

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). One-pot interfacial engineering of $\text{ZnMn}_2\text{O}_7/\text{N-rGO}$ nanocomposites as anode materials for high-performance lithium-ion batteries. *Journal of Electroanalytical Chemistry*, 1018, Article 120415. <https://doi.org/10.1016/j.jelechem.2026.120415>

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.



One-pot interfacial engineering of $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites as anode materials for high-performance lithium-ion batteries

Bharath Chandran^a, Reshma S. Babu^a, Durga S. Nair^c, O. Padmaraj^c, 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 (MSE), Faculty of Mechanical Engineering (ME), Delft University of Technology, Mekelweg 2, 2628, CD, Delft, the Netherlands

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

ARTICLE INFO

Keywords:

ZnMn_2O_4
Nitrogen-doped reduced graphene oxide
lithium-ion batteries
Anode materials
Interfacial engineering
Charge-transfer kinetics
Hydrothermal synthesis

ABSTRACT

In recent years, spinel-structured transition-metal oxide ZnMn_2O_4 has attracted attention as a low-cost anode material with high lithium-ion storage capacity. However, its practical application is limited by poor intrinsic electrical conductivity, sluggish reaction kinetics, and large volume changes during repeated lithiation and delithiation, leading to unstable cycling behavior. Although several strategies have been explored to improve cyclic stability, many reported systems still suffer from limited rate performance, multistep synthesis routes, and an incomplete understanding of nitrogen-doped graphene oxide (N-rGO)-induced interfacial effects. In this work, hybrid $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites with controlled graphene oxide additions of 20 and 30 wt% were synthesized via a simple one-pot hydrothermal route, enabling intimate oxide–N-rGO interfacial contact. Structural, microscopic, and X-ray photoelectron spectroscopy analyses confirmed the formation of phase-pure tetragonal ZnMn_2O_4 nanoparticles uniformly distributed on the N-rGO framework. XPS revealed a redistribution of nitrogen bonding configurations at higher GO loading, with increased graphitic nitrogen contribution that may enhance electronic conductivity, while pyridinic and pyrrolic nitrogen species provide interfacial active sites. Brunauer–Emmett–Teller analysis showed that increasing GO content enhanced the specific surface area and pore volume while preserving mesoporous architecture. The $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposite containing 30 wt% graphene oxide (ZMO-30) delivered a reversible discharge capacity of 859.02 mAh g^{−1} after 100 cycles at 100 mA g^{−1} with superior rate performance and reduced charge-transfer resistance, demonstrating the beneficial role of oxide–N-rGO interfacial engineering in improving the kinetics and durability of ZnMn_2O_4 anodes.

1. Introduction

Over the past few decades, sustainable energy solutions have driven significant research into the development of reliable and efficient energy storage systems. Among the energy-storing technologies explored so far, rechargeable lithium-ion batteries (LIBs) continue to dominate both academic research and commercial applications due to their high energy density, long cycle life, and well-established production infrastructure [1–4]. Consequently, LIBs remain the primary power source for most portable electronic devices and are closely linked to the continued growth of electric vehicles (EVs) and large-scale energy storage technologies [1,2]. However, the overall performance of LIBs is increasingly

constrained by the limitations of currently available anode materials. Graphite remains the most widely used commercial anode material because of its excellent cycling stability and long service life. Nevertheless, its low theoretical capacity of 372 mAh g^{−1} has become a major obstacle to achieving high-energy-density lithium-ion batteries. Consequently, considerable research efforts have been devoted to developing alternative anode materials that can simultaneously deliver higher capacity, improved rate capability, and long-term cycling stability [5–7].

Among the various alternative anode materials investigated, transition metal oxides (TMOs) have received significant attention as potential anode materials because of their very high theoretical capacities associated with conversion-type lithium storage reactions. However, the

* Corresponding authors.

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

<https://doi.org/10.1016/j.jelechem.2026.120415>

Received 4 June 2026; Received in revised form 5 July 2026; Accepted 8 July 2026

Available online 8 July 2026

1572-6657/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

practical use of these TMOs has serious drawbacks, including poor intrinsic electrical conductivity and large volume changes during repeated lithiation and delithiation processes [8,9]. Over continuous cycling, these effects lead to electrode pulverization due to unstable electrode-electrolyte interfaces and rapid capacity fading. Among TMOs, mixed transition-metal oxides (MTMOs) with spinel structured- AB_2O_4 type, where $A = \text{Zn, Co, Ni, etc.}$, and $B = \text{Mn, Fe, Co, etc.}$, have been proposed as more viable alternatives. The presence of two different A and B metal cations introduces synergistic redox behavior and facilitates electron transport between multiple valence states. As a result, the conductivity can be improved compared to that of single-metal oxides [10–12]. Among the reported MTMOs, ZnMn_2O_4 has gained notable attention as an anode for LIBs due to its high theoretical capacity ($\sim 1008 \text{ mAh g}^{-1}$), low cost, abundance of Zn and Mn, environmentally benign nature, and low Li-ion extraction potential (1.3–1.5 V), compared to cobalt-based oxide [13,14]. However, despite these advantages, ZnMn_2O_4 also exhibits poor electrical conductivity and volume expansion during lithium insertion and extraction, which cause electrode pulverization and cracking along with the formation of an unstable solid-electrolyte interphase, leading to gradual capacity degradation [14].

To address the aforementioned issues, many approaches have focused on modifying the nano- and micro-scale morphologies of ZnMn_2O_4 , which include loaf-like nanorods [15], ball-in-ball hollow microspheres [16], nanofibers [17], hollow microrods [18], etc. Such designs can shorten lithium-ion diffusion paths and provide additional space to accommodate volume changes during cycling. However, despite these structural improvements, the electrochemical performance of most pristine ZnMn_2O_4 architectures remained below the theoretical capacity, particularly during prolonged cycling and high-rate operation. To overcome this, Cai et al [14], demonstrated the synthesis of graphene-wrapped porous ZnMn_2O_4 nanospheres, in which ZnMn_2O_4 was first prepared via hydrothermal treatment followed by calcination, and subsequently wrapped with reduced graphene oxide (rGO) using 3-aminopropyltrimethoxysilane (APTMS). Similarly, Zhang et al [19] reported the preparation of graphene-wrapped ZnMn_2O_4 hollow microspheres by a hydrothermal method, followed by APS-assisted graphene wrapping and calcination. These graphene-wrapped ZnMn_2O_4 nanocomposites demonstrated strong interfacial contact, resulting in effective charge transfer, improved lithium-ion diffusion paths, cycling stability, and rate performance [20]. In addition to graphene-wrapping techniques, three-dimensional hybrid carbon frameworks incorporating both reduced graphene oxide and carbon nanotubes have also been explored to enhance conductivity and structural robustness. For instance, the $\text{ZnMn}_2\text{O}_4/\text{CNT}/\text{rGO}$ network architectures reported by Tang et al [21] showed improved cycling stability by physically interconnecting conductive pathways around the active particles. In all these reports, rGO serves as a conductive and flexible support matrix due to its high electrical conductivity, large surface area, mechanical strength, and chemical stability.

