28 cm^{-1} and 2851.23 cm^{-1} are attributed to the asymmetric and symmetric C–H stretching vibrations, possibly originating from residual organic impurities from ethanol used in the washing process or from partially reduced graphene oxide sheets. The peak appearing near 1737.31 cm^{-1} can be assigned to C=O stretching vibrations from graphene oxide. The weak band observed around 1637.26 cm^{-1} may arise from C=C vibrations of residual carbonaceous species or skeletal vibrations of sp^2 -bonded carbon within oxidized graphitic domains. In contrast, the peak at 1569.29 cm^{-1} corresponds to the C=C stretching vibration of graphitic domains, indicating the presence of reduced graphene oxide in the composite [43–45]. The band appearing at 1406.81 cm^{-1} may be attributed to the symmetric

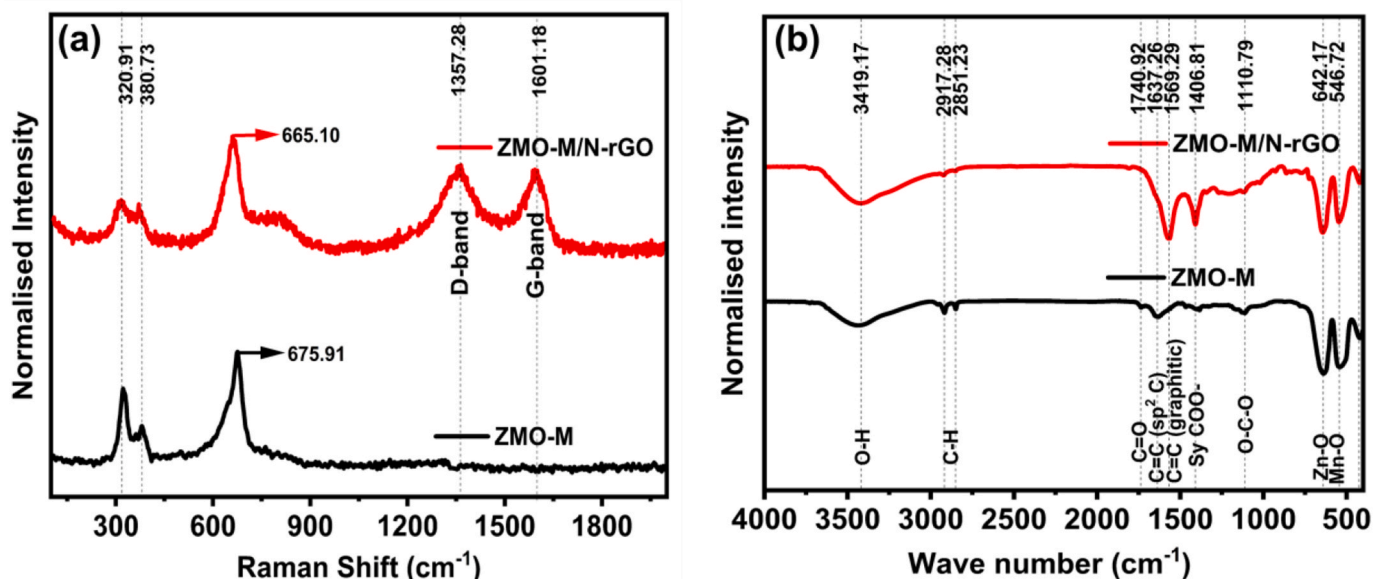


Fig. 5. (a) Raman and (b) FTIR spectra of the as-prepared ZMO-M and the nanocomposite, ZMO-M/N-rGO.

stretching vibration of carboxylate (COO^-) groups associated with residual oxygen-containing functional groups of graphene-based materials [46]. For ZMO-M/N-rGO, the peak at 1110.79 cm^{-1} is attributed to O–C–O stretching vibrations from epoxy or alkoxy functional groups present in GO. In contrast, for ZMO-M, this band is most likely due to C–O stretching vibrations from residual organic species, such as acetate or alcohol-derived fragments, or from surface carbonates formed through the adsorption of atmospheric CO_2 [43]. More importantly, the characteristic bands at 642.17 cm^{-1} and 548 cm^{-1} correspond to the Zn–O and Mn–O lattice vibrations, respectively, confirming the formation of the spinel ZnMn_2O_4 structure in ZMO-M and ZMO-M/N-rGO [11, 47]. The coexistence of these metal–oxygen vibrations together with graphene-related functional groups indicates the successful integration of the rGO framework with the ZnMn_2O_4 structure.

3.1.4. XPS

Fig. 6(a) presents the XPS survey spectra of pristine ZnMn_2O_4 (ZMO-

M) and the ZnMn_2O_4 /N-rGO nanocomposite (ZMO-M/N-rGO). The survey spectra confirm the presence of Zn, Mn, and O elements in both samples, verifying the formation of ZnMn_2O_4 . In addition, a distinct C 1s signal is observed in both samples, while the ZMO-M/N-rGO sample exhibits an additional N 1s peak, confirming the successful incorporation of nitrogen-doped reduced graphene oxide (N-rGO). The higher carbon intensity in the ZMO-M/N-rGO further indicates the presence of the graphene framework surrounding the ZnMn_2O_4 particles in the nanocomposite.

Fig. 6(b) and (f) show the high-resolution Zn 2p spectra of ZMO-M and ZMO-M/N-rGO, respectively. For the pristine ZMO-M sample, two characteristic peaks located at 1021.3 eV and 1044.4 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, with a spin-orbit splitting of 23.1 eV, which is consistent with the typical binding energy values of Zn^{2+} in spinel ZnMn_2O_4 . For the ZMO-M/N-rGO, the Zn 2p peaks appear at 1021.8 eV and 1045.0 eV, maintaining a similar spin-orbit separation of 23.2 eV, confirming Zn^{2+} oxidation state in the nanocomposite [48,49].

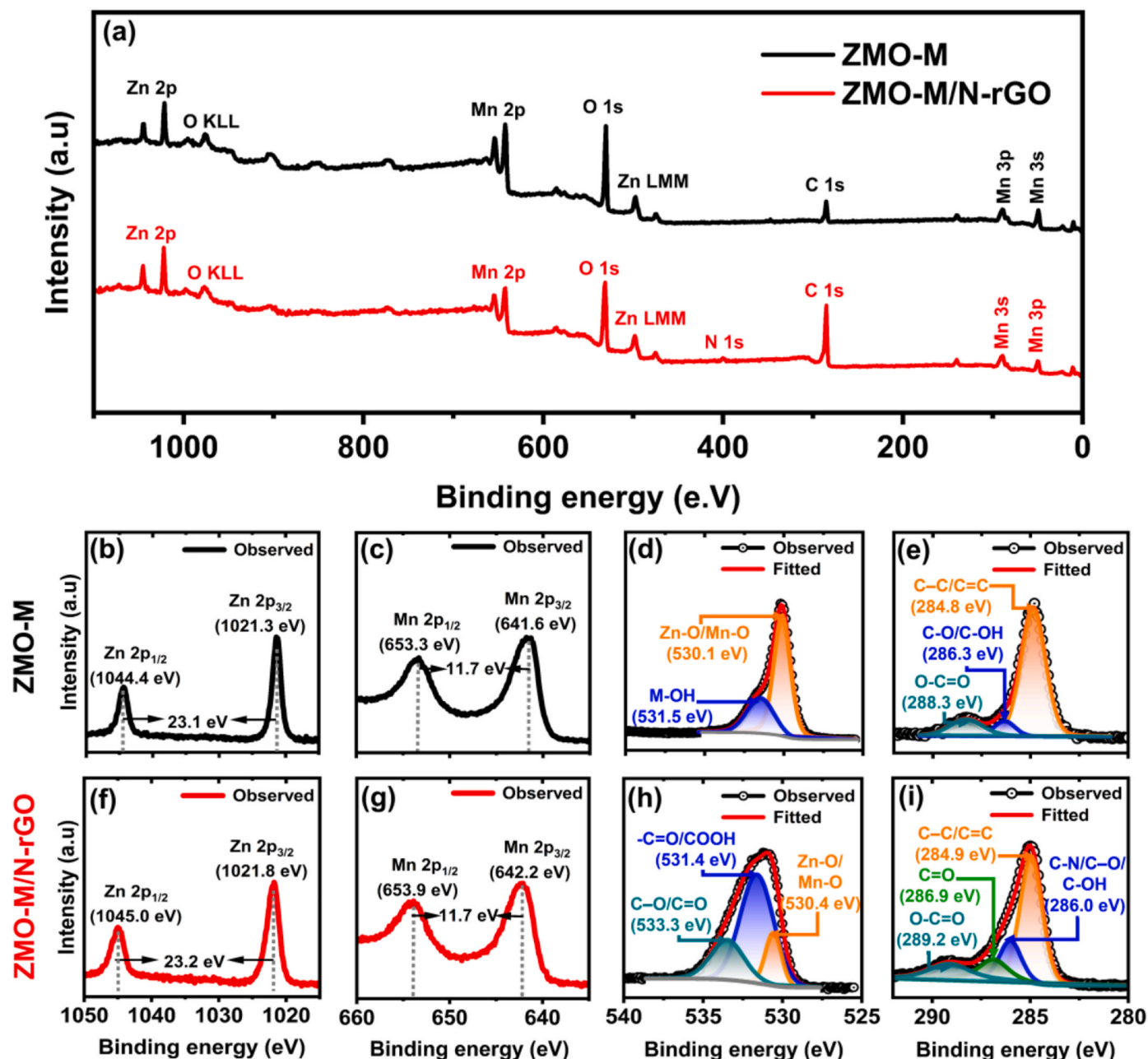


Fig. 6. XPS spectra of ZMO-M and ZMO-M/N-rGO: (a) Survey spectra, High-resolution Zn 2p, Mn 2p, O 1s, and C 1s spectra of (b–e) ZMO and (f–i) ZMO-M/N-rGO.

A slight positive shift in the Zn 2p binding energy compared to pristine ZMO-M suggests a modification in the local electronic environment of Zn ions due to strong interfacial interaction between ZnMn_2O_4 nanoparticles and the conductive N-rGO framework [50]. Similarly, Fig. 6(c) and (g) show the high-resolution Mn 2p spectra of ZMO-M and ZMO-M/N-rGO. Due to the complex spectral features associated with transition metals, particularly Mn 2p, spectra are interpreted based on characteristic binding energies and spin-orbit splitting, without detailed peak deconvolution [51]. In the pristine ZMO-M sample, the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks appear at 641.6 eV and 653.3 eV, respectively, with a spin-orbit separation of 11.7 eV, which is a characteristic of Mn^{3+} in ZnMn_2O_4 [52,53]. In the ZMO-M/N-rGO sample, the Mn 2p peaks shift slightly toward higher binding energies, appearing at 642.2 eV and 653.9 eV while maintaining the same spin-orbit splitting of 11.7 eV. Such a slight positive shift suggests a modification in the local electronic environment of Mn ions. The slight positive shift in the Mn 2p binding energy may arise from subtle changes in the local ligand field, Mn–O covalency, or surface coordination environment, as well as interfacial charge redistribution between the oxide and graphene framework [54, 55]. Furthermore, although the Mn 2p spectra are dominated by features consistent with Mn^{3+} , the possible presence of minor surface Mn^{2+} and/or Mn^{4+} species cannot be completely excluded. However, reliable quantitative determination of the relative contributions of different Mn oxidation states from the Mn 2p spectra requires reference-based multiplet fitting because the Mn 2p region exhibits complex multiplet and satellite structures, even for materials containing a single Mn valence state [56,57]. Moreover, variations in the multiplet-fitting parameters can introduce significant uncertainty in the calculated Mn oxidation-state composition [56]. Therefore, the present XPS analysis is best interpreted as indicating Mn^{3+} as the predominant Mn oxidation state, without assigning quantitative fractions to possible minor $\text{Mn}^{2+}/\text{Mn}^{4+}$ surface species.

Fig. 6(d) and (h) present the deconvoluted O 1s spectra of ZMO-M and ZMO-M/N-rGO, respectively. For the pristine ZMO-M sample, the O 1s spectrum can be resolved into two main components. The dominant peak located at 530.1 eV is assigned to lattice oxygen (Zn–O/Mn–O) in the spinel ZnMn_2O_4 structure, consistent with previously reported values [11,58]. The second component, centered at 531.5 eV, corresponds to surface hydroxyl species (M – OH), which are commonly associated with adsorbed water molecules or hydroxylated surface sites formed during the hydrothermal synthesis process [11,58]. In contrast, the ZMO-M/N-rGO nanocomposite exhibits three distinct oxygen components. The peak at 530.4 eV is attributed to lattice oxygen (Zn–O/Mn–O) within the ZnMn_2O_4 framework [58]. The intermediate peak centered at 531.4 eV is associated with C=O and COOH functional groups on the graphene sheets [59]. The relatively higher intensity of this component in the ZMO-M/N-rGO nanocomposite indicates that graphene oxide wraps around the ZnMn_2O_4 nanoparticles. A third peak at 533.3 eV is assigned to oxygen-containing functional groups, such as C–O–C and C–OH, originating from the N-rGO sheets [59]. The presence of these additional oxygenated groups confirms the successful incorporation of the N-rGO framework and suggests strong interfacial interaction between ZnMn_2O_4 nanoparticles and the graphene sheets.

Fig. 6(e) and (i) show the deconvoluted high-resolution C 1s spectra of ZMO-M and ZMO-M/N-rGO, respectively. For the pristine ZMO-M sample, the C 1s spectrum can be resolved into three components located at 284.8, 286.3, and 288.3 eV, corresponding to C–C/C=C, C–O/C–OH, and O–C=O species, respectively. These carbon signals mainly arise from adventitious carbon adsorbed on the surface during sample handling and exposure to ambient atmosphere air [60]. In contrast, the ZMO-M/N-rGO nanocomposite exhibits a dominant peak centered at 284.9 eV, corresponding to the sp^2 -hybridized graphitic C–C/C=C bonds of the reduced graphene oxide structure, along with additional peaks at 286.0, 286.9, and 289.2 eV, which are attributed to C–N/C–O/C–OH, C=O, and O–C=O functional groups, respectively [61,62]. Because the binding energy ranges of C–N and C–O species are

very close in the C 1s region, distinguishing these two contributions reliably is challenging [61,62]. Therefore, the presence of nitrogen within the graphene framework is more convincingly verified through analysis of the high-resolution N 1s spectrum, which is commonly used to confirm nitrogen doping in reduced graphene oxide systems [43, 61–63].