Although the previous approaches effectively improved the conductivity and structural stability of ZnMn_2O_4 , they generally rely on multistep synthetic procedures involving separate oxide synthesis, surface functionalization, and subsequent graphene wrapping or assembly. Such processing increases fabrication complexity and may limit the scalability of composite production. Recently, one-pot synthesis strategies have also been explored to simplify the fabrication of ZnMn_2O_4 -based composite anodes while simultaneously improving their electrochemical performance through rational structural design. For instance, Chandran et al. [13] reported a one-pot microwave-assisted $\text{ZnMn}_2\text{O}_4/\alpha\text{-MnO}_2$ nanocomposite with improved electrochemical performance. However, the composite did not incorporate a conductive carbon framework to enhance electrical conductivity and oxide-carbon interfacial charge-transfer characteristics. Nevertheless, the improvement in rate performance achieved using undoped rGO remains limited, as recent in situ electrochemical Raman studies have clearly demonstrated

that Li^+ storage in rGO is largely due to non-specific lattice defects and electrostatic charge accumulation, resulting in weakly localized Li^+ -carbon interactions and restricted interfacial charge-transfer efficiency [22]. In contrast, nitrogen-doped reduced graphene oxide (N-rGO) can introduce chemically active nitrogen-induced defect sites that act as preferential Li^+ anchoring centers within the carbon framework [22–24]. These nitrogen functionalities, particularly pyridinic-N, can strengthen Li^+ -surface interactions and improve charge-transfer behavior, thereby reducing kinetic polarization during cycling [22,23]. Moreover, nitrogen incorporation modifies the electronic structure of graphene. The graphitic nitrogen enhances the intrinsic electrical conductivity of the carbon network, while pyridinic nitrogen has been reported to promote strong metal-nitrogen (N) interfacial electronic coupling through orbital hybridization and charge redistribution in transition-metal/nitrogen-doped carbon systems [25,26]. Consequently, nitrogen doping in rGO improves Li-ion storage kinetics and high-rate electrochemical performance compared to undoped rGO, resulting in superior rate capability and cycling stability under high current densities [24]. Based on these considerations, integrating N-rGO with ZnMn_2O_4 through a one-pot in situ hydrothermal synthesis offers an effective strategy for simultaneously constructing a conductive graphene network and promoting the direct nucleation and growth of ZnMn_2O_4 nanoparticles on the N-rGO sheets, thereby establishing an intimate ZnMn_2O_4 -N-rGO interface. In the present work, the term “interfacial engineering” refers to the deliberate formation of this intimate ZnMn_2O_4 -N-rGO interface through one-pot in situ synthesis rather than by post-synthetic physical mixing or wrapping. Such an in situ interfacial architecture is expected to facilitate electron transport, reduce interfacial charge-transfer resistance, promote Li-ion transport, and improve the structural stability of the electrode during repeated lithiation/delithiation, thereby enhancing the capacity, rate capability, and cycling performance of ZnMn_2O_4 -based lithium-ion battery anodes.

Motivated by these considerations, a scalable one-pot synthesis strategy was employed to develop $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites, aiming to promote intimate interfacial contact between ZnMn_2O_4 and N-rGO while overcoming the limitations of previously reported multistep composite fabrication routes. The influence of N-rGO-induced interfacial effects on the electrochemical behavior of the composites was systematically investigated at different graphene oxide loadings (20 and 30 wt%) using complementary structural, morphological, surface, and electrochemical characterization techniques. XRD, Raman, FTIR, and XPS analyses were employed to confirm phase formation, graphene oxide reduction, nitrogen incorporation, and oxide-graphene interfacial interactions, whereas FESEM, TEM, and BET analyses were used to evaluate the morphology and textural characteristics of the composites. Furthermore, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), cycling stability, rate capability, and electrochemical impedance spectroscopy (EIS) were performed to elucidate the influence of conductive network density and oxide-N-rGO interfacial interactions on charge-transfer kinetics and lithium-ion storage performance, particularly under high-rate operating conditions.

2. Experimental

2.1. Materials

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$], manganese acetate tetrahydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$], ethanol [$\text{C}_2\text{H}_5\text{OH}$], and ammonia solution [$\text{NH}_3(\text{aq})$, 25%] were used as received without further purification. Deionized (DI) water [H_2O] was used throughout the experiments. Graphene oxide [GO] used was prepared by the modified Hummers' method as described in the supplementary information.

2.2. Synthesis of ZnMn_2O_4 (ZMO) nanoparticles

Pure ZnMn_2O_4 (ZMO) nanoparticles were synthesized by dissolving 2.5 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 5 mmol $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in 100 mL of a mixed solvent mixture comprising 10 mL ethanol and 90 mL DI water under magnetic stirring for 1 h at room temperature. The resultant solution was ultrasonicated for 30 min, followed by dropwise addition of 20 mL NH_3 solution to bring the total volume to 120 mL under continuous stirring for an additional 1 h. The mixture was transferred to a 200 mL Teflon-lined stainless-steel autoclave and heated at 160°C for 12 h in a hydrothermal reactor. After natural cooling, the precipitate was collected by centrifugation, washed several times with DI water and ethanol, and dried to obtain pristine ZMO material.

2.3. Synthesis of $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites

Fig. 1 shows the schematic illustration of the synthesis process for the $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposite via a one-pot hydrothermal method. First, 2.5 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 5 mmol $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 mL of a mixed solvent mixture comprising 10 mL of ethanol and 90 mL of DI water, under magnetic stirring for 1 h at room temperature. Then, the required amount of GO, specifically 120 mg and 180 mg for different mass loadings of 20% and 30%, respectively, was added to the aforementioned $\text{Zn}^{2+}/\text{Mn}^{2+}$ precursor solution under continuous stirring and ultrasonication for 1 h at room temperature. This was followed by the dropwise addition of 20 mL aqueous ammonia $[\text{NH}_3(\text{aq})]$ under continuous stirring for an additional hour at room temperature. The resultant mixture was then transferred to a 200 mL Teflon-lined stainless-steel autoclave and heated at 160°C for 12 h. During the hydrothermal treatment, aqueous ammonia served both as the precipitating agent for ZnMn_2O_4 formation and as the nitrogen source for the in situ nitrogen functionalization of graphene oxide. Under these conditions, ammonia can react with the oxygen-containing functional groups and defect sites of graphene oxide, promoting its simultaneous reduction and the incorporation of nitrogen-containing functionalities into the graphene framework [27]. After hydrothermal treatment, the autoclave was naturally cooled to room temperature. The resulting precipitate was collected by centrifugation, washed several times with a deionized water–ethanol mixture, and dried to obtain $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites with graphene oxide loadings of 20 and 30 wt%, designated as ZMO-20 and ZMO-30, respectively. The obtained nanocomposites were subsequently characterized using various structural, morphological, surface, and electrochemical techniques.

2.4. Material characterization

The as-prepared pristine ZnMn_2O_4 (ZMO) nanoparticles and the two

different $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites, denoted as ZMO-20 and ZMO-30 samples, were analyzed through different characterization techniques in order to confirm the phase formation, examine the presence of graphene-metal oxide components, and evaluate the morphological and surface chemical features of both pure and nanocomposite samples. A set of complementary characterization techniques was employed, including diffraction and spectroscopic methods for phase and bonding analysis, and microscopic techniques for morphology and microstructure investigation.

Crystallographic phase analysis was performed by X-ray diffraction. The diffraction patterns of the samples were recorded on a Bruker D8 Advance diffractometer employing $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated in Bragg-Brentano geometry. The diffracted patterns were collected over a 2θ range of 5° – 80° using a Lynxeye position-sensitive detector. Raman spectroscopy was used to probe the structural features and disorder of reduced graphene oxide (rGO) in the composites. Raman spectra were acquired using a laser confocal Raman spectrometer equipped with a 514 nm excitation laser. Fourier-transform infrared spectroscopy was further employed to examine chemical bonding and surface functional groups. FTIR spectra were recorded in a Thermo Nicolet 6700 spectrometer in transmittance mode using KBr pellets. The surface morphology and particle distribution in the samples were examined by field-emission scanning electron microscopy (FESEM) using a JEOL JSM-6500F instrument.

operating at 20 kV with a working distance of approximately 10 mm. Elemental composition and its spatial distribution were analyzed by energy-dispersive X-ray spectroscopy using a JEOL JSM-IT800 FESEM system. Microstructural features of ZMO30 were investigated in greater detail by high-resolution transmission electron microscopy (HRTEM). The HRTEM images and selected area electron diffraction patterns were obtained using a JEOL JEM-2100 microscope operated at 200 kV to assess lattice features and crystallinity. The HRTEM instrument 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 carried out under ultra-high vacuum conditions of 10^{-9} mbar, with the X-ray source operated at 200 W power and an accelerating voltage of 13.5 kV. The survey spectra were recorded at a pass energy of 89.45 eV, while high-resolution spectra were acquired at 71.55 eV. All the obtained XPS data were processed using MultiPak v8.0 software. Textural properties of the samples were evaluated by nitrogen adsorption-desorption measurements performed on a Micromeritics Tristar II 3020 analyzer. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while the pore size distribution and total pore volume were determined from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method.

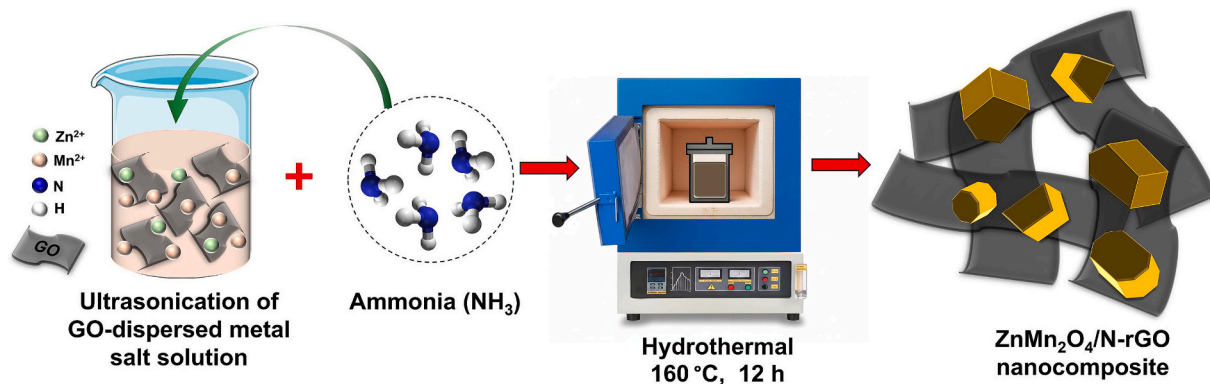


Fig. 1. Schematic illustration for the preparation of $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ nanocomposites by a simple one-pot hydrothermal route, involving GO dispersion in the $\text{Zn}^{2+}/\text{Mn}^{2+}$ precursor solution, followed by aqueous ammonia addition.

2.5. Electrode preparation

The working electrode slurry was prepared by mixing the active material, Super P conductive carbon, and polyvinylidene fluoride (PVDF) binder in the weight ratio of 70:20:10 in *N*-methyl-2-pyrrolidone (NMP). The prepared homogeneous slurry was coated over the copper foil using the doctor blade technique and dried in a hot-air oven at 80 °C for 12 h. The dried working electrodes were cut into circular disks with a diameter of 8 mm. The active material loading was 1.25 mg cm⁻² for ZMO, 0.48 mg cm⁻² for ZMO-20, and 0.46 mg cm⁻² for ZMO-30.

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, O₂ < 1 ppm, H₂O ~ 0.01 ppm), using lithium metal (10 mm diameter) as the counter/reference electrode and newly prepared pure ZMO, ZMO-20, and ZMO-30 nanocomposites coated copper discs as the working electrode. A Whatman glass micro-fiber filter (16 mm diameter) was used as a separator, and 1 M LiPF₆ dissolved in a 1:1 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) served as the electrolyte. Electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were performed using a Biologic BCS 810 workstation. CV curves were recorded between 0.01 and 3.0 V (vs. Li/Li⁺) at a scan rate of 0.1 mV s⁻¹. GCD measurements were carried out within the same potential window to evaluate cycling stability and rate capability at different current densities. EIS spectra were recorded in the frequency range of 10 kHz to 1 Hz using a sinusoidal 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, morphological, and textural analysis

3.1.1. XRD

Fig. 2 shows the XRD patterns of as-prepared graphene oxide (GO), pristine ZnMn₂O₄ (ZMO), and its nanocomposites prepared by the addition of 20 wt% and 30 wt% of graphene oxide, denoted as ZMO-20 and ZMO-30, respectively, along with the standard JCPDS (Card No. 24-1133; *a* = *b* = 5.722 Å, *c* = 9.236 Å) data for ZnMn₂O₄.