Fig. 7(a) shows the deconvoluted high-resolution N 1s XPS spectrum of the ZMO-M/N-rGO nanocomposite. The spectrum can be resolved into three characteristic components centered at approximately 398.98 eV, 400.18 eV, and 401.68 eV, which are assigned to pyridinic, pyrrolic, and graphitic nitrogen, respectively, consistent with previously reported nitrogen-doped graphene systems [64–68]. The presence of these three nitrogen configurations confirms the successful incorporation of nitrogen atoms within the reduced graphene oxide framework of the nanocomposite. The identified nitrogen bonding configurations from the N 1s deconvolution are schematically illustrated in Fig. 7(b). Pyridinic nitrogen atoms, represented in green, are typically located at the edge or defect sites of the graphene lattice and are bonded to two sp^2 -hybridized carbon atoms. These atoms possess a localized lone pair of electrons and contribute one π -electron to the conjugated π system of graphene. The presence of pyridinic nitrogen is known to increase defect density and modify the local electronic structure of the carbon framework [65,69]. Such defect-rich sites enhance surface polarity and improve electrolyte wettability, thereby facilitating interfacial charge-transfer processes during electrochemical reactions [65,69]. Meanwhile, the Pyrrolic nitrogen atoms, shown in pink, are incorporated within five-membered ring structures associated with defect regions of the graphene lattice and contribute two π -electrons to the aromatic π network. The presence of pyrrolic N increases the chemical reactivity of the carbon framework and provides additional adsorption sites for lithium ions, thereby promoting surface-controlled and pseudocapacitive lithium storage behavior [65,69]. In contrast, graphitic nitrogen atoms, shown in red, result from the substitution of carbon atoms within the basal plane of the graphene lattice and are bonded to three sp^2 -hybridized carbon atoms. This configuration contributes delocalized π -electrons to the graphene framework and is widely reported to enhance the electronic conductivity of nitrogen-doped carbon materials [64,65]. To quantify the distribution of these nitrogen species, the relative contribution of each component was calculated from the integrated peak area of the fitted N 1s peaks. As shown in Fig. 7(c), pyridinic N is the dominant nitrogen species ($\approx 58.96\%$), followed by graphitic N ($\approx 24.89\%$) and pyrrolic N ($\approx 15.99\%$). The predominance of pyridinic nitrogen indicates the presence of abundant edge and defect sites within the N-rGO structure, while the presence of graphitic nitrogen suggests nitrogen incorporation within the graphene basal plane, which can contribute to improved electronic conductivity of the nanocomposite.

Thus, XPS analysis confirms the presence of Zn, Mn, and O, along with a small amount of adventitious carbon in the pristine ZMO-M sample, confirming the formation of ZnMn_2O_4 . In contrast, the ZMO-M/N-rGO nanocomposite exhibits a strong C signal and a weak N signal due to the incorporation of the N-doped graphene framework. Importantly, the deconvolution of the high-resolution N 1s spectrum further confirms the successful incorporation of nitrogen into the reduced graphene oxide, indicating the formation of N-rGO within the nanocomposite.

3.1.5. FESEM and EDX

FESEM was employed to investigate the surface morphology of the pristine ZMO-M and ZMO-M/N-rGO nanocomposite. Fig. 8(a–c) present the FESEM images of pristine ZMO-M at different magnifications. The images reveal that ZMO-M consists of agglomerated nanoparticles forming a porous architecture. The presence of numerous interparticle voids and pores is clearly observed, originating from the decomposition of the carbonate precursor during calcination [12,35]. Such porous structures are beneficial for lithium-ion diffusion and electrolyte penetration [17,70]. Fig. 8(d–f) show FESEM images of ZMO-M/N-rGO,

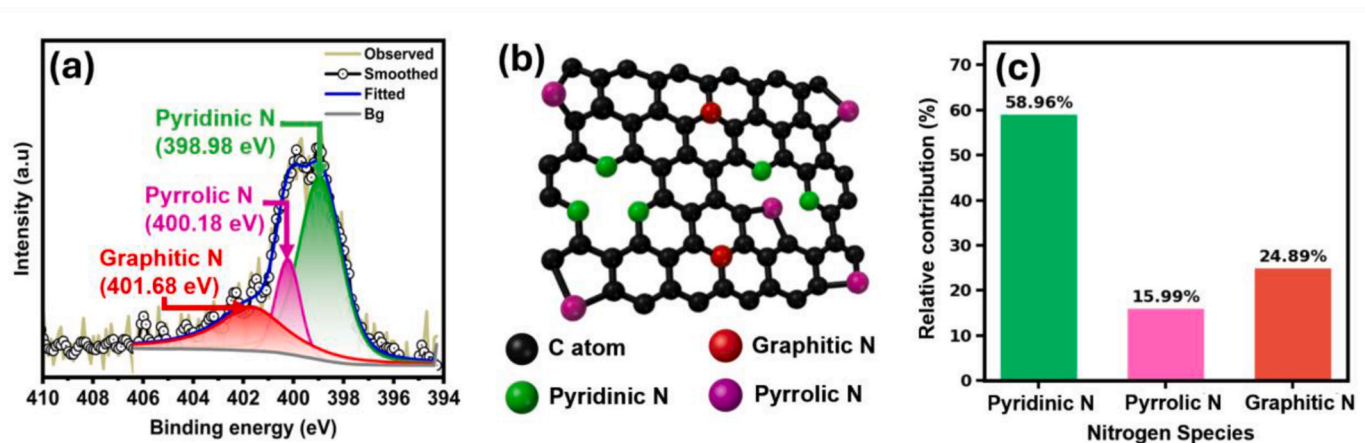


Fig. 7. (a) Deconvoluted high-resolution N 1s XPS spectrum of the ZMO-M/N-rGO nanocomposite, (b) Schematic illustration of the identified nitrogen configurations within the graphene lattice. (c) Relative contribution of different nitrogen species calculated from the integrated peak areas of the fitted N 1s components.

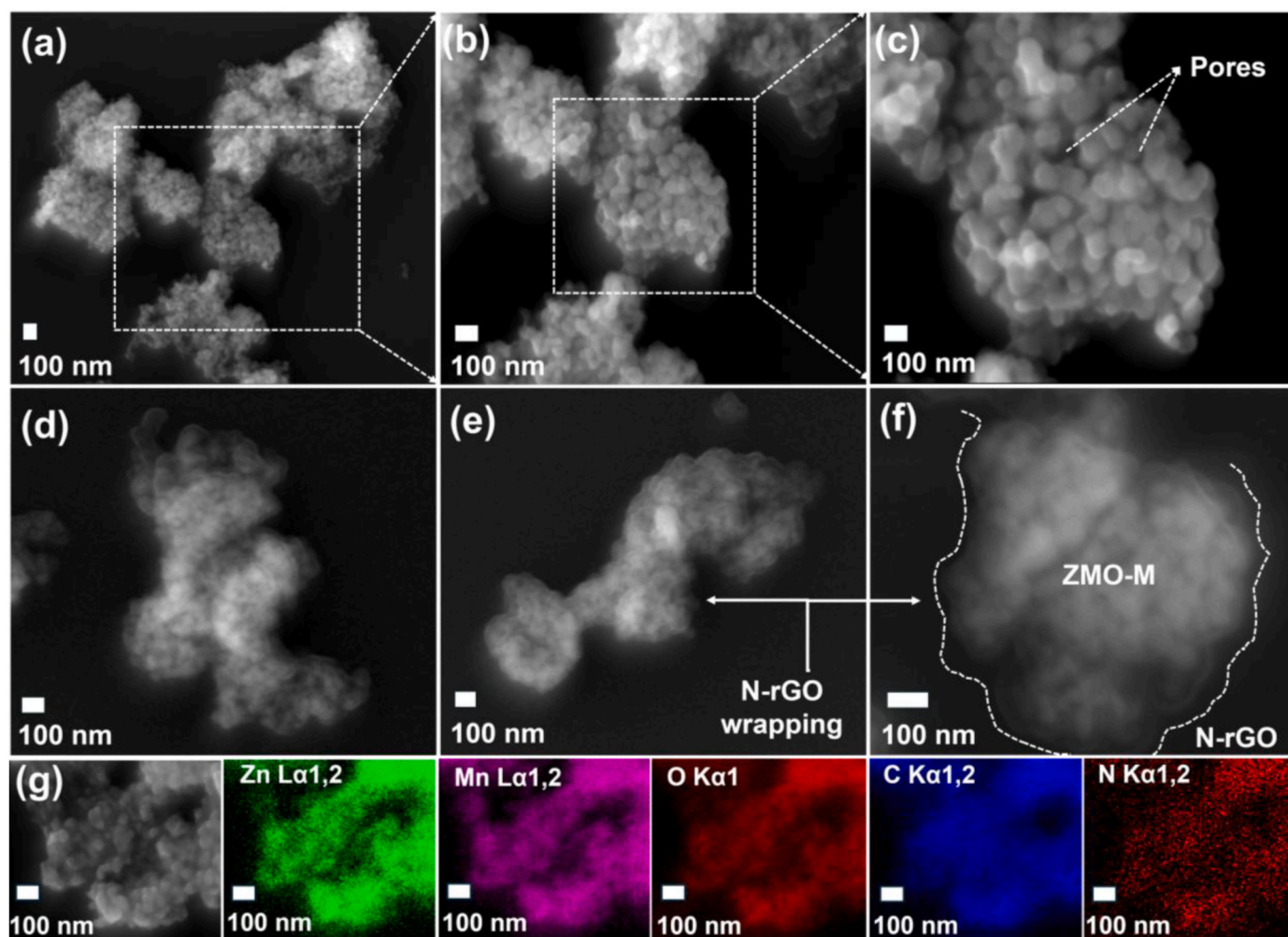


Fig. 8. FESEM images of (a-c) pristine ZMO-M and (d-f) ZMO-M/N-rGO nanocomposite (g) FESEM image of ZMO-M/N-rGO and corresponding elemental mapping images showing the distribution of Zn, Mn, O, C, and N elements throughout the nanocomposite.

revealing the nanocomposite morphology. Compared with pristine ZMO-M, N-rGO sheets are observed in close association with and extending around the ZMO-M nanoparticle aggregates, forming an interconnected oxide-carbon framework. The graphene sheets appear around and in close contact with the ZMO-M aggregates, suggesting

partial association and wrapping of the ZMO-M nanoparticle aggregates by N-rGO sheets during the second microwave-assisted hydrothermal treatment. This interconnected N-rGO framework is expected to facilitate electron transport and may help maintain structural integrity by accommodating volume variations of ZnMn_2O_4 during repeated

lithiation–delithiation.

To further examine the elemental composition and distribution of the pristine and composite materials, EDX elemental mapping was performed. Fig. S2 shows the FESEM image acquired during the EDX measurement of pristine ZMO-M together with the corresponding elemental maps, confirming the distribution of Zn, Mn, O, and C throughout the material. Fig. 8(g) displays the FESEM image of ZMO-M/N-rGO and the corresponding elemental mapping images showing the distribution of Zn, Mn, O, C, and N elements throughout the nanocomposite. The spatial distribution of carbon and nitrogen signals further supports the incorporation and distribution of the N-containing carbon framework in the nanocomposite. The N-rGO wrapping together with the porous ZMO-M architecture may provide efficient electron-transport pathways, improved electrolyte accessibility, and enhanced structural stability, thereby contributing to the superior rate capability and long-term cycling performance of the ZMO-M/N-rGO electrode [23].

3.1.6. HRTEM and SAED

To further investigate the nanoscale morphology and interfacial structure of the ZMO-M/N-rGO nanocomposite, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed. The FESEM observations indicate the close association of N-rGO sheets with the ZMO-M nanoparticle aggregates. However, the nanoscale features of the ZnMn_2O_4 -N-rGO interface cannot be fully resolved by FESEM. TEM provides higher spatial resolution, thereby enabling more direct visualization of the ZMO-M–N-rGO interfacial contact. Prior to TEM analysis, the ZMO-M/N-rGO sample was ultrasonicated in ethanol to disperse agglomerated particles and partially exfoliate the N-rGO sheets, facilitating better observation of the interfacial structure.

Fig. 9(a), (b), and (d) show TEM images of the ultrasonicated ZMO-M/N-rGO nanocomposite at different magnifications. The low-magnification TEM image in Fig. 9(a) reveals loosely agglomerated ZnMn_2O_4 nanoparticles dispersed after ultrasonication. Although the porous architecture observed in the FESEM images is not directly distinguishable owing to particle dispersion during TEM sample preparation, the image confirms the nanoparticulate nature of the ZnMn_2O_4 phase. Fig. 9(b) and (d) present enlarged views of the selected regions

from Fig. 9(a). At lower magnification, as shown in Fig. 9(b), the graphene layers are not clearly distinguishable; however, higher-magnification imaging reveals thin N-rGO sheets in intimate contact with the ZnMn_2O_4 nanoparticles, as shown in Fig. 9(c) and (d).

As shown in Fig. 9(c), an N-rGO layer with an estimated thickness of approximately 2.3 nm can be observed adjacent to the ZnMn_2O_4 particle, indicating successful coating of the oxide surface. The lattice spacing was determined from the HRTEM image using FFT and inverse FFT analysis. A filtered inverse FFT image of the boxed region is shown in the inset of Fig. 9(c), exhibiting well-defined lattice fringes with an interplanar spacing of 0.31 nm, corresponding to the (112) plane of tetragonal ZnMn_2O_4 , confirming the crystalline nature of the nanoparticles [71]. Further evidence of the wrapping configuration is provided in Fig. 9(d), where an N-rGO sheet with an estimated thickness of approximately 3.3 nm is observed partially covering the ZnMn_2O_4 particle. These observations suggest that the second time microwave-assisted hydrothermal treatment promotes intimate wrapping of N-rGO sheets around the ZnMn_2O_4 nanoparticles, leading to the formation of a well-integrated oxide–carbon interface.