The pure ZMO sample and nanocomposites ZMO-20 and ZMO-30 showed sharp, well-defined diffraction peaks at 18.4°, 29.4°, 31.13°, 33.18°, 36.31°, 39.17°, 44.69°, 50.92°, 52.20°, 54.39°, 56.78°, 58.98°, 61.03°, 65.09°, and 75.05°, which are compared with standard JCPDS

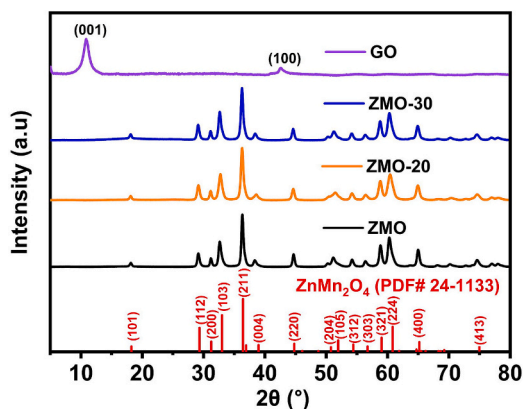


Fig. 2. XRD patterns of the as-prepared pure ZMO, nanocomposites ZMO-20 and ZMO-30, and GO, along with the standard JCPDS data for the ZnMn₂O₄ phase.

data for the ZnMn₂O₄ phase and are assigned to the crystallographic planes (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224), (440), and (413), respectively, of the tetragonal spinel ZnMn₂O₄ phase with space group I4₁/amd [28,29]. The excellent agreement between the observed diffraction patterns and the standard JCPDS data confirms the formation of the pure ZnMn₂O₄ phase in ZMO, ZMO-20, and ZMO-30. Further, no additional peaks corresponding to crystalline impurities were detected. Moreover, no distinct diffraction peaks of rGO were observed, which may be attributed to its amorphous nature and relatively low content of rGO in the nanocomposites.

Furthermore, the crystallite sizes were estimated using the Williamson-Hall (W-H) method from the obtained XRD data. The obtained W-H plots are shown in Fig. S1. The average crystallite sizes were found to be 21 nm for ZMO, 19 nm for ZMO-20, and 21 nm for ZMO-30. These results indicate that the different mass loadings of 20 & 30 wt% GO have a negligible effect on the crystallite size of the ZnMn₂O₄ phase. The estimated lower average crystallite size is highly relevant, as nanoscale crystalline domains facilitate lithium-ion diffusion and thereby significantly influence the electrochemical performance of lithium-half cells when they are used as anode materials.

3.1.2. Raman and FTIR

Fig. 3(a) shows the Raman spectra obtained for pristine ZMO, nanocomposites ZMO-20 and ZMO-30, and GO. For pristine ZMO, the peaks observed at 325.1 cm⁻¹, 383.5 cm⁻¹, and 671.8 cm⁻¹ correspond to Mn—O bending vibration with E_g symmetry, Mn—O stretching vibration in octahedral units with T_{2g} symmetry, and the A_{1g} symmetric stretching vibration of oxygen in Zn—O₄ tetrahedra, respectively, consistent with the previously reported Raman-active modes of tetragonal spinel ZnMn₂O₄ [30–33]. Similar peaks were also observed in the newly prepared nanocomposites, as shown in Fig. 3(a). In the case of the ZMO-20 sample, the characteristic ZnMn₂O₄ modes appear at 325.2 cm⁻¹, 380.7 cm⁻¹, and 669.0 cm⁻¹, while for the ZMO-30 sample, they occur at 326.6 cm⁻¹, 383.5 cm⁻¹, and 669.0 cm⁻¹. In addition, the Raman spectra of ZMO-20, ZMO-30, and GO showed graphitic D and G bands. The D band depicted at approximately 1358.56 cm⁻¹ corresponds to the A_{1g} breathing mode of disordered sp² carbon, and the G band at around 1604.83 cm⁻¹ corresponds to the E_{2g} stretching vibration of the sp² carbon network [34]. From the estimated I_D/I_G ratios, values are found to be from 0.85 for GO to 1.05 and 1.02 for ZMO-20 and ZMO-30, respectively, indicating an increase in the degree of disorder and defects in the graphene network. This may be due to the successful reduction of GO, as well as the strong interfacial interactions between ZMO and GO in the nanocomposites, which is consistent with previous reports [34,35]. Furthermore, it is also worth noting that ZMO-20 and ZMO-30, and GO exhibited higher-order modes, such as the 2D band (2700 cm⁻¹), the D + G band (2950 cm⁻¹), and the 2G overtone (3200 cm⁻¹), as described in a previous report [36]. The presence of a broad 2D band confirms multilayer stacking of graphene sheets, and its position is known to be sensitive to stacking order and the presence of oxygen-containing functional groups. These observations are consistent with the expected behavior of GO and rGO-like materials embedded within the composite [32,35,36]. Overall, the Raman analysis reveals that the fundamental vibrational modes of the ZnMn₂O₄ phase are preserved in all samples, while the presence of graphitic features in the composites indicates the effective integration of ZnMn₂O₄-rGO in the nanocomposite structure.

Fig. 3(b) presents the FTIR spectra of the as-prepared ZMO and nanocomposites ZMO-20 and ZMO-30, along with pristine GO. The broad band centered at approximately 3436.20 cm⁻¹ is attributed to the stretching vibrations of hydroxyl (—OH) functional groups on partially reduced GO, as well as physically adsorbed moisture present on the surface of the metal oxide [37]. For pristine ZnMn₂O₄ (ZMO), this observed vibrational band is relatively intense due to the adsorption of atmospheric moisture and surface hydroxyl groups (—OH) [37,38]. In

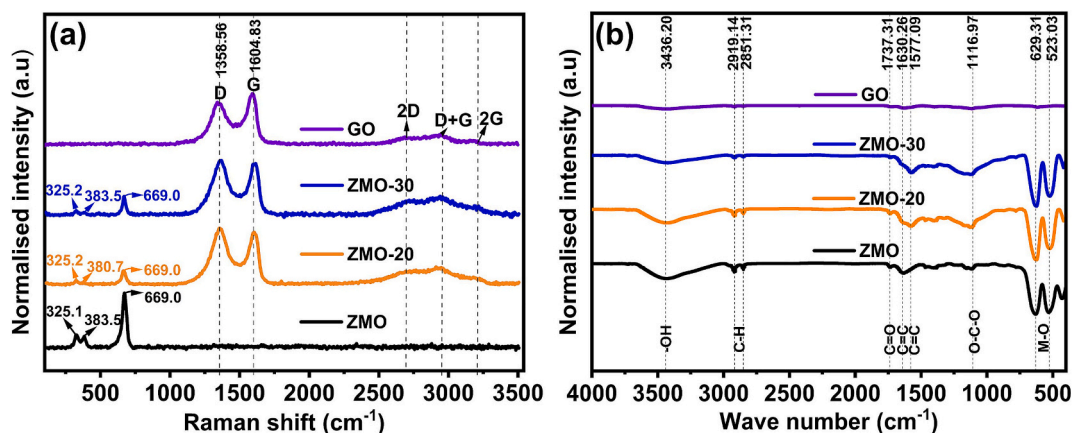


Fig. 3. (a) Raman and (b) FTIR spectra of the as-prepared pure ZMO, nanocomposites ZMO-20 and ZMO-30, and GO.