The HRTEM image shown in Fig. 9(e) further confirms the crystalline nature of the ZnMn_2O_4 nanoparticle. The corresponding FFT/inverse FFT processed inset image exhibits well-defined lattice fringes with an interplanar spacing of 0.19 nm, which can be indexed to the (123) plane of tetragonal ZnMn_2O_4 . The observed lattice spacings from the HRTEM images are in good agreement with the XRD results, further confirming the formation of crystalline spinel ZnMn_2O_4 . The SAED pattern shown in Fig. 9(f) consists of a series of concentric diffraction rings, indicating the polycrystalline nature of the ZnMn_2O_4 nanoparticles. The measured ring-radius ratios of 1:1.69:2.51 agree well with the theoretical ratios corresponding to the (011), (020), and (123) planes of tetragonal ZnMn_2O_4 , thereby confirming the formation of the spinel crystal structure.

Overall, the TEM, HRTEM, and SAED analyses confirm the successful integration of N-rGO with ZnMn_2O_4 nanoparticles and the formation of intimate oxide–graphene sheet interfacial contact. This wrapping structure may enhance electron transport, facilitate Li^+ diffusion, and improve the rate capability and cycling stability of the ZMO-M/N-rGO electrode [12,23,72].

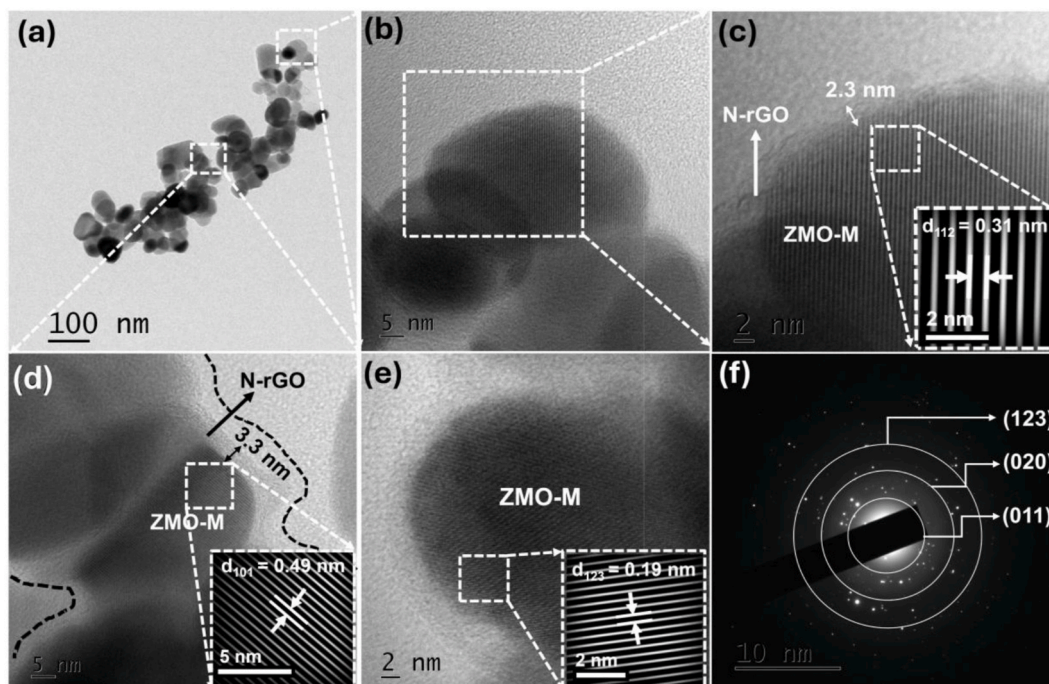


Fig. 9. (a, b, d) TEM images, (c, e) HRTEM images, and (f) SAED pattern of the ZMO-M/N-rGO nanocomposite.

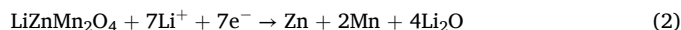
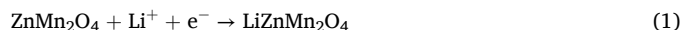
3.2. Electrochemical performance of pristine ZMO-M and ZMO-M/N-rGO nanocomposite

The electrochemical performance of ZMO-M and ZMO-M/N-rGO electrodes is discussed in detail in the following sections.

3.2.1. Cyclic voltammetry

Fig. 10(a) and (c) show the cyclic voltammograms of the pristine ZMO-M electrode and ZMO-M/N-rGO, respectively, while Fig. 10(b) and (d) show the corresponding magnified views of the boxed regions.

For the pristine ZMO-M electrode, the first cathodic scan exhibits two broad reduction peaks at 1.26 V and 0.73 V, along with a sharp, intense peak at 0.23 V, as shown in Fig. 10(a). The peak at 1.26 V corresponds to the initial insertion of Li^+ into the ZnMn_2O_4 lattice, accompanied by the reduction of Mn^{3+} to Mn^{2+} , leading to the formation of an intermediate $\text{LiZnMn}_2\text{O}_4$ (intercalation process) phase as represented in Equation (1) [73] and marking the onset of structural transformation prior to the subsequent conversion reaction. The smaller broad feature at 0.73 V is attributed to electrolyte decomposition and the formation of the solid electrolyte interphase (SEI) layer [11,12,21,73]. The sharp cathodic peak at 0.23 V is associated with the subsequent conversion reaction of Zn^{2+} and Mn^{2+} to their metallic states, Zn^0 and Mn^0 , accompanied by the formation of Li_2O as represented by Equation (2), followed by alloying of Zn with Li [11,12,74] as represented by Equation (3). The complete reduction processes can be represented as follows:



During the first anodic scan, two distinct oxidation peaks are observed at 1.23 V and 1.56 V, which can be associated with the oxidation of Mn^0 and Zn^0 , respectively, together with the dealloying of LiZn [21]. These reactions collectively represent the reversible delithiation process, which can be summarized as:



In the second cycle, the cathodic peak at 1.26 V disappears, indicating the irreversible nature of the initial intercalation and structural transformation process, while the SEI-related peak persists with minor shifts. A single prominent cathodic peak appears at 0.50 V, corresponding to the reversible conversion reaction of Zn^{2+} and Mn^{2+} to their metallic states [21,73,74]. In the subsequent third, fourth, and fifth cycles, similar peaks are observed with slight shifts and poor overlap. The gradual shift of the cathodic peak from 0.50 V to 0.49 V and the reduction in peak intensity indicate increased polarization and limited reversibility of the pristine ZMO-M electrode, consistent with previous reports [11,73,75]. The persistence and growth of the SEI-related feature further indicate unstable interfacial behavior during the initial 5 cycles.

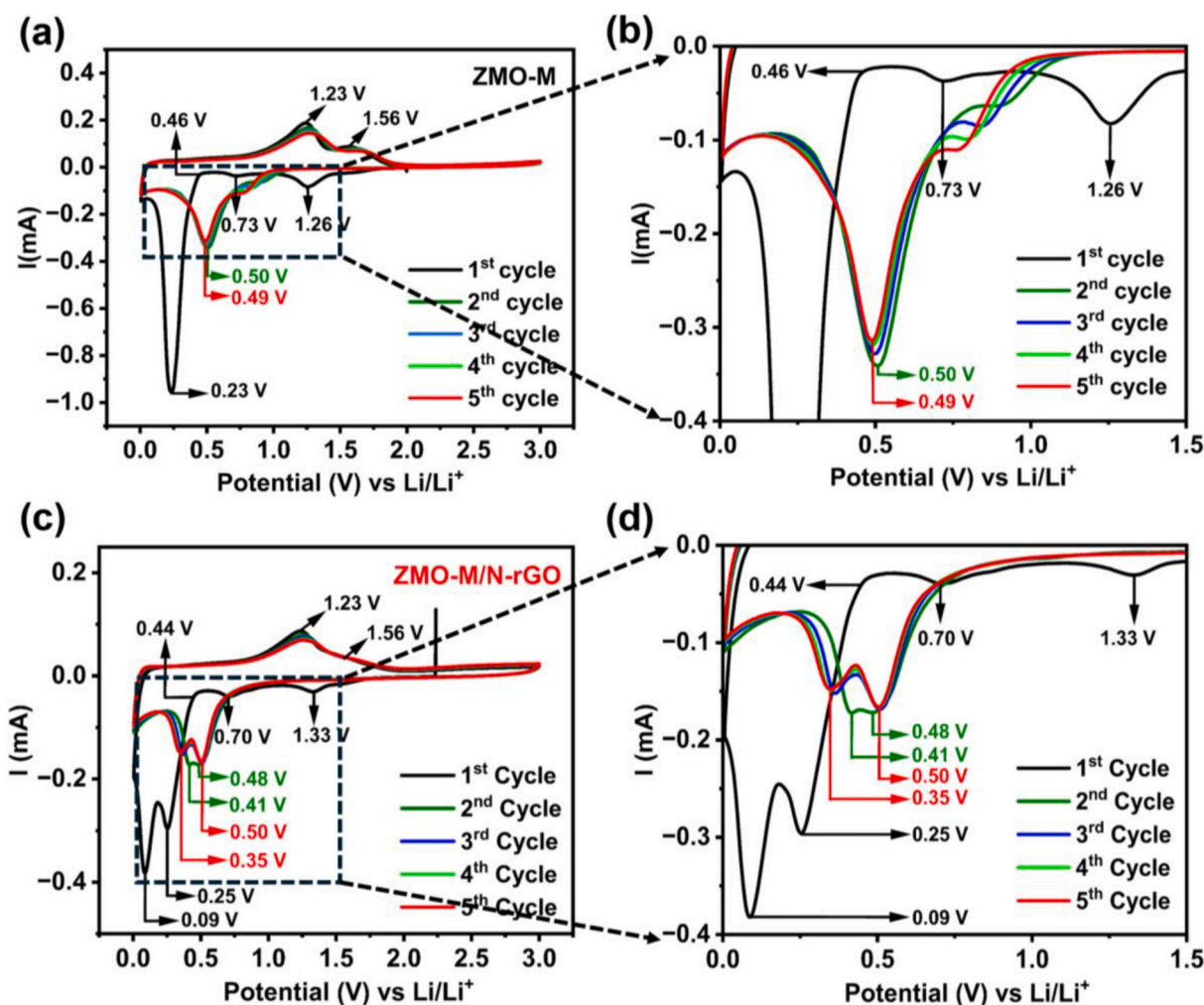


Fig. 10. Cyclic voltammograms of (a,b) ZMO-M and (c,d) ZMO-M/N-rGO electrodes recorded for the first five cycles with their respective magnified views highlighting the low-potential cathodic region.

For the ZMO-M/N-rGO nanocomposite electrode, the first cathodic scan exhibits two reduction peaks at 1.33 V and 0.70 V, corresponding to Mn^{3+} reduction and SEI formation, respectively, as shown in Fig. 10(c) and (d). The positive shift in the Mn^{3+} reduction peak relative to ZMO-M indicates reduced polarization and improved reaction kinetics, due to the conductive N-rGO framework [76,77]. Interestingly, at lower potentials, instead of a single sharp peak (0.23 V) observed for pristine ZMO-M, two distinct cathodic peaks at 0.25 V and 0.09 V are observed. This clearly indicates that the lithiation process proceeds through a stepwise mechanism involving conversion followed by alloying, rather than a single overlapping process. The peak at ~ 0.25 V may correspond to the primary conversion reaction [73] described by Equation (2), and the additional peak at 0.09 V can be attributed to Li–Zn alloy formation, in agreement with Zn-based alloying behavior [78]. During the first anodic scan, oxidation peaks at 1.23 V and 1.56 V correspond to the reversible oxidation of Mn^0 and Zn^0 , as described by Equation (4). In the second cycle, during the cathodic scan, the SEI-related peak (0.73 V) disappears, indicating the formation of a stable SEI layer during the first cycle when compared to pristine ZMO-M. The single cathodic peak observed at 0.50 V for pristine ZMO-M evolves into two closely spaced peaks at 0.48 V and 0.41 V in the ZMO-M/N-rGO electrode, as shown in Fig. 10(d). This suggests that the reversible conversion reaction of Zn^{2+} and Mn^{2+} to their metallic states in the second cycle also occurs through

partially separated electrochemical processes rather than a single overlapping step. As shown in Fig. 10 (d), in the subsequent third, fourth, and fifth cycles, the peak splitting became more prominent with well-resolved peaks at 0.50 V and 0.35 V at the fifth cycle. More importantly, the SEI-related peak was absent, and the CV curves exhibit excellent overlap with negligible peak shifts, as shown in Fig. 10(c) and (d). The absence of persistent SEI-related features indicates improved interfacial stability, the well-defined peak splitting reflects a fully established stepwise conversion-alloying mechanism, and the excellent overlap of CV curves with negligible peak shifts indicates enhanced reversibility and reduced polarization. The improved electrochemical performance of the ZMO-M/N-rGO nanocomposite can be attributed to the synergistic effect of N-rGO wrapping, which enhances electronic conductivity, facilitates charge transfer, and promotes surface-controlled pseudocapacitive lithium storage, resulting in improved kinetics and cycling stability compared to the pristine ZMO-M electrode [25,79–83].

Overall, the ZMO-M/N-rGO electrode demonstrates significantly improved electrochemical kinetics, reduced polarization, enhanced reversibility, and stable SEI formation, with the conversion reaction proceeding through a well-defined stepwise mechanism compared to the pristine ZMO-M electrode.

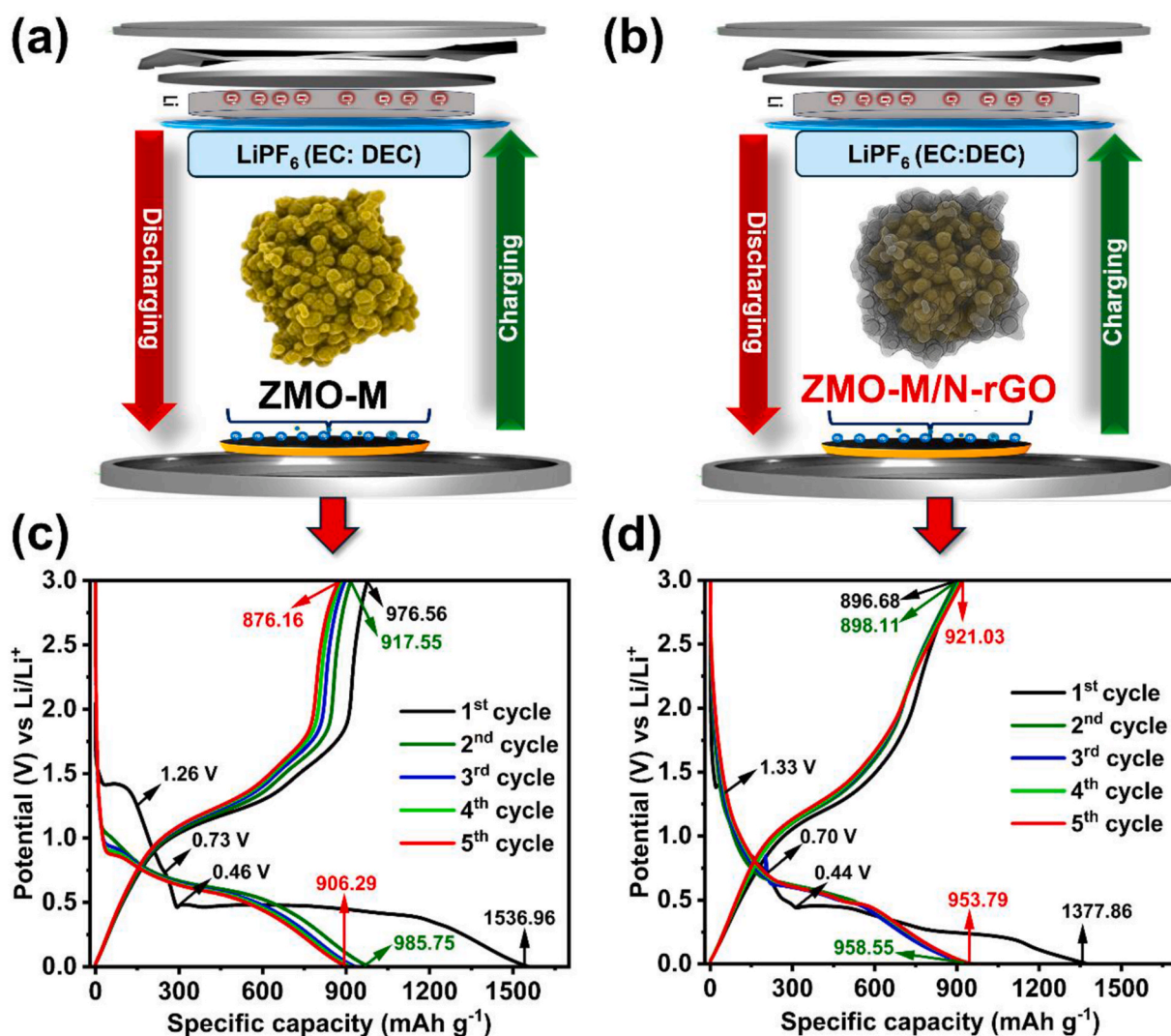


Fig. 11. Schematic illustration of the fabricated Li-ion half-cells with (a) pristine ZMO-M and (b) ZMO-M/N-rGO as the anode materials, along with the corresponding galvanostatic charge-discharge curves of (c) ZMO-M and (d) ZMO-M/N-rGO recorded for the first five cycles at a current density of 100 mA g⁻¹.

3.2.2. Galvanostatic charge–discharge

Fig. 11(a) and (b) show the schematic illustrations with various components of the fabricated Li-ion half-cells using pristine ZMO-M and ZMO-M/N-rGO as the anode materials, respectively. The galvanostatic charge–discharge (GCD) curves of these cells are presented in Fig. 11(c) and (d), where Fig. 11(c) corresponds to the pristine ZMO-M electrode and Fig. 11(d) corresponds to the ZMO-M/N-rGO electrode.

As shown in Fig. 11(c), the pristine ZMO-M electrode exhibits two distinct discharge plateaus in the voltage range 1.42–0.01 V during the first lithiation process. The initial plateau from ~1.42 to 0.46 V corresponds to the combined contributions of Mn^{3+} reduction to Mn^{2+} and SEI formation [11].

The second, long and prominent discharge plateau extending from ~0.46 V toward lower potentials corresponds to the irreversible conversion reaction of ZnMn_2O_4 into metallic Zn and Mn, along with Li_2O and Li–Zn alloy formation as represented in Equations (1) and (2) [73]. Accordingly, the first discharge capacity reaches $1536.96 \text{ mA h g}^{-1}$, which is significantly higher than the theoretical capacity ($\sim 1008 \text{ mA h g}^{-1}$) due to additional contributions from the reduction of Mn^{3+} to Mn^{2+} and SEI formation [11] as discussed in the previous chapter. During the first charging process, a capacity of $976.56 \text{ mA h g}^{-1}$ is obtained, indicating substantial irreversible Li^+ consumption during the first discharge, resulting in a low initial coulombic efficiency of 63.5% in the first cycle. In the second cycle, the discharge and charge specific capacities further decrease to $985.75 \text{ mA h g}^{-1}$ and $917.55 \text{ mA h g}^{-1}$, respectively, resulting in an improved coulombic efficiency of 93.1%. The excess capacity beyond the theoretical limit ($\sim 784 \text{ mA h g}^{-1}$) may be due to synergistic contributions of surface-controlled pseudocapacitive lithium storage and reversible lithium storage in the SEI layer, rather than solely from SEI formation [73,84]. However, noticeable voltage hysteresis and poor overlap of charge–discharge curves in subsequent cycles indicate increased polarization, unstable SEI formation, and structural degradation, possibly due to particle pulverization and loss of electrical contact, consistent with the CV results [11,73,75]. After the fifth cycle, the specific discharge and charge capacities further decrease to 906.29 and $876.16 \text{ mA h g}^{-1}$, respectively, corresponding to a coulombic efficiency of 96.7%, confirming the limited cycling stability of the ZMO-M electrode during the initial cycles.

In contrast, as shown in Fig. 11(d), the ZMO-M/N-rGO nanocomposite electrode exhibits distinct and improved charge–discharge characteristics compared to ZMO-M. During the first discharge, two well-defined discharge plateaus are observed in the voltage range ~1.39–0.01 V. The initial plateau in the ~1.39–0.44 V range corresponds to the reduction of Mn^{3+} to Mn^{2+} along with SEI formation, consistent with the CV results. The subsequent long plateau extending from ~0.44 to ~0.25 V is attributed to the primary conversion reaction of ZnMn_2O_4 into metallic Zn and Mn, accompanied by Li_2O formation [73]. In addition, the low-potential region is influenced by subsequent lithiation processes, as evidenced by the CV peak at 0.09 V, which corresponds to Li–Zn alloy formation [78]. The first discharge and charge capacities are significantly enhanced to $1377.86 \text{ mA h g}^{-1}$ and $896.68 \text{ mA h g}^{-1}$, respectively, resulting in an initial coulombic efficiency of 65.1%, which is slightly higher than that of pristine ZMO-M (63.5%). The observed marginal improvement indicates the partial suppression of irreversible Li^+ consumption and improved interfacial stability, both enabled by the N-rGO framework. In the second cycle, the discharge and charge capacities stabilize at $958.55 \text{ mA h g}^{-1}$ and $898.11 \text{ mA h g}^{-1}$, respectively, corresponding to a coulombic efficiency of 93.7%, indicating improved reversibility of the electrochemical reactions. More importantly, as observed in the CV results, after the second cycle, the GCD curves exhibit excellent overlap with minimal voltage hysteresis, indicating reduced polarization and stable electrochemical behavior. After the fifth cycle, the specific discharge and charge capacities reached 953.79 and $921.03 \text{ mA h g}^{-1}$, respectively, corresponding to a coulombic efficiency of 96.6%, which is comparable to that of pristine ZMO-M (96.7%).

From the comparison of the GCD curves of the pristine ZMO-M and the ZMO-M/N-rGO nanocomposite, it can be concluded that, despite similar coulombic efficiency, the nanocomposite delivers slightly higher capacity and improved capacity retention than the pristine electrode. This indicates that, although the reversibility of the electrochemical reactions remains comparable, the nanocomposite enables improved utilization of active material, enhanced structural stability, and additional surface-controlled pseudocapacitive lithium storage, as discussed in the previous chapter [26,27,79]. These enhancements arise from the synergistic effect of N-rGO wrapping, which provides a conductive network for efficient electron transport and introduces defect-rich pyridinic and pyrrolic nitrogen species, thereby creating additional active sites for lithium storage and promoting pseudocapacitive behavior [27, 79,82,85]. Furthermore, microscopic studies confirm the formation of a porous architecture composed of agglomerated ZnMn_2O_4 nanoparticles, while the effective N-rGO wrapping of these agglomerates in the ZMO-M/N-rGO nanocomposite facilitates electrolyte penetration and buffers volume changes during repeated lithiation–delithiation processes. Thus, the superior electrochemical performance of the ZMO-M/N-rGO nanocomposite may be attributed to the synergistic effects of improved electronic conductivity, enhanced structural stability, and additional pseudocapacitive lithium storage, resulting in higher capacity, reduced polarization, and improved cycling stability compared to the pristine ZMO-M electrode.

3.2.3. Rate capability

After the galvanostatic charge–discharge (GCD) analysis, the same assembled cells were further subjected to rate capability testing by gradually increasing the applied current density. The rate performance of the fabricated Li-ion half-cells using pristine ZMO-M and ZMO-M/N-rGO nanocomposite electrodes was systematically evaluated to examine the influence of high-rate operation on specific capacity and structural stability. Both cells were sequentially cycled at current densities of 100, 200, 500 mA g^{-1} , 1 A g^{-1} , and 2 A g^{-1} , with 10 cycles at each current density, followed by a return to 100 mA g^{-1} to assess the capacity recovery after prolonged high-rate cycling. The corresponding rate performance profiles are presented in Fig. 12.

At an initial current density of 100 mA g^{-1} , both electrodes exhibit relatively high specific capacities. The ZMO-M/N-rGO nanocomposite delivers a higher reversible capacity and better capacity retention than pristine ZMO-M, indicating improved structural stability and greater utilization of the active material, as discussed in the GCD analysis. With increasing current density, a gradual decrease in specific capacity is observed for both electrodes, which is expected due to kinetic

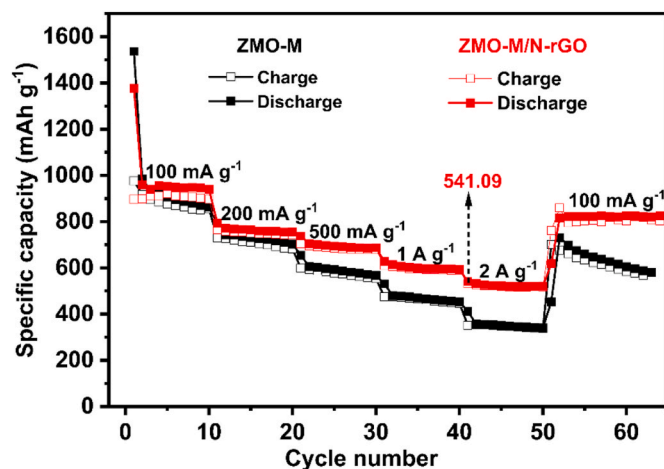


Fig. 12. Rate performance comparison of pristine ZMO-M and ZMO-M/N-rGO nanocomposite electrodes at varying current densities from 100 mA g^{-1} to 2 A g^{-1} , followed by recovery at 100 mA g^{-1} .

limitations in lithium-ion diffusion and charge-transfer processes at higher rates [11]. However, the capacity decay in the ZMO-M/N-rGO electrode is less pronounced than that of pristine ZMO-M. When the current density was gradually increased to 200 mA g⁻¹ and 500 mA g⁻¹, the nanocomposite maintained higher capacities, indicating improved rate tolerance. Also, the coulombic efficiency (CE) started increasing as the current rate increased. As the current density is further increased to 1 A g⁻¹ and 2 A g⁻¹, the CE approaches ~100% for both electrodes, and, more importantly, the capacity difference between the two electrodes becomes more pronounced, as shown in Fig. 12. The pristine ZMO-M electrode exhibits a sharp drop in capacity, falling below 400 mA h g⁻¹, whereas the ZMO-M/N-rGO nanocomposite retains a comparatively higher capacity of ~541.09 mA h g⁻¹ at 2 A g⁻¹, demonstrating superior high-rate capability. It is also worth noting that the active-material loading of the ZMO-M/N-rGO electrode (0.78 mg cm⁻²) was lower than that of pristine ZMO-M (1.25 mg cm⁻²). Since electrode loading can influence ion-transport distance and electrode resistance, the lower loading of ZMO-M/N-rGO may have also contributed to its improved high-rate response [24,86]. After returning to 100 mA g⁻¹, the ZMO-M/N-rGO nanocomposite recovers a substantial fraction of the initial capacity, indicating improved structural robustness and reversibility compared to the pristine ZMO-M [12]. This improved rate performance indicates enhanced charge-transfer kinetics and faster lithium-ion diffusion in the nanocomposite electrode. Although there was an initial capacity decrease as the current rate was gradually increased, the ZMO-M/N-rGO nanocomposite exhibits excellent rate performance. A comparison with previously reported ZnMn₂O₄/rGO-based nanocomposites under high-current-density conditions is presented in Table 1. The comparison provides a general assessment of the high-rate electrochemical performance of the present ZMO-M/N-rGO electrode relative to previously reported rGO-based systems.

It should be noted that the values presented in Table 1 were obtained under different electrochemical testing protocols and are therefore intended for contextual comparison rather than direct one-to-one quantitative comparison. As shown in Table 1, Zheng et al. [22] reported a capacity of ~440 mA h g⁻¹ at 2 A g⁻¹, while Cai et al. [12] reported ~560.8 mA h g⁻¹ at 1.2 A g⁻¹ during the rate-capability test. Zhang et al. [23] reported ~280 mA h g⁻¹ at 2 A g⁻¹, whereas Feng et al. [72] reported ~481 mA h g⁻¹ at the same current density using a three-dimensional CNT/rGO conductive network. In comparison, the present ZMO-M/N-rGO electrode delivered ~541.09 mA h g⁻¹ at 2 A

g⁻¹. Gao et al. [87] reported ~659 mA h g⁻¹ at 2 A g⁻¹ after prolonged cycling, representing a long-term cycling result rather than a rate-capability measurement. Although the capacity reported by Gao et al. [87] is higher than that of the present electrode, differences in composite architecture, testing protocol, and cycling history should be considered when comparing these values.