the case of nanocomposite ZMO-20 and ZMO-30 samples, the observed O—H band intensity was gradually decreasing with an increase in GO content, which attributes the partial reduction of GO under hydrothermal conditions, due to the consumption of surface hydroxyl groups during oxide–graphene interfacial coupling and the reduced adsorption of moisture on the composite surface [37,38]. The observed weak bands at 2919.14 cm^{-1} and 2851.31 cm^{-1} correspond to the asymmetric and symmetric C—H stretching vibrations, respectively. These bands are commonly associated with residual organic species, which may originate from adsorbed ethanol used during washing processes or from remaining aliphatic carbon moieties present in partially reduced GO [13,37,38]. The peak appearing at 1737.31 cm^{-1} can be assigned to C=O stretching vibrations from graphene oxide. The band observed at 1630.26 cm^{-1} is attributed to the skeletal vibration of sp^2 -bonded carbon (C=C) within oxidized graphitic domains of graphene oxide, and due to carbon impurity, whereas the peak at 1577.09 cm^{-1} corresponds to the C=C stretching vibration of partially restored graphitic domains, indicating the structural evolution of graphene sheets during reduction [37,39,40]. The peak appearing at 1116.97 cm^{-1} is attributed to O—C—O stretching vibrations, characteristic of epoxy or alkoxy functional groups present in GO [37]. For pure ZMO, this band is most plausibly attributed to C—O stretching vibrations arising from residual organic species originating from precursor salts such as acetate or alcohol-derived fragments, or from surface carbonates formed via adsorption of atmospheric CO_2 [37]. Importantly, the pure ZMO and nanocomposites ZMO-20 and ZMO-30 samples showed two prominent low-wavenumber absorption bands at 629.31 cm^{-1} and 523.03 cm^{-1} , which can be assigned to Mn—O stretching and Zn—O vibrations, respectively, within the spinel ZnMn_2O_4 crystal structure, as reported in the literature [13,38]. The presence and consistency of these vibrational bands, along with the observed XRD patterns of the ZMO, ZMO-20, and ZMO-30 samples, confirm the successful formation of the ZnMn_2O_4 crystal structure and indicate the incorporation of a graphene-metal-oxygen framework.

Thus, the Raman and FTIR results, together with the XRD patterns, confirm the presence of partially reduced GO with residual oxygen-containing functional groups and a preserved metal-oxide framework, indicating the successful coexistence and integration of the ZnMn_2O_4 phase and rGO in the nanocomposites.

3.1.3. XPS

Fig. 4(a) shows the XPS survey spectra of ZMO, ZMO-20, and ZMO-30, confirming the presence of Zn, Mn, O, and C in all samples, thus indicating the formation of ZnMn_2O_4 . However, N 1s peaks were not prominently visible in the survey spectra of ZMO-20 and ZMO-30, as shown in Fig. 4(a). Figs. 4(b), (f), and (j) show the high-resolution Zn 2p spectra of ZMO, ZMO-20, and ZMO-30, respectively.

For ZMO, the Zn 2p peaks, Zn $2\text{p}_{1/2}$ and Zn $2\text{p}_{3/2}$ as shown in Figs. 4

(b), (f) and (j), appeared at 1044.53 eV and 1021.49 eV, respectively, with a spin orbital splitting of 23.04 eV, and are in excellent agreement with literature values for Zn^{2+} in the ZnMn_2O_4 sample ($\Delta \approx 23$ eV), confirming the existence of +2-oxidation state of Zn in the spinel lattice [13,41–43]. 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 [44]. From Fig. 4(c), the high-resolution Mn 2p of pristine ZnMn_2O_4 (ZMO) showed Mn $2\text{p}_{3/2}$ and Mn $2\text{p}_{1/2}$ peaks at 641.95 and 653.75 eV with an energy difference of $\Delta = 11.80$ eV, consistent with the Mn^{3+} state as expected for ZnMn_2O_4 [45,46]. In the ZMO-20 and ZMO-30 nanocomposites, the Mn 2p peaks exhibit a slight shift toward higher binding energies at 642.29 eV and 653.89 eV, respectively, along with a marginal decrease in spin-orbit splitting to 11.60 eV compared to 11.80 eV for pristine ZMO. According to Biesinger et al [47], such small variations in binding energy and spin-orbit separation can arise from subtle changes in the local Mn—O coordination environment, including variations in ligand field and surface electronic structure, without any change in oxidation state. In this context, the observed shift and reduced splitting in the nanocomposites can be attributed to slight modifications in the surface Mn—O environment. Similar Mn 2p binding-energy shifts have also been reported for graphene-integrated metal oxide systems, where they were associated with changes in the local bonding environment at the oxide–carbon interface [48]. Therefore, the present results indicate a mild surface-level perturbation of Mn coordination rather than any change in oxidation state, which remains Mn^{3+} in the ZnMn_2O_4 lattice. These observations are consistent with subtle modifications in the local electronic environment at the ZnMn_2O_4 /N-rGO interface. However, more direct interface-sensitive characterization techniques would be required to conclusively establish the nature of the interfacial electronic interaction.

Figs. 4(d), (h), and (l) show the deconvoluted high-resolution O 1s spectra of ZMO, ZMO-20, and ZMO-30, respectively. As shown in Fig. 4(d), the O 1s spectrum of pristine ZMO consists of a dominant peak at 530.04 eV, assigned to lattice oxygen (Zn—O/Mn—O) [42], and a weaker component at 531.80 eV attributed to surface hydroxyl groups (M—OH) [13]. Fig. 4(h), the O 1s spectrum of ZMO-20 exhibits peaks at 531.39 eV and 533.59 eV, corresponding to carbonyl/carboxyl (C=O/COOH) and C—O functional groups (epoxy/hydroxyl), respectively [49,50]. The contribution from surface hydroxyl groups is expected to overlap within the ~ 531 eV region. As shown in Fig. 4(l), the relative contribution of the C=O/COOH component increases, while the lattice oxygen contribution slightly decreases in ZMO-30 compared to ZMO-20, indicating a higher presence of oxygenated carbon species on the surface with increasing GO content. The persistence of the epoxy/hydroxyl component confirms the presence of residual oxygen functionalities in the

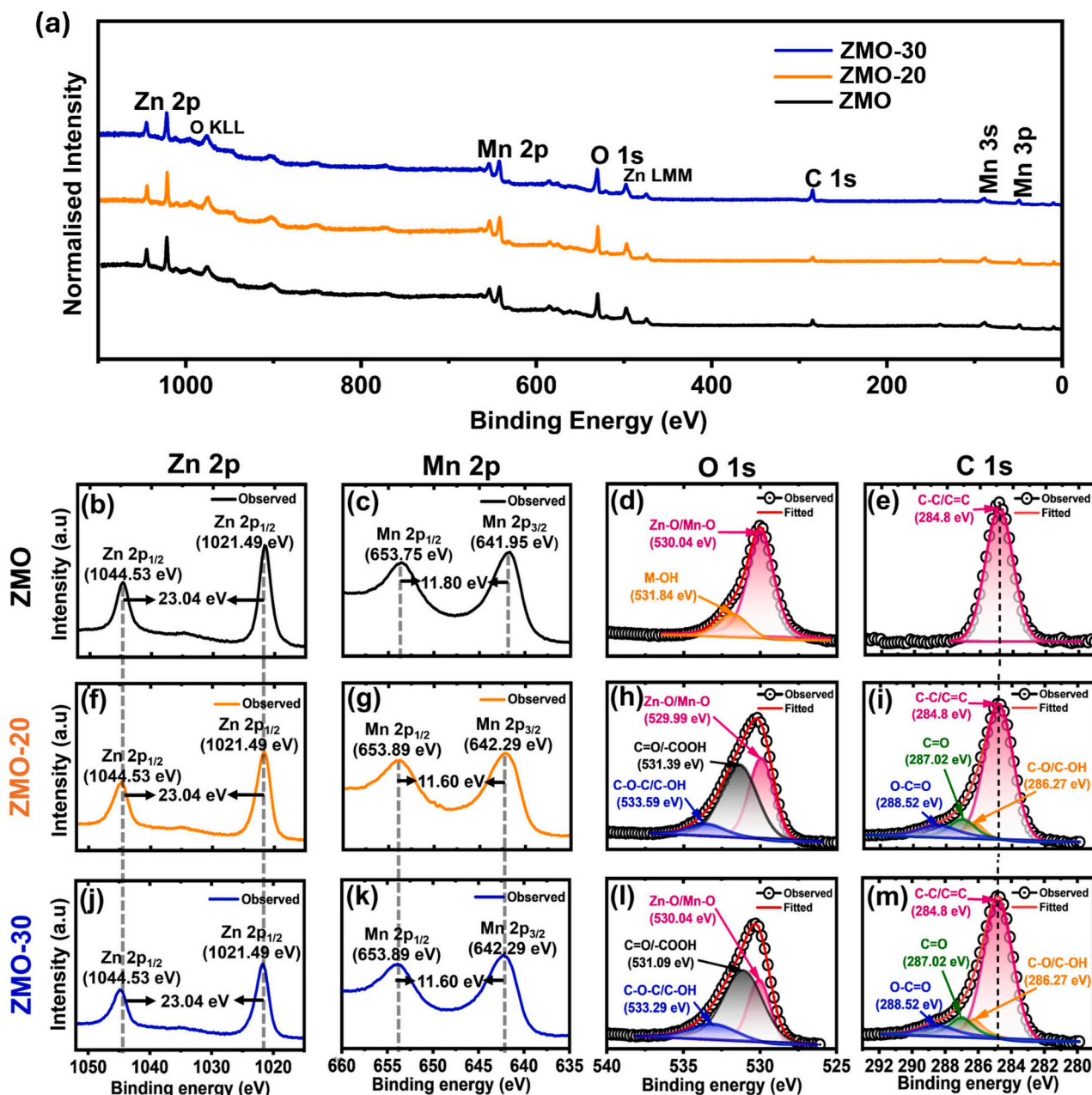


Fig. 4. XPS spectra of ZMO, ZMO-20, and ZMO-30: (a) Survey spectra, High-resolution Zn 2p, Mn 2p, O 1 s, and C 1 s spectra of (b-e) ZMO, (f-i) ZMO-20, and (j-m) ZMO-30.

graphene framework. Overall, the O 1 s analysis confirms an increasing contribution of carbon-related oxygen species with higher GO content, suggesting modification of the surface oxygen environment associated with metal oxide-N-rGO interaction.

Figs. 4(e), (i), and (m) show the deconvoluted high-resolution C 1 s spectra of ZMO, ZMO-20, and ZMO-30, respectively. As shown in Fig. 4 (e), the C 1 s spectrum of pristine ZMO exhibits a single dominant peak at 284.8 eV, attributed to adventitious carbon (C–C/C=C) originating from surface contamination during sample handling and exposure to air [51]. Upon incorporation of graphene oxide, the C 1 s spectrum of ZMO-20 shows an intense peak at 284.8 eV corresponding to sp²-hybridized C–C/C=C, along with additional components at 286.27 eV (C–O/C–OH), 287.02 eV (C=O), and 288.52 eV (O–C=O), as shown in Fig. 4(i) [52,53]. A similar distribution of components is observed for ZMO-30 (Fig. 4(m)), with an overall increase in C 1 s intensity due to higher graphene content. However, the relative contributions of individual

components remain largely unchanged compared to ZMO-20, indicating that increasing GO content primarily increases surface carbon concentration without introducing new chemical states of carbon. Due to the overlap between C–N and C–O contributions in the C 1 s region [52,53], reliable identification of C–N bonding is difficult. Therefore, nitrogen incorporation into the graphene framework is more conclusively confirmed from the analysis of high-resolution N 1 s spectra [37,52–54].

Fig. 5(a) shows the deconvoluted N 1 s spectrum of the ZMO-20 sample, which exhibits three characteristic components located at approximately 398.5, 399.9, and 401.06 eV. The binding energy positions obtained for ZMO-20 were used as a reference for the deconvolution of ZMO-30, enabling a consistent comparison of nitrogen bonding configurations. Fig. 5(b) shows the corresponding N 1 s spectrum of ZMO-30, with peaks at similar positions assigned to pyridinic, pyrrolic, and graphitic nitrogen, respectively, in agreement with previous reports