3.2.4. Cyclic performance

The high-current electrochemical performance of the ZMO-M/N-rGO nanocomposite suggests its potential for stable long-term cycling. Therefore, the cyclic stability of the fabricated Li-ion half-cells using pristine ZMO-M and ZMO-M/N-rGO electrodes was systematically evaluated under high current conditions. Initially, the fabricated Li-Half cells were cycled at a lower current density of 100 mA g⁻¹ for the first 10 cycles to facilitate proper electrolyte infiltration, electrode wetting, and stabilization of the electrode-electrolyte interface through the formation of a stable solid electrolyte interphase (SEI) layer [70]. Subsequently, the current density was increased to 1 A g⁻¹ to investigate the long-term cycling stability under high-current-rate conditions. Fig. 13 shows the cycling performance and coulombic efficiency of pristine ZMO-M and ZMO-M/N-rGO nanocomposite electrodes cycled at 1 A g⁻¹ following initial stabilization for the first 10 cycles at 100 mA g⁻¹. As shown in Fig. 13, both electrodes exhibit comparable cycling behavior initially, consistent with the rate performance results. After the transition to 1 A g⁻¹ at approximately the 11th cycle, the ZMO-M and ZMO-M/N-rGO electrodes deliver initial discharge capacities of ~629.77 and ~612.76 mA h g⁻¹, respectively. Notably, both electrodes exhibit relatively stable cycling behavior up to ~35 cycles under high-current-density conditions. Beyond this stage, a clear divergence in long-term cycling behavior becomes evident. The pristine ZMO-M electrode initially shows a gradual decrease in capacity from ~35 to ~60 cycles, followed by a continuous increase, reaching ~981.34 mA h g⁻¹ at approximately the 147th cycle. This increase can be attributed to progressive electrochemical activation, improved electrolyte penetration, and the gradual utilization of previously inaccessible active sites [11]. However, this apparent capacity enhancement is accompanied by noticeable fluctuations and the absence of a stable capacity plateau during prolonged cycling, indicating unstable electrochemical behavior at high current densities.

In contrast, the ZMO-M/N-rGO nanocomposite exhibits a stable and controlled electrochemical response under high current density conditions. Following the transition from 100 mA g⁻¹ to 1 A g⁻¹, the electrode maintains a nearly constant discharge capacity of ~619.10 mA h g⁻¹ up to the 300th cycle, indicating good electrochemical stability. Beyond this stage, a gradual capacity decay is observed, with the electrode retaining a discharge capacity of ~268.14 mA h g⁻¹ after 633 cycles. The extended cycling behavior is presented in Fig. S3 (Supplementary Information). Despite this decline, the nanocomposite demonstrates significantly improved capacity stability and retention compared to the pristine ZMO-M electrode over extended cycling. The coulombic efficiency of both electrodes rapidly approaches ~100% after the initial cycles and remains stable, indicating highly reversible electrochemical reactions. Notably, the ZMO-M/N-rGO electrode exhibits more consistent coulombic efficiency behavior, suggesting a more stable electrode-electrolyte interface [11]. Fig. S4 shows the post-cycling FESEM images of the ZMO-M and ZMO-M/N-rGO electrodes. Both electrodes exhibit noticeable morphological changes after prolonged electrochemical cycling compared with their pristine counterparts. In particular, the ZMO-M/N-rGO electrode shows a more fragmented surface morphology after extended cycling, which may be associated with the gradual capacity decay observed during long-term cycling.

The unstable cyclic stability, accompanied by rapid capacity fluctuations, of the pristine ZMO-M electrode indicates poor structural robustness during repeated lithiation-delithiation processes. Significant volume variations during the conversion reaction at high current rates can induce mechanical stress, leading to particle pulverization and

Table 1

Comparison of the electrochemical performance of previously reported ZnMn₂O₄/rGO-based nanocomposites and the present ZMO-M/N-rGO electrode at high current densities.

Material	Architecture	Current Density (A g ⁻¹)	Capacity (mAh g ⁻¹)	Reference
rGO/ZnMn ₂ O ₄ porous nanorods	Graphene-wrapped Porous nanorods	2.0	~440	[22]
rGO/ZnMn ₂ O ₄ porous nanospheres	Graphene-wrapped Porous nanospheres	1.2	~560.8	[12]
rGO/ZnMn ₂ O ₄ hollow porous microspheres	Graphene-wrapped Hollow microspheres	2.0	~280	[23]
ZnMn ₂ O ₄ /rGO/CNFs	Graphene-wrapped ZnMn ₂ O ₄ /carbon nanofibers	2.0	~659	[87]
ZnMn ₂ O ₄ /rGO/CNT composite	CNT/rGO 3D conductive network	2.0	~481	[72]
N-rGO/ZnMn ₂ O ₄ nanocomposite	N-rGO-wrapped nanoparticle network	2.0	541.09	This work

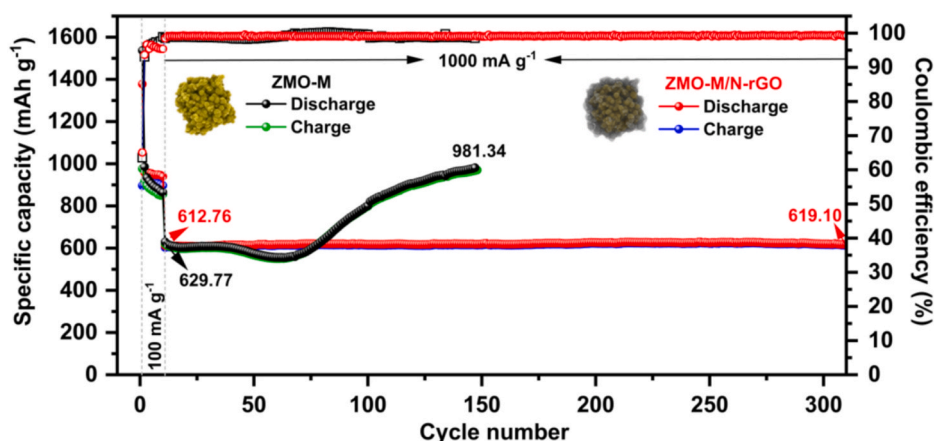


Fig. 13. Cycling performance and coulombic efficiency comparison of pristine ZMO-M and ZMO-M/N-rGO nanocomposite electrodes cycled at 1 A g^{-1} for 300 cycles after initial stabilization at 100 mA g^{-1} for 10 cycles.

unstable SEI formation. These factors could contribute to fluctuating and unreliable electrochemical behavior during prolonged cycling [11]. Therefore, although the pristine ZMO-M electrode exhibits a high capacity at intermediate cycles, capacity stability is more critical for practical applications. In contrast, the stable electrochemical performance of the ZMO-M/N-rGO nanocomposite originates from the controlled stepwise synthesis strategy. The calcination-assisted formation of porous ZnMn_2O_4 ensures high crystallinity and phase purity, providing a stable structural framework. However, such structural stability alone is insufficient to withstand the large volume changes and uncontrolled side reactions associated with repeated lithiation-delithiation processes. The improved electrochemical stability of ZMO-M/N-rGO can be attributed to the N-rGO wrapping, which buffers volume variations and maintains electrical connectivity during cycling [12]. As discussed in the synthesis mechanism (Fig. 2), APTMS-assisted functionalization facilitates the integration of graphene with the oxide aggregates, resulting in a conductive and mechanically interconnected network.

Furthermore, Table 2 compares the long-term cycling performance of the present ZMO-M/N-rGO nanocomposite with previously reported ZnMn_2O_4 -based composite anodes. Cai et al. [12] reported a capacity of $\sim 587.4 \text{ mA h g}^{-1}$ after 120 cycles at 1 A g^{-1} , while Zhang et al. [23]

reported $\sim 580 \text{ mA h g}^{-1}$ after 150 cycles at the same current density. Feng et al. [71] reported $\sim 606 \text{ mA h g}^{-1}$ after 1000 cycles at 1 A g^{-1} using a three-dimensional CNT/rGO hybrid network. In comparison, the present ZMO-M/N-rGO electrode maintained $\sim 619.10 \text{ mA h g}^{-1}$ after 300 cycles at 1 A g^{-1} . Gao et al. [87] reported $\sim 659 \text{ mA h g}^{-1}$ after 1000 cycles at 2 A g^{-1} using a $\text{ZnMn}_2\text{O}_4/\text{rGO}/\text{CNF}$ architecture. Although Gao et al. [87] achieved a higher capacity after a substantially longer cycling period, their electrode was evaluated at a higher current density, and employed a more complex carbon architecture. Overall, the present ZMO-M/N-rGO electrode exhibits competitive long-term cycling performance at 1 A g^{-1} , with a comparatively simple N-rGO/ ZnMn_2O_4 architecture.

3.2.5. Electrochemical impedance spectroscopy

To further elucidate the electrochemical kinetics and interfacial evolution during cycling, electrochemical impedance spectroscopy (EIS) was performed on pristine ZMO-M and ZMO-M/N-rGO nanocomposite electrodes at different stages: before cycling, after 5 cycles, after 10 cycles, and after prolonged cycling. The corresponding Nyquist plots are shown in Fig. 14(a), (c), (e), and (g), while the linear fits of the low-frequency Warburg region are presented in Fig. 14(b)–(d), (f), and (h).

As observed in Fig. 14(a), (c), (e), and (g), all Nyquist plots exhibit a depressed semicircle in the high-to-medium frequency region, followed by a straight inclined line in the low-frequency region.

The obtained impedance spectra were fitted using Biologic EC-Lab software to analyze the different resistive components within the cell, and the corresponding equivalent circuit is shown in Fig. 15.

The high-frequency intercept corresponds to the electrolyte resistance (R_{el}), whereas the semicircle represents the combined interfacial resistance (R_{int}), associated with charge-transfer processes and SEI layer contributions, coupled with a constant phase element reflecting non-ideal capacitive behavior [12,20,88]. It should be noted that the impedance spectra after the first cycle do not exhibit well-defined multiple semicircles, making the reliable separation of charge-transfer resistance (R_{CT}) and SEI resistance (R_{SEI}) difficult. Therefore, a combined interfacial resistance (R_{int}) is used for fitting, representing the overall interfacial impedance contribution. The constant phase element (Q_{CPE}) accounts for the non-ideal double-layer capacitance arising from surface roughness and heterogeneity [88]. The low-frequency linear region corresponds to the Warburg impedance (W), which is associated with lithium-ion diffusion within the electrode. In addition, a constant phase element (Q_{int}) is included in the low-frequency region to account for pseudocapacitive or bulk interfacial storage contributions arising from surface-controlled lithium storage processes [89]. The extracted impedance parameters are summarized in Table 3, which serves as the basis for the following explanation.

Table 2

Comparison of the cyclic performance of the newly prepared ZMO-M/N-rGO nanocomposite with previously reported ZnMn_2O_4 -based composites under high-current-density conditions.

Material	Architecture	Current Density (A g^{-1})	Cycle Number	Capacity (mAh g^{-1})	Reference
$\text{ZnMn}_2\text{O}_4/\text{rGO}/\text{CNFs}$	rGO-wrapped carbon nanofiber network	2.0	1000	~ 659	[87]
$\text{ZnMn}_2\text{O}_4/\text{CNT}/\text{rGO}$	3D CNT/rGO hybrid network	1.0	1000	~ 606	[72]
$\text{ZnMn}_2\text{O}_4/\text{rGO}$	Graphene-wrapped hollow structure	1.0	150	~ 580	[23]
$\text{ZnMn}_2\text{O}_4/\text{rGO}$	Graphene-wrapped Porous nanospheres	1	120	587.4	[12]
$\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ (ZMO-M/N-rGO)	N-rGO-wrapped nanoparticle network	1.0	300	~ 619.10	This work

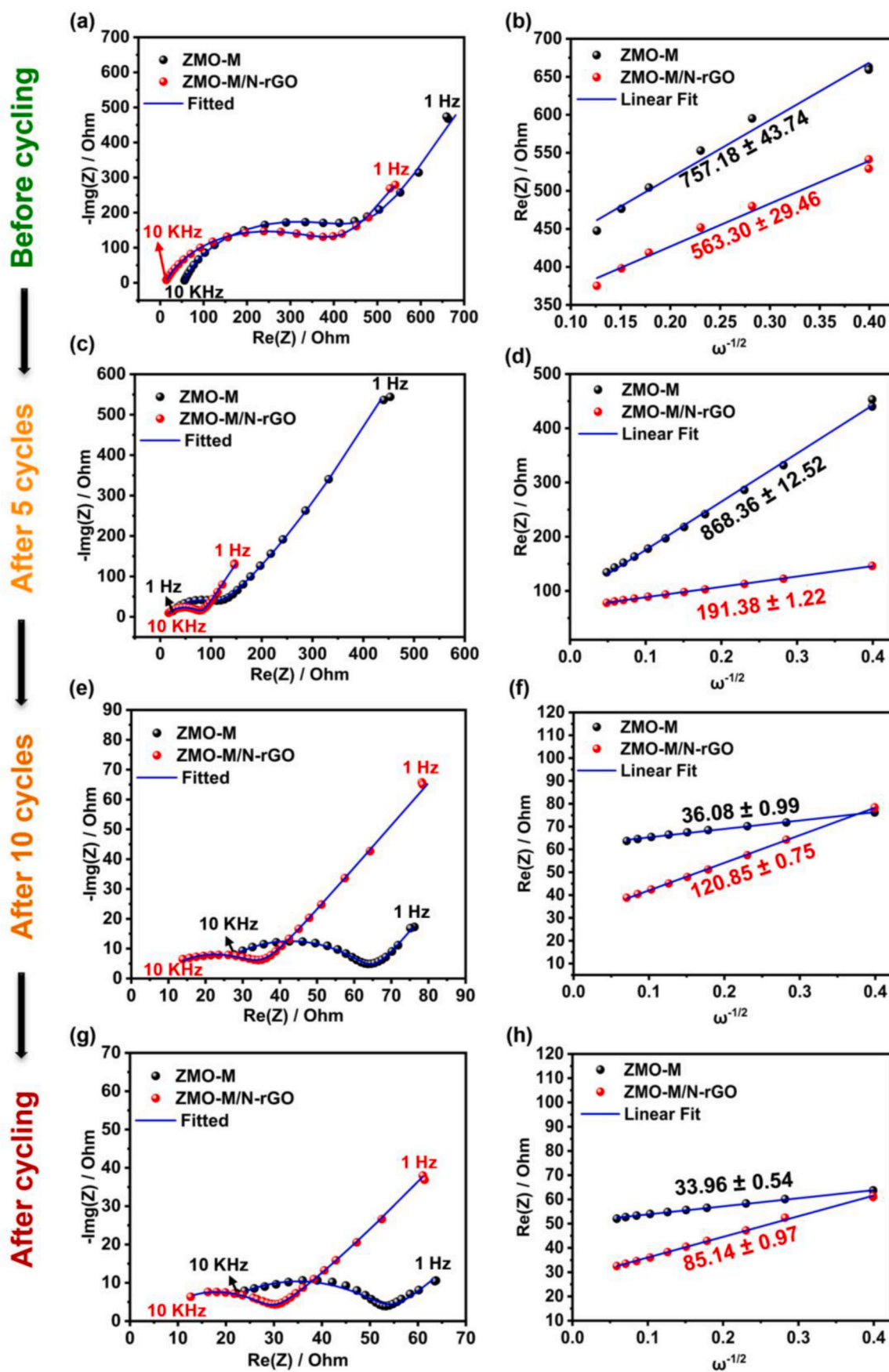


Fig. 14. Nyquist plots and corresponding linear fits of the low-frequency Warburg region for ZMO-M and ZMO-M/N-rGO electrodes at different stages: (a,b) before cycling, (c,d) after 5 cycles, (e,f) after 10 cycles, and (g,h) after prolonged cycling.