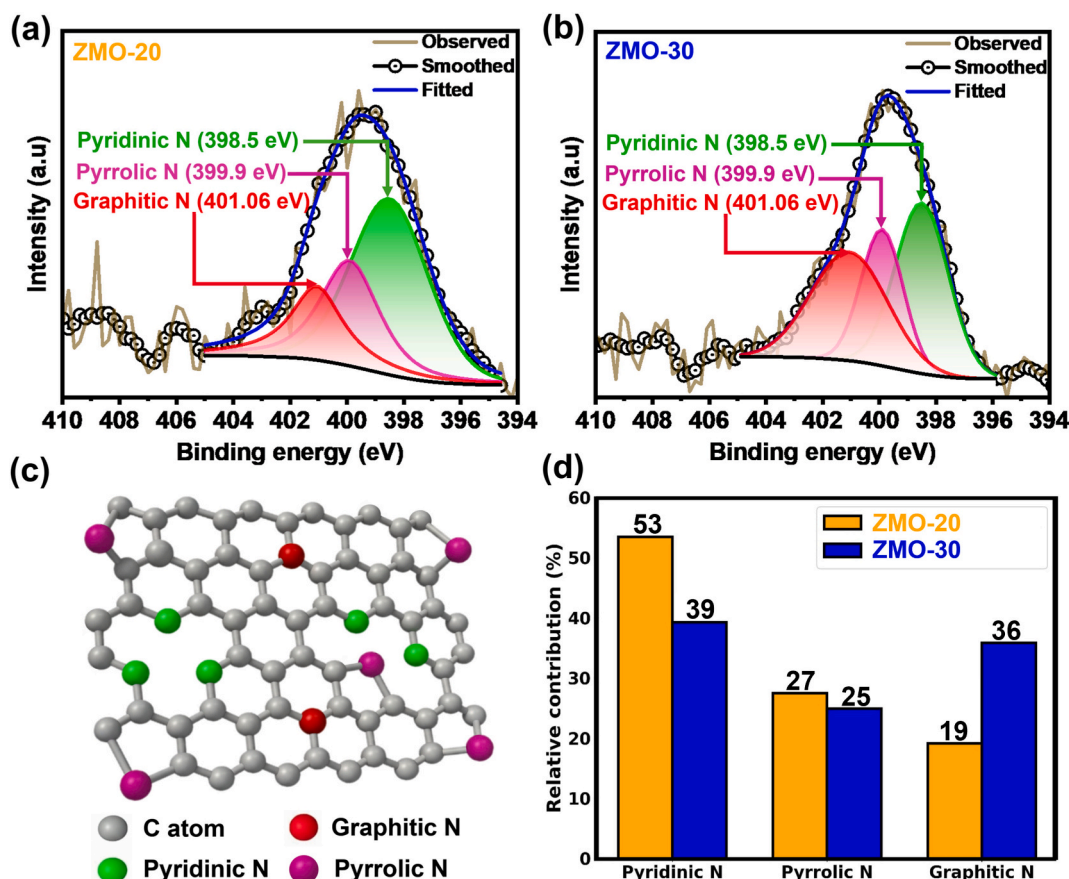


Fig. 5. Deconvoluted N 1s spectra of (a) ZMO-20 and (b) ZMO-30, (c) schematic illustration of the three identified nitrogen configurations within the graphene lattice, and (d) relative percentage contributions of pyridinic N, pyrrolic N, and graphitic N obtained from XPS analysis of ZMO-20 and ZMO-30 nanocomposites.

[55–57]. The simultaneous presence of these nitrogen configurations is a common feature of nitrogen-doped graphene and carbon materials, and has been shown to exert a synergistic influence on electrochemical energy storage behavior [56,58]. Fig. 5(c) schematically illustrates the three identified nitrogen atoms and their doping environments within the graphene lattice. Pyridinic N, shown in green, is located at edge or defect sites and enhances surface polarity and interfacial charge-transfer kinetics, whereas Pyrrolic N, shown in pink, is incorporated into five-membered ring structures and contributes to defect formation and surface activity, thereby promoting lithium-ion adsorption and pseudocapacitive storage behavior [56]. Graphitic N, shown in red, results from substitution within the graphene basal plane and enhances the intrinsic electrical conductivity of the carbon framework [55,56].

The relative contributions of these nitrogen species were quantified from the integrated peak areas as shown in Fig. 5(d). For ZMO-20, pyridinic N is dominant (53%), followed by pyrrolic N (27%) and graphitic N (19%). In contrast, ZMO-30 exhibits a more balanced distribution, with pyridinic N decreasing to 39%, pyrrolic N remaining comparable (25%), and graphitic N increasing significantly to 36%. This redistribution indicates that increasing GO content promotes nitrogen incorporation not only at defect sites but also within the graphene basal plane, resulting in a more uniform nitrogen coordination environment in ZMO-30. Thus, XPS analysis confirms the presence of Zn, Mn, and O in pristine ZMO, while the nanocomposites additionally exhibit carbon along with detectable nitrogen species. More importantly, the high-resolution N 1s spectra confirm successful incorporation of nitrogen into the graphene framework, leading to the formation of N-rGO in the nanocomposites.

3.1.4. FESEM and EDX

Fig. 6(a–c) shows FESEM images of pure ZMO, confirming the formation of irregularly shaped nanosized polyhedral particles due to instantaneous precipitation induced by the NH_3 solution on the precursor salt solution. Fig. 6(d–f) presents the FESEM images of the ZMO-20 nanocomposite sample. As shown in Fig. 6(d), the addition of 20 wt% GO to the precursor solution resulted in ZnMn_2O_4 nanoparticles that are locally wrapped or covered by sheet-like N-rGO, likely formed during the one-pot hydrothermal synthesis route. However, in other regions, as shown in Figs. 6(e) and (f), only partial anchoring was observed rather than complete wrapping. Further, Figs. 6(e) and (f) revealed that, while certain regions exhibit intimate contact between ZnMn_2O_4 nanoparticles and N-rGO sheets, other areas display numerous exposed ZnMn_2O_4 nanoparticles and isolated graphene nanosheets, resulting in ineffective nanoparticle anchoring. This observation indicates non-uniform utilization of graphene in ZMO-20, with interfacial contact forming only at certain locations within the nanocomposite.

Figs. 6(g–i) display FESEM images of the ZMO-30 nanocomposite. The ZnMn_2O_4 nanoparticles in ZMO-30 appear partially agglomerated and interconnected, as observed in Figs. 6(g) and (h). In these regions, the sheet-like features of N-rGO become less distinguishable, suggesting a more intimate and uniform integration of ZnMn_2O_4 nanoparticles within the N-rGO matrix during the one-pot synthesis. Nevertheless, in certain regions, the transparent and wrinkled morphology associated with N-rGO sheets remains visible, as highlighted in Fig. 6(g) and the magnified image shown in Fig. 6(i). The FESEM image of ZMO-30 nanocomposite, along with corresponding EDX elemental mappings, is shown in Fig. 6(j). The EDX image of ZMO-30 shows the spatial distribution of Zn, Mn, O, C, and N in the nanocomposite. The element mappings confirm a uniform distribution of Zn, Mn, and O, indicating