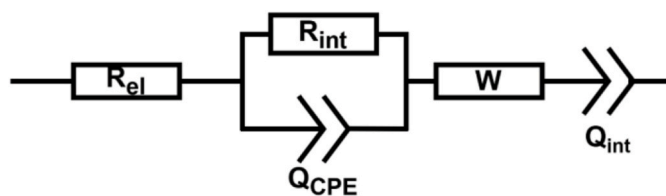


Fig. 15. Equivalent circuit model used for fitting the EIS spectra of ZMO-M and ZMO-M/N-rGO electrodes.

Table 3

EIS fitting parameters of ZMO-M and ZMO-M/N-rGO electrodes at different cycling stages.

Cycle Stage	Electrode	$R_{el}(\Omega)$	$R_{int}(\Omega)$	$\sigma(\Omega s^{-1/2})$
Before cycling	ZMO-M	53.52 ± 1	394.4 ± 1	757.18 ± 43.74
	ZMO-M/N-rGO	10.6 ± 1	389.4 ± 1	563.30 ± 29.46
After 5 cycles	ZMO-M	15.95 ± 1	81.87 ± 1	886.36 ± 12.52
	ZMO-M/N-rGO	10.38 ± 1	70.14 ± 1	191.38 ± 1.22
After 10 cycles	ZMO-M	20.2 ± 1	44.07 ± 1	36.08 ± 0.99
	ZMO-M/N-rGO	7.71 ± 1	26.4 ± 1	120.85 ± 0.75
After cycling	ZMO-M	15.24 ± 1	38.02 ± 1	33.96 ± 0.54
	ZMO-M/N-rGO	5.60 ± 1	22.71 ± 1	85.14 ± 0.97

Before electrochemical cycling, the pristine ZMO-M electrode exhibits a relatively high electrolyte resistance of $R_{el} = 53.52 \pm 1 \Omega$ compared to the ZMO-M/N-rGO nanocomposite ($R_e = 10.6 \pm 1 \Omega$), indicating improved electrical conductivity and better electrode-electrolyte contact in the presence of the conductive N-rGO framework. The interfacial resistance values for both electrodes are comparable, with $394.4 \pm 1 \Omega$ for ZMO-M and $389.4 \pm 1 \Omega$ for ZMO-M/N-rGO, suggesting that the intrinsic charge-transfer behavior is primarily governed by the $ZnMn_2O_4$ framework at this stage. However, a clear difference is observed in the Warburg coefficient (σ), where ZMO-M shows a higher value ($757.18 \pm 43.74 \Omega s^{1/2}$) compared to ZMO-M/N-rGO ($563.30 \pm 29.46 \Omega s^{1/2}$), indicating relatively sluggish lithium-ion diffusion in the pristine electrode. The lower σ value in the nanocomposite reflects enhanced ion transport facilitated by the conductive N-rGO network and defect-rich graphene structure, which provides additional diffusion pathways and improved interfacial contact.

Interestingly, after 5 cycles, both electrodes exhibit a significant reduction in interfacial resistance, with ZMO-M and ZMO-M/N-rGO showing R_{int} values of $81.87 \pm 1 \Omega$ and $70.14 \pm 1 \Omega$, respectively. This reduction indicates electrode activation and improved electrode-electrolyte interaction after the initial cycle [11]. In contrast, a distinct difference is observed in lithium-ion diffusion behavior. The Warburg coefficient of ZMO-M increases significantly to $886.36 \pm 12.52 \Omega s^{1/2}$, indicating hindered diffusion, likely due to unstable SEI formation and structural degradation during the initial cycles. On the other hand, the ZMO-M/N-rGO electrode exhibits a substantially lower σ ($\sim 191.38 \pm 1.22 \Omega s^{1/2}$), suggesting enhanced diffusion kinetics and a more stable interfacial environment [20]. This behavior is consistent with the cyclic voltammetry results, which show that the ZMO-M/N-rGO nanocomposite exhibits improved reversibility in the first 5 cycles, with excellent overlap of successive CV curves and the absence of persistent SEI-related peaks, indicating stable SEI formation. In contrast, the pristine ZMO-M electrode shows poor overlap, noticeable polarization, and persistent SEI-related features during the initial cycles.

After 10 cycles, both electrodes show further reduction in interfacial resistance, indicating improved charge-transfer kinetics. The ZMO-M electrode exhibits $R_{int} = 44.07 \pm 1 \Omega$, whereas the ZMO-M/N-rGO nanocomposite shows a significantly lower value of $26.4 \pm 1 \Omega$, confirming faster interfacial kinetics in the nanocomposite system. The Warburg coefficient of ZMO-M decreases sharply to $\sim 36.08 \pm 0.99 \Omega s^{1/2}$, suggesting electrochemical activation and increased accessibility of active sites. However, such a drastic reduction may also indicate

structural rearrangement or degradation, thereby artificially enhancing ion transport pathways. In contrast, the nanocomposite maintains a moderate σ of $\sim 120.85 \pm 0.75 \Omega s^{1/2}$, indicating stable and controlled lithium-ion diffusion.

After prolonged cycling (633 cycles), even though the capacity of the ZMO-M/N-rGO electrode decreases to $268.14 \text{ mA h g}^{-1}$, it continues to exhibit superior electrochemical characteristics. The electrolyte resistance (R_{el}) decreases to $5.60 \pm 1 \Omega$, and the interfacial resistance ($22.71 \pm 1 \Omega$) remains significantly lower than that of the pristine ZMO-M electrode ($38.02 \pm 1 \Omega$ at the 147th cycle), indicating a stable electrode-electrolyte interface.

The Warburg coefficient further highlights the difference in diffusion behavior. The pristine ZMO-M electrode exhibits a lower σ ($\sim 33.96 \pm 0.54 \Omega s^{1/2}$), which can be attributed to structural degradation, increased porosity, and the formation of unstable diffusion pathways rather than true enhancement in lithium-ion transport. In contrast, the ZMO-M/N-rGO nanocomposite maintains a controlled σ ($\sim 85.14 \pm 0.97 \Omega s^{1/2}$), indicating stable lithium-ion diffusion and preserved structural integrity during prolonged cycling.

The EIS results strongly correlate with the electrochemical performance discussed in the previous sections. The unstable evolution of impedance parameters in the pristine ZMO-M electrode, particularly the fluctuating Warburg coefficient and relatively higher interfacial resistance, is consistent with its poor cycling stability and capacity fluctuations. These behaviors may arise from structural degradation, unstable SEI formation, and loss of electrical connectivity during repeated lithiation-delithiation processes. In comparison, the ZMO-M/N-rGO nanocomposite exhibits consistently lower resistance values and a gradual, controlled evolution of the Warburg coefficient throughout cycling, as shown in Table 3. These stable impedance characteristics correlate well with the observed superior cycling stability, improved capacity retention, and enhanced rate capability. The improved electrochemical performance may be attributed to the synergistic effect of the N-rGO framework, which enhances electronic conductivity, provides continuous electron transport pathways, facilitates lithium-ion diffusion, and effectively buffers volume changes during cycling [26].

Overall, the EIS analysis clearly demonstrates that the pristine ZMO-M electrode undergoes unstable impedance evolution, accompanied by fluctuating charge-transfer resistance and irregular lithium-ion diffusion behavior, which directly correlates with its unstable cycling stability and capacity fluctuations. In contrast, the ZMO-M/N-rGO nanocomposite exhibits consistently lower interfacial resistance and a gradual controlled evolution of the Warburg coefficient, indicating stable lithium-ion diffusion pathways and improved electrochemical kinetics. These results confirm that N-rGO wrapping effectively enhances interfacial charge-transfer processes, maintains structural integrity, and ensures stable long-term electrochemical performance.

4. Conclusion

In this work, $ZnMn_2O_4$ (ZMO-M) and its N-rGO nanocomposite (ZMO-M/N-rGO) were successfully synthesized through a microwave-assisted hydrothermal route followed by controlled calcination and APTMS-assisted interfacial engineering. Structural and spectroscopic analyses confirmed the formation of phase-pure tetragonal $ZnMn_2O_4$ and the successful incorporation of N-rGO containing pyridinic, pyrrolic, and graphitic nitrogen species. FESEM and TEM investigations revealed an intimate oxide-N-rGO interfacial contact, with thin N-rGO sheets distributed around the $ZnMn_2O_4$ nanoparticles, forming a conductive network that facilitates charge transport and enhances structural stability.

Electrochemical studies demonstrated that N-rGO incorporation significantly influences the lithium-storage behavior of $ZnMn_2O_4$. Cyclic voltammetry revealed improved electrochemical reversibility and reduced polarization, while galvanostatic charge-discharge measurements confirmed enhanced rate capability for the ZMO-M/N-rGO

nanocomposite. Although the pristine ZMO-M electrode attained higher discharge capacities during cycling, it exhibited pronounced capacity fluctuations and irregular electrochemical behavior. In contrast, the ZMO-M/N-rGO electrode delivered a more stable electrochemical response and maintained a discharge capacity of $619.10 \text{ mA h g}^{-1}$ after 300 cycles at a current density of 1000 mA g^{-1} . Furthermore, electrochemical impedance spectroscopy revealed lower electrolyte and interfacial resistance for the ZMO-M/N-rGO nanocomposite, together with a more gradual and controlled evolution of lithium-ion diffusion behavior compared with pristine ZMO-M. The improved diffusion characteristics indicate the presence of more stable lithium-ion transport pathways and a better-maintained electrode-electrolyte interface during prolonged cycling. The enhanced electrochemical performance of the nanocomposite is therefore attributed to the synergistic effects of the conductive N-rGO framework, improved oxide-carbon interfacial contact, and more stable charge-transfer and diffusion processes. Overall, the present study demonstrates that N-rGO-based interfacial engineering is an effective strategy for improving the electrochemical performance and reaction kinetics of ZnMn_2O_4 anodes. The results highlight the importance of rational oxide-carbon interface design for achieving stable lithium storage behavior and provide useful insights for the development of high-performance transition-metal-oxide-based anodes for lithium-ion batteries.

CRedit authorship contribution statement

Bharath Chandran: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Reshma S. Babu:** Writing – review & editing, Data curation. **Durga S. Nair:** Writing – review & editing, Data curation. **O. Padmaraj:** Writing – review & editing, Data curation. **Prasad Gonugunta:** Supervision, Methodology, Investigation, Formal analysis, Data curation. **Thamayanthi Panneerselvam:** Resources. **R. Murugan:** Resources. **Gangineni Ramesh Babu:** Writing – review & editing. **Ruud Hendrikx:** Methodology, Investigation, Data curation. **Peyman Taheri:** Writing – review & editing, Resources. **Arjan Mol:** Writing – review & editing, Resources, Formal analysis, Data curation. **N. Satyanarayana:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Data curation. **Pra-saanth Ravi Anusuyadevi:** Writing – review & editing, Visualization, Supervision, Project administration, Formal analysis, Data curation, Conceptualization.

Funding

B.C has received research fellowship support from Pondicherry University. N.S. has received UGC-BSR Faculty Fellowship support from the UGC, Government of India (No. F.18-1/2011 (BSR), Date: 07-03-2019).

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.

Acknowledgements

The authors are grateful to the Central Instrumentation Facility (CIF), Pondicherry University, for providing access to various characterization facilities. N.S. acknowledges the University Grants Commission (UGC), Government of India, for awarding the UGC-BSR Faculty Fellowship (No. F.18-1/2011(BSR), dated 07-03-2019). The authors also express their sincere thanks to DST-FIST Phase-II for supporting the GIXRD facility in the Department of Physics, Pondicherry University. B. C. acknowledges Pondicherry University for providing the research

fellowship.

Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2026.133161>.

Data availability

Data will be made available on request.

References

- [1] D. Kasprzak, C.C. Mayorga-Martinez, M. Pumera, Sustainable and flexible energy storage devices: a review, *Energy Fuels* 37 (2023) 74–97, <https://doi.org/10.1021/acs.energyfuels.2c03217>.
- [2] L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, A review on the key issues for lithium-ion battery management in electric vehicles, *J. Power Sources* 226 (2013) 272–288, <https://doi.org/10.1016/j.jpowsour.2012.10.060>.
- [3] J.W. Choi, D. Aurbach, Promise and reality of post-lithium-ion batteries with high energy densities, *Nat. Rev. Mater.* 1 (2016), <https://doi.org/10.1038/natrevmater.2016.13>.
- [4] J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *www.nature.com*, 2001.
- [5] R.M. Humana, M.G. Ortiz, J.E. Thomas, S.G. Real, M. Sedlarikova, J. Vondrák, A. Visintin, Preparation and characterization of graphite anode for lithium ion batteries, *ECS Trans.* 63 (2014) 91–97, <https://doi.org/10.1149/06301.0091ecst>.
- [6] K. Ullah, N. Shah, R. Wadood, B.M. Khan, W.C. Oh, Recent trends in graphene based transition metal oxides as anode materials for rechargeable lithium-ion batteries, *Nano Trends* 1 (2023), <https://doi.org/10.1016/j.nwnano.2023.100004>.
- [7] C. Zhao, S. Yao, C. Li, Y. An, S. Zhao, X. Sun, K. Wang, X. Zhang, Y. Ma, Recent advances in transition metal oxides as anode materials for high-performance lithium-ion capacitors, *Chem. Eng. J.* 497 (2024), <https://doi.org/10.1016/j.cej.2024.154535>.
- [8] Y. Zhao, X. Li, B. Yan, D. Xiong, D. Li, S. Lawes, X.L. Sun, Recent developments and understanding of novel mixed transition-metal oxides as anodes in lithium ion batteries, *Adv. Energy Mater.* 6 (2016), <https://doi.org/10.1002/aenm.201502175>.
- [9] Y. Zhu, X. Liao, H. Qiu, S. An, Y. Zhang, W. He, Mixed metals oxides with strong synergistic electrochemistry as battery-type electrodes for ultrafast energy storage, *J. Alloys Compd.* 848 (2020), <https://doi.org/10.1016/j.jallcom.2020.156395>.
- [10] S. Yuvaraj, R.K. Selvan, Y.S. Lee, An overview of AB_2O_4 - and A_2BO_4 -structured negative electrodes for advanced Li-ion batteries, *RSC Adv.* 6 (2016) 21448–21474, <https://doi.org/10.1039/c5ra23503k>.
- [11] B. Chandran, R.S. Babu, P. Gonugunta, O. Padmaraj, T. Panneerselvam, R. Murugan, G.R. Babu, R. Hendrikx, P. Taheri, A. Mol, N. Satyanarayana, P. R. Anusuyadevi, Self-adaptive $\text{ZnMn}_2\text{O}_4/\alpha\text{-MnO}_2$ nanocomposite as an anode material for high-performance lithium-ion batteries, *Appl. Surf. Sci.* 712 (2025), <https://doi.org/10.1016/j.apsusc.2025.164175>.
- [12] D. Cai, D. Wang, H. Huang, X. Duan, B. Liu, L. Wang, Y. Liu, Q. Li, T. Wang, Rational synthesis of ZnMn_2O_4 porous spheres and graphene nanocomposite with enhanced performance for lithium-ion batteries, *J. Mater. Chem. A Mater.* 3 (2015) 11430–11436, <https://doi.org/10.1039/c5ta00539f>.
- [13] Z. Bai, N. Fan, C. Sun, Z. Ju, C. Guo, J. Yang, Y. Qian, Facile synthesis of loaf-like ZnMn_2O_4 nanorods and their excellent performance in Li-ion batteries, *Nanoscale* 5 (2013) 2442–2447, <https://doi.org/10.1039/c3nr33211j>.
- [14] L. Luo, H. Qiao, K. Chen, Y. Fei, Q. Wei, Fabrication of electrospun ZnMn_2O_4 nanofibers as anode material for lithium-ion batteries, *Electrochim. Acta* 177 (2015) 283–289, <https://doi.org/10.1016/j.electacta.2015.01.100>.
- [15] J. Zou, B. Liu, H. Liu, Y. Ding, T. Xin, Y. Wang, Facile synthesis of interconnected mesoporous ZnMn_2O_4 nano-peanuts for Li-storage via distinct structure design, *Mater. Res. Bull.* 107 (2018) 468–476, <https://doi.org/10.1016/j.materresbull.2018.08.019>.
- [16] G. Zhang, L. Yu, H. Bin Wu, H.E. Hoster, X.W. Lou, Formation of ZnMn_2O_4 ball-in-ball hollow microspheres as a high-performance anode for lithium-ion batteries, *Adv. Mater.* 24 (2012) 4609–4613, <https://doi.org/10.1002/adma.201201779>.
- [17] Q. Fang, C. Chen, Z. Yang, X. Chen, X. Chen, T. Liu, Synthesis and electrochemical performance of pomegranate-like ZnMn_2O_4 porous microspheres, *J. Alloys Compd.* 826 (2020), <https://doi.org/10.1016/j.jallcom.2020.154084>.
- [18] N. Wang, X. Ma, H. Xu, L. Chen, J. Yue, F. Niu, J. Yang, Y. Qian, Porous ZnMn_2O_4 microspheres as a promising anode material for advanced lithium-ion batteries, *Nano Energy* 6 (2014) 193–199, <https://doi.org/10.1016/j.nanoen.2014.04.001>.
- [19] B. Fan, A. Hu, X. Chen, S. Zhang, Q. Tang, J. Wang, W. Deng, Z. Liu, K. Xiao, Hierarchical porous ZnMn_2O_4 microspheres as a high-performance anode for lithium-ion batteries, *Electrochim. Acta* 213 (2016) 37–45, <https://doi.org/10.1016/j.electacta.2016.07.030>.
- [20] J. Chen, H. Zuo, C. Wang, Y.-C. Zhang, W. Gao, N. Zhao, Y. Huang, S. Xiao, Synthesis and electrochemical properties of ZnMn_2O_4 with hollow porous pap-pine-like structure as anode material for Li-ion battery, *Electrochim. Acta* 426 (2022) 140780, <https://doi.org/10.1016/j.electacta.2022.140780>.
- [21] P. Zhou, L. Zhong, Z. Liu, M. Liu, T. Zhou, Y. Zhao, X. Lai, J. Bi, D. Gao, Porous ZnMn_2O_4 hollow microrods: facile construction and excellent electrochemical

- performances for lithium ion batteries, *Appl. Surf. Sci.* 578 (2022), <https://doi.org/10.1016/j.apsusc.2021.152087>.
- [22] Z. Zheng, Y. Cheng, X. Yan, R. Wang, P. Zhang, Enhanced electrochemical properties of graphene-wrapped ZnMn_2O_4 nanorods for lithium-ion batteries, *J. Mater. Chem. A Mater* 2 (2014) 149–154, <https://doi.org/10.1039/c3ta13511j>.
- [23] T. Zhang, H. Yue, H. Qiu, K. Zhu, L. Zhang, Y. Wei, F. Du, G. Chen, D. Zhang, Synthesis of graphene-wrapped ZnMn_2O_4 hollow microspheres as high performance anode materials for lithium ion batteries, *RSC Adv.* 5 (2015) 99107–99114, <https://doi.org/10.1039/c5ra16667e>.
- [24] B. Chandran, R.S. Babu, D.S. Nair, O. Padmaraj, P. Goungunta, T. Panneerselvam, R. Murugan, G.R. Babu, R. Hendrikx, P. Taheri, A. Mol, N. Satyanarayana, P. R. Anusuyadevi, One-pot interfacial engineering of ZnMn_2O_4 /N-rGO nanocomposites as anode materials for high-performance lithium-ion batteries, *J. Electroanal. Chem.* 1018 (2026), <https://doi.org/10.1016/j.jelechem.2026.120415>.
- [25] R. Yadav, P. Joshi, M. Hara, M. Yoshimura, In situ electrochemical raman investigation of charge storage in rGO and N-doped rGO, *Phys. Chem. Chem. Phys.* 23 (2021) 11789–11796, <https://doi.org/10.1039/d1cp00248a>.
- [26] M. Du, J. Sun, J. Chang, F. Yang, L. Shi, L. Gao, Synthesis of nitrogen-doped reduced graphene oxide directly from nitrogen-doped graphene oxide as a high-performance lithium ion battery anode, *RSC Adv.* 4 (2014) 42412–42417, <https://doi.org/10.1039/c4ra05544f>.
- [27] A. Tasdemir, B. Bulut Kopuklu, A.C. Kirlioglu, S. Alkan Gursel, A. Yurum, The influence of nitrogen doping on reduced graphene oxide as highly cyclable Li-ion battery anode with enhanced performance, *Int. J. Hydrogen Energy* 46 (2021) 11865–11877, <https://doi.org/10.1016/j.ijhydene.2021.01.099>.
- [28] H. Xue, A. Meng, T. Lian, T. Yang, J. Gao, C.V. Singh, Z. Geng, L. Chen, Z. Li, Co-Pyridinic-N bond constructed at the interface of Co_3P and N-Doped carbon to effectively facilitate oxygen reduction, *ACS Sustain. Chem. Eng.* 11 (2023) 5238–5249, <https://doi.org/10.1021/acsschemeng.2c07734>.
- [29] E.M.E. Kristensen, F. Niederberg, H. Rensmo, T. Bowden, J. Hilborn, H. Siegbahn, Photoelectron spectroscopy studies of the functionalization of a silicon surface with a phosphorylcholine-terminated polymer grafted onto (3-Aminopropyl) trimethoxysilane, *Langmuir* 22 (2006) 9651–9657, <https://doi.org/10.1021/la060586o>.
- [30] F. Mo, M. Cui, L. Yang, H. Lei, S. Chen, J. Wei, L. Kang, Phase-transformation-activated MnCO_3 as cathode material of aqueous zinc-ion batteries, *Batteries* 8 (2022), <https://doi.org/10.3390/batteries8110239>.
- [31] T. Feng, J. Wang, G. Yang, J. Yang, M. Wu, Pomegranate-structured ZnMn_2O_4 microspheres for long cycle life lithium ion anode and elucidation of its conversion mechanism, *J. Electrochem. Soc.* 167 (2020) 060507, <https://doi.org/10.1149/1945-7111/ab79a9>.
- [32] X. Chen, Y. Zhang, H. Lin, P. Xia, X. Cai, X. Li, X. Li, W. Li, Porous ZnMn_2O_4 nanospheres: facile synthesis through microemulsion method and excellent performance as anode of lithium ion battery, *J. Power Sources* 312 (2016) 137–145, <https://doi.org/10.1016/j.jpowsour.2016.02.056>.
- [33] X. Zhu, J. Quan, J. Huang, Z. Ma, Y. Chen, D. Zhu, C. Ji, D. Li, A new approach to improve the electrochemical performance of ZnMn_2O_4 through a charge compensation mechanism using the substitution of Al^{3+} for Zn^{2+} , *RSC Adv.* 8 (2018) 7361–7368, <https://doi.org/10.1039/c8ra00310f>.
- [34] Y. Jin, L. Wang, Q. Jiang, X. Du, C. Ji, X. He, Morphology controllable synthesis of CoMn_2O_4 structures by adjusting the urea concentration: from microflowers to microspheres, *Mater. Lett.* 168 (2016) 166–170, <https://doi.org/10.1016/j.matlet.2016.01.077>.
- [35] W. Dang, F. Wang, Y. Ding, C. Feng, Z. Guo, Synthesis and electrochemical properties of ZnMn_2O_4 microspheres for lithium-ion battery application, *J. Alloys Compd.* 690 (2017) 72–79, <https://doi.org/10.1016/j.jallcom.2016.07.304>.
- [36] L. Malavasi, P. Galinetto, M.C. Mozzati, C.B. Azzoni, G. Flor, Raman spectroscopy of AMn_2O_4 (A = Mn, Mg and Zn) spinels, *Phys. Chem. Chem. Phys.* 4 (2002) 3876–3880, <https://doi.org/10.1039/b203520k>.
- [37] H. Li, B. Song, W.J. Wang, X.L. Chen, Facile synthesis, thermal, magnetic, raman characterizations of spinel structure ZnMn_2O_4 , *Mater. Chem. Phys.* 130 (2011) 39–44, <https://doi.org/10.1016/j.matchemphys.2011.04.072>.
- [38] Q. Sun, M. Bijelić, A.B. Djurišić, C. Suchomski, X. Liu, M. Xie, A.M.C. Ng, H. Kong Li, K. Shih, S. Burazer, Z. Skoko, I. Djerdj, J. Popović, Graphene-oxide-wrapped ZnMn_2O_4 as a high performance lithium-ion battery anode, *Nanotechnology* 28 (2017), <https://doi.org/10.1088/1361-6528/aa8a5b>.
- [39] E.S. Guillén-López, F. López-Urías, E. Muñoz-Sandoval, M. Courel-Piedrahita, M. Sanchez-Tizapa, H. Guillén-Bonilla, V.M. Rodríguez-Betancourt, O. Blanco-Alonso, A. Guillén-Bonilla, J.P. Morán-Lázaro, High performance isopropanol sensor based on spinel ZnMn_2O_4 nanoparticles, *Mater. Today Commun.* 26 (2021), <https://doi.org/10.1016/j.mtcomm.2021.102138>.
- [40] P. Ahuja, R.K. Sharma, G. Singh, Solid-state, high-performance supercapacitor using graphene nanoribbons embedded with zinc manganite, *J. Mater. Chem. A Mater* 3 (2015) 4931–4937, <https://doi.org/10.1039/c4ta05865h>.
- [41] M. Iliut, C. Leordean, V. Canpean, C.M. Teodorescu, S. Astilean, A new green, ascorbic acid-assisted method for versatile synthesis of Au-graphene hybrids as efficient surface-enhanced raman scattering platforms, *J. Mater. Chem. C Mater* 1 (2013) 4094–4104, <https://doi.org/10.1039/c3tc30177j>.
- [42] L. He, J. Peng, X. Liu, P. Liu, J. Yang, Y. Tang, X. Wang, The reduced graphene oxide conductive additives with a certain defect concentration enabling rate-capability of lithium-ion batteries, *Electrochim. Acta* 511 (2025), <https://doi.org/10.1016/j.electacta.2024.145353>.
- [43] P. Anil, V.V.R.K. Kumar, B. Chandran, N. Satyanarayana, R.S.P. Goud, Structural and dielectric characteristics of CoFe_2O_4 /nitrogen-enriched reduced graphene oxide composites via a one-pot solvothermal method, *J. Mater. Sci.* 60 (2025) 4687–4711, <https://doi.org/10.1007/s10853-025-10712-0>.
- [44] N. Kumar, V.C. Srivastava, Simple synthesis of large graphene oxide sheets via electrochemical method coupled with oxidation process, *ACS Omega* 3 (2018) 10233–10242, <https://doi.org/10.1021/acsomega.8b01283>.
- [45] Y.X. Liou, S.L. Li, K.Y. Hsieh, S.J. Li, L.J. Hu, Investigating the extracellular-electron-transfer mechanisms and kinetics of Shewanella decolorationis NTOU1 reducing graphene oxide via lactate metabolism, *Bioengineering* 10 (2023), <https://doi.org/10.3390/bioengineering10030311>.
- [46] J. Cui, J. Liu, C. Wang, F. Rong, L. He, Y. Song, Z. Zhang, S. Fang, Efficient electrocatalytic water oxidation by using the hierarchical 1D/2D structural nanohybrid of CoCu-based zeolitic imidazolate framework nanosheets and graphdiyne nanowires, *Electrochim. Acta* 334 (2020), <https://doi.org/10.1016/j.electacta.2019.135577>.
- [47] A. Venkatesan, A. Nizam, A.R. Cherian, R. Patel, J. Xavier, K.R. Pooja, R. Harini, G. Nagaraju, Molecular energy transfer: utilizing biogenically-synthesized ZnMn_2O_4 nanoparticles from *Arachis hypogaea* seeds for photoluminescence, adsorption, and photocatalytic applications, *RSC Adv.* 15 (2025) 32638–32653, <https://doi.org/10.1039/d5ra05696a>.
- [48] I.V. Ivanova, N.A. Zaitseva, R.F. Samigullina, T.I. Krasnenko, Solid-state synthesis of ZnMn_2O_4 spinel: sequence of phase transformations, thermal stability, localization and charge state of manganese ions in the intermediate and final reaction products, *Solid State Sci.* 136 (2023), <https://doi.org/10.1016/j.solidstatesciences.2023.107110>.
- [49] P. Zhang, X. Li, Q. Zhao, S. Liu, Synthesis and optical property of one-dimensional spinel ZnMn_2O_4 nanorods, *Nanoscale Res. Lett.* 6 (2011), <https://doi.org/10.1186/1556-276X-6-323>.
- [50] N. Mirikaram, Á. Pérez-molina, S. Morales-Torres, A. Salemi, F.J. Maldonado-hódar, L.M. Pastrana-Martínez, Photocatalytic performance of ZnO -graphene oxide composites towards the degradation of vanillic acid under solar radiation and visible LED, *Nanomaterials* 11 (2021), <https://doi.org/10.3390/nano11061576>.
- [51] A.E. Hughes, C.D. Easton, P.R. Anusuyadevi, T.J. Raeber, N.C. Wilson, A. Mol, Widespread erroneous analysis of the Fe 2p peak in X-ray photoelectron spectroscopy examination in corrosion studies, *Corros. Sci.* 257 (2025), <https://doi.org/10.1016/j.corsci.2025.113357>.
- [52] A. Pramanik, S. Chattopadhyay, S. Maiti, G. De, S. Mahanty, Hollow-porous nanospheres of ZnMn_2O_4 spinel: a high energy density cathode for rechargeable aqueous battery, *Mater. Chem. Phys.* 263 (2021), <https://doi.org/10.1016/j.matchemphys.2021.124373>.
- [53] Y.Q. Lin, X.M. Chen, Dielectric relaxation and polaronic conduction in double perovskite $\text{La}_2\text{MgMnO}_6$, *Appl. Phys. Lett.* 96 (2010), <https://doi.org/10.1063/1.3377906>.
- [54] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.* 257 (2011) 2717–2730, <https://doi.org/10.1016/j.apsusc.2010.10.051>.
- [55] S. Wang, X. Guo, K. Huang, A. Achari, J. Safaei, Y. Lei, D. Li, Q. Gu, C. Sun, L. Gloag, S. Langford, A. Geim, R.R. Nair, G. Wang, Cooperative jahn-teller effect and engineered long-range strain in manganese oxide/graphene superlattice for aqueous zinc-ion batteries, *Nat. Commun.* 16 (2025), <https://doi.org/10.1038/s41467-025-60558-y>.
- [56] V. Chakrapani, C. Wang, Q. Wang, N. Smieszek, Direct determination of Mn valence states in mixed-valent manganates by photoluminescence spectroscopy, *Surf. Interface Anal.* 54 (2022) 1192–1202, <https://doi.org/10.1002/sia.7144>.
- [57] Y.J. Sa, S. Kim, Y. Lee, J.M. Kim, S.H. Joo, Mesoporous manganese oxides with high-valent Mn species and disordered local structures for efficient oxygen electrocatalysis, *ACS Appl. Mater. Interfaces* 15 (2023) 31393–31402, <https://doi.org/10.1021/acsaami.3c03358>.
- [58] H. Cao, X. Xiao, X. Wang, J. Liu, P. Si, Morphology engineering of self-assembled porous zinc manganate hexagons for lithium ion storage, *Electrochim. Acta* 330 (2020), <https://doi.org/10.1016/j.electacta.2019.135260>.
- [59] Y.J. Oh, J.J. Yoo, Y. Il Kim, J.K. Yoon, H.N. Yoon, J.H. Kim, S. Bin Park, Oxygen functional groups and electrochemical capacitive behavior of incompletely reduced graphene oxides as a thin-film electrode of supercapacitor, *Electrochim. Acta* 116 (2014) 118–128, <https://doi.org/10.1016/j.electacta.2013.11.040>.
- [60] Carbon | XPS periodic table - IN, (n.d.). <https://www.thermofisher.com/in/en/home/materials-science/learning-center/periodic-table/non-metal/carbon.html> (accessed December 12, 2025).
- [61] M.S. Ratsoma, H. Mathebula, K.T. Boikanyo, M.A. Kebede, K.D. Modibane, G. Kubheka, M.D.S. Lekgoathi, K. Makgopa, Investigation of N-rGO/ $\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O}$ as battery-type electrode material for high-performance supercapacities, *Electrochim. Acta* 524 (2025), <https://doi.org/10.1016/j.electacta.2025.146079>.
- [62] M. Serhan, M. Sprowls, D. Jackemeyer, M. Long, I.D. Perez, W. Maret, N. Tao, E. Forzani, Total iron measurement in human serum with a smartphone, in: Aiche Annual Meeting, Conference Proceedings, American Institute of Chemical Engineers, 2019, <https://doi.org/10.1039/x0xx00000x>.
- [63] P.L. Yap, S. Kabiri, Y.L. Auyong, D.N.H. Tran, D. Losic, Tuning the multifunctional surface chemistry of reduced graphene oxide via combined elemental doping and chemical modifications, *ACS Omega* 4 (2019) 19787–19798, <https://doi.org/10.1021/acsomega.9b02642>.
- [64] A.H. Pasanaje, A.C. Lokhande, D.S. Choi, N. Singh, Structural engineering of nitrogen-doped reduced graphene oxide for high-performance lithium-ion batteries: an experimental and theoretical study, *ACS Appl. Energy Mater.* 8 (2025) 15692–15705, <https://doi.org/10.1021/acsaem.5c01980>.

- [65] D. Xiong, X. Li, Z. Bai, H. Shan, L. Fan, C. Wu, D. Li, S. Lu, Superior cathode performance of nitrogen-doped graphene frameworks for lithium ion batteries, *ACS Appl. Mater. Interfaces* 9 (2017) 10643–10651, <https://doi.org/10.1021/acsami.6b15872>.
- [66] J.D. Bagley, D.K. Kumar, K.A. See, N.C. Yeh, Selective formation of pyridinic-type nitrogen-doped graphene and its application in lithium-ion battery anodes, *RSC Adv.* 10 (2020) 39562–39571, <https://doi.org/10.1039/d0ra06199a>.
- [67] J. Zhang, Z. Xia, L. Dai, Carbon-based electrocatalysts for advanced energy conversion and storage, *Sci. Adv.* 1 (2015), <https://doi.org/10.1126/sciadv.1500564>.
- [68] T. Peng, H. Sun, T. Peng, B. Liu, X. Zhao, Structural regulation and electroconductivity change of nitrogen-doping reduced graphene oxide prepared using p-phenylene diamine as modifier, *Nanomaterials* 7 (2017), <https://doi.org/10.3390/nano7100292>.
- [69] W. Zhang, K. Kang, J. Duan, P. Li, R. Zhang, J. Wang, Y. Liu, High content pyridine nitrogen-doped carbon nanosheets derived from ZIF-L as anode materials of lithium-ion batteries with excellent capacity and rate performance, *J. Alloys Compd.* 992 (2024), <https://doi.org/10.1016/j.jallcom.2024.174591>.
- [70] Y. Zhang, P. Zhang, Y. Xu, X. Song, H. Wang, T. Ma, Synthesis of pomegranate-shaped micron ZnMn_2O_4 with enhanced lithium storage capability, *J. Mater. Chem.* 7 (2021) 699–707, <https://doi.org/10.1016/j.jmat.2021.01.005>.
- [71] L. Dong, J. Hao, H. Liu, W. Shi, J. Yang, J. Lian, Three-dimensional ZnMn_2O_4 nanoparticles/carbon cloth anodes for high-performance flexible lithium-ion batteries, *ChemistrySelect* 5 (2020) 2372–2378, <https://doi.org/10.1002/slct.202000037>.
- [72] Q. Tang, Y. Shi, Z. Ding, T. Wu, J. Wu, V. Mattick, Q. Yuan, H. Yu, K. Huang, Three-dimensional hierarchical graphene and CNT-Coated spinel ZnMn_2O_4 as a high-stability anode for lithium-ion batteries, *Electrochim. Acta* 338 (2020), <https://doi.org/10.1016/j.electacta.2020.135853>.
- [73] Z. Zhao, G. Tian, A. Sarapulova, V. Trouillet, Q. Fu, U. Geckle, H. Ehrenberg, S. Dsoke, Elucidating the energy storage mechanism of ZnMn_2O_4 as promising anode for Li-ion batteries, *J. Mater. Chem. A Mater* 6 (2018) 19381–19392, <https://doi.org/10.1039/c8ta06294c>.
- [74] C. Feng, W. Wang, X. Chen, S. Wang, Z. Guo, Synthesis and electrochemical properties of ZnMn_2O_4 anode for lithium-ion batteries, *Electrochim. Acta* 178 (2015) 847–855, <https://doi.org/10.1016/j.electacta.2015.08.070>.
- [75] X.H. Huang, J.P. Tu, B. Zhang, C.Q. Zhang, Y. Li, Y.F. Yuan, H.M. Wu, Electrochemical properties of NiO-Ni nanocomposite as anode material for lithium ion batteries, *J. Power Sources* 161 (2006) 541–544, <https://doi.org/10.1016/j.jpowsour.2006.03.039>.
- [76] R. Ding, J. Zhang, J. Qi, Z. Li, C. Wang, M. Chen, N-Doped dual carbon-confined 3D architecture rGO/ Fe_3O_4 /AC nanocomposite for high-performance lithium-ion batteries, *ACS Appl. Mater. Interfaces* 10 (2018) 13470–13478, <https://doi.org/10.1021/acsami.8b00353>.
- [77] W. Qiu, Z. Lin, H. Xiao, G. Zhang, H. Gao, H. Feng, X. Lu, Construction of chemical self-charging zinc ion batteries based on defect coupled nitrogen modulation of zinc manganite vertical graphene arrays, *Mater. Adv.* 2 (2021) 6694–6702, <https://doi.org/10.1039/d1ma00727k>.
- [78] M. Możdzierz, Z. Feng, A. Brzoza-Kos, P. Czaja, B. Fu, K. Świerczek, Understanding the electrochemical reaction mechanism to achieve excellent performance of the conversion-alloying Zn_2SnO_4 anode for Li-ion batteries, *J. Mater. Chem. A Mater* 11 (2023) 20686–20700, <https://doi.org/10.1039/d3ta02549g>.
- [79] P. Bharathidasan, M.B. Idris, D.W. Kim, S.R. Sivakkumar, S. Devaraj, Enhanced capacitance properties of nitrogen doped reduced graphene oxide obtained by simultaneous reduction and nitrogen doping, *FlatChem* 11 (2018) 24–31, <https://doi.org/10.1016/j.flatc.2018.10.001>.
- [80] S. Liang, M. Luo, Y.Y. Dou, L. Guo, B. Liang, H.B. Li, J. Li, Fabrication and electrochemical performance of nitrogen-doped graphene synthesized by hydrothermal method, in: *Materials Science Forum*, Trans Tech Publications Ltd, 2015, pp. 35–38, <https://doi.org/10.4028/www.scientific.net/MSF.804.35>.
- [81] Z.S. Wu, W. Ren, L. Xu, F. Li, H.M. Cheng, Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries, *ACS Nano* (2011) 5463–5471, <https://doi.org/10.1021/nn2006249>.
- [82] H. Xu, L. Ma, Z. Jin, Nitrogen-doped graphene: synthesis, characterizations and energy applications, *J. Energy Chem.* 27 (2018) 146–160, <https://doi.org/10.1016/j.ijechem.2017.12.006>.
- [83] T. Van Khai, H.G. Na, D.S. Kwak, Y.J. Kwon, H. Ham, K.B. Shim, H.W. Kim, Significant enhancement of blue emission and electrical conductivity of N-doped graphene, *J. Mater. Chem.* 22 (2012) 17992–18003, <https://doi.org/10.1039/c2jm33194b>.
- [84] Q. Li, H. Li, Q. Xia, Z. Hu, Y. Zhu, S. Yan, C. Ge, Q. Zhang, X. Wang, X. Shang, S. Fan, Y. Long, L. Gu, G.X. Miao, G. Yu, J.S. Moosera, Extra storage capacity in transition metal oxide lithium-ion batteries revealed by in situ magnetometry, *Nat. Mater.* 20 (2021) 76–83, <https://doi.org/10.1038/s41563-020-0756-y>.
- [85] T.S. Sreeprasad, V. Berry, How do the electrical properties of graphene change with its functionalization? *Small* 9 (2013) 341–350, <https://doi.org/10.1002/sml.201202196>.
- [86] J. Chen, M. Asachi, A. Hassanpour, M. Babaie, M. Jabbari, Modelling of lithium-ion battery electrode calendaring: a critical review, *J. Energy Storage* 123 (2025), <https://doi.org/10.1016/j.est.2025.116702>.
- [87] Q. Gao, Z. Yuan, L. Dong, G. Wang, X. Yu, Reduced graphene oxide wrapped ZnMn_2O_4 /carbon nanofibers for long-life lithium-ion batteries, *Electrochim. Acta* 270 (2018) 417–425, <https://doi.org/10.1016/j.electacta.2018.03.107>.
- [88] B. Kurc, M. Pigłowska, An influence of temperature on the lithium ions behavior for starch-based carbon compared to graphene anode for LIBs by the electrochemical impedance spectroscopy (EIS), *J. Power Sources* 485 (2021), <https://doi.org/10.1016/j.jpowsour.2020.229323>.
- [89] R.S. Babu, E. Madai, D.S. Nair, P. Gonugunta, S.M. Armaki, R. Hendriks, T. Panneerselvam, R. Murugan, V.V.R.K. Kumar, P. Taheri, A. Mol, N. Satyanarayana, P.R. Anusuyadevi, Effect of synthesis conditions on morphology, surface chemistry and electrochemical performance of nickel ferrite nanoparticles for lithium-ion battery applications, *J. Mater. Sci. Mater. Electron.* 36 (2025), <https://doi.org/10.1007/s10854-025-14886-w>.