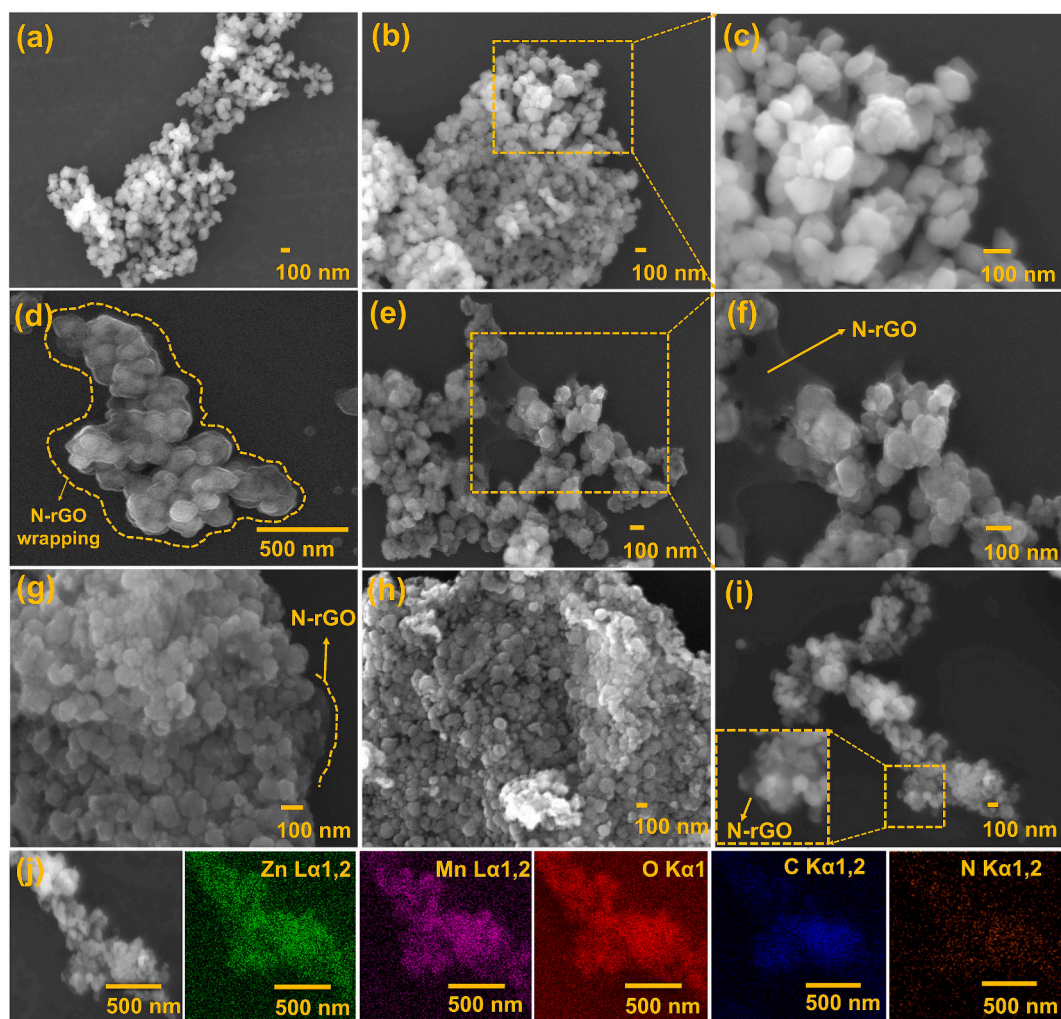


Fig. 6. FESEM images of (a–c) pure ZMO, and two nanocomposites (d–f) ZMO-20, (g–i) ZMO-30 with different mass loadings of GO recorded at various magnifications, and (j) Higher-magnification image of ZMO-30 along with the corresponding EDX elemental mappings of Zn, Mn, O, C, and N.

the formation of ZnMn_2O_4 phase, while the carbon contrast was more in some selective areas. Additionally, a relatively weak nitrogen signal was also detected, consistent with slightly higher contrast in carbon-rich regions.

Due to the agglomeration of nanoparticles and the presence of a dominant carbon contrast in certain regions, FESEM image and EDX mappings of ZMO-30 alone do not provide sufficient resolution to clearly observe the nanoscale metal oxide–N-rGO interfacial structure. Therefore, HRTEM images of the ultrasonicated ZMO-30 nanocomposite were obtained for a more detailed understanding of the structural arrangement and interfacial interactions between ZnMn_2O_4 nanoparticles and N-rGO sheets.

3.1.5. HRTEM and SAED

Figs. 7(a–d) show the TEM images of ultrasonicated ZMO-30 nanocomposite at different magnifications, in which Figs. 7(b) and (d) are magnified TEM images of (a) and (c), respectively.

The TEM micrographs clearly revealed that all irregular-shaped nanoparticles are well distributed and tightly anchored to the N-rGO sheet matrix, confirming the formation of a more uniform ZnMn_2O_4 /N-rGO hybrid structure in ZMO-30 compared to ZMO-20. The HRTEM image shown in Fig. 7(e) demonstrates the multiple intimate interfacial contacts between the nanosized ZnMn_2O_4 particles and N-rGO sheet with slit-shaped voids, and this strong interfacial contact is considered favorable for enhanced Li-ion diffusion during electrochemical

performance [14,20]. Figs. 7(f) and (g) show the corresponding magnified lattice fringes observed in the ZMO-30 nanocomposite, which clearly display well-resolved lattice fringes with interplanar spacings of 0.304 nm and 0.484 nm corresponding to the (112) and (101) lattice planes of ZnMn_2O_4 , respectively, as calculated from XRD data, and are in good agreement with previously reported values [59]. Furthermore, the SAED patterns, as shown in Fig. 7(h), clearly exhibit three distinct diffraction rings that can be indexed to the (220), (004), and (112) planes of the tetragonal ZnMn_2O_4 phase, consistent with previously reported literature [59].

Overall, the TEM and HRTEM images, together with the SAED patterns, confirm the formation of irregularly shaped nanosized ZnMn_2O_4 particles homogeneously anchored on N-rGO sheets, resulting in a higher degree of intimate ZnMn_2O_4 /N-rGO interfacial contact achieved through the one-pot hydrothermal synthesis strategy. These observations are in good agreement with XRD results, Raman spectra, FESEM, and EDAX elemental mappings of Zn, Mn, O, C, and N, further verifying the successful synthesis of the crystalline ZnMn_2O_4 /N-rGO nanocomposite ZMO-30.

3.1.6. BET and BJH

The N_2 adsorption-desorption isotherms of pure ZMO, and nanocomposites ZMO-20, and ZMO-30 are shown in Figs. 8(a–c). All the samples exhibit type-IV isotherms with a distinct H3 hysteresis loop over the relative pressure (P/P_0) range of 0–1, and no clear adsorption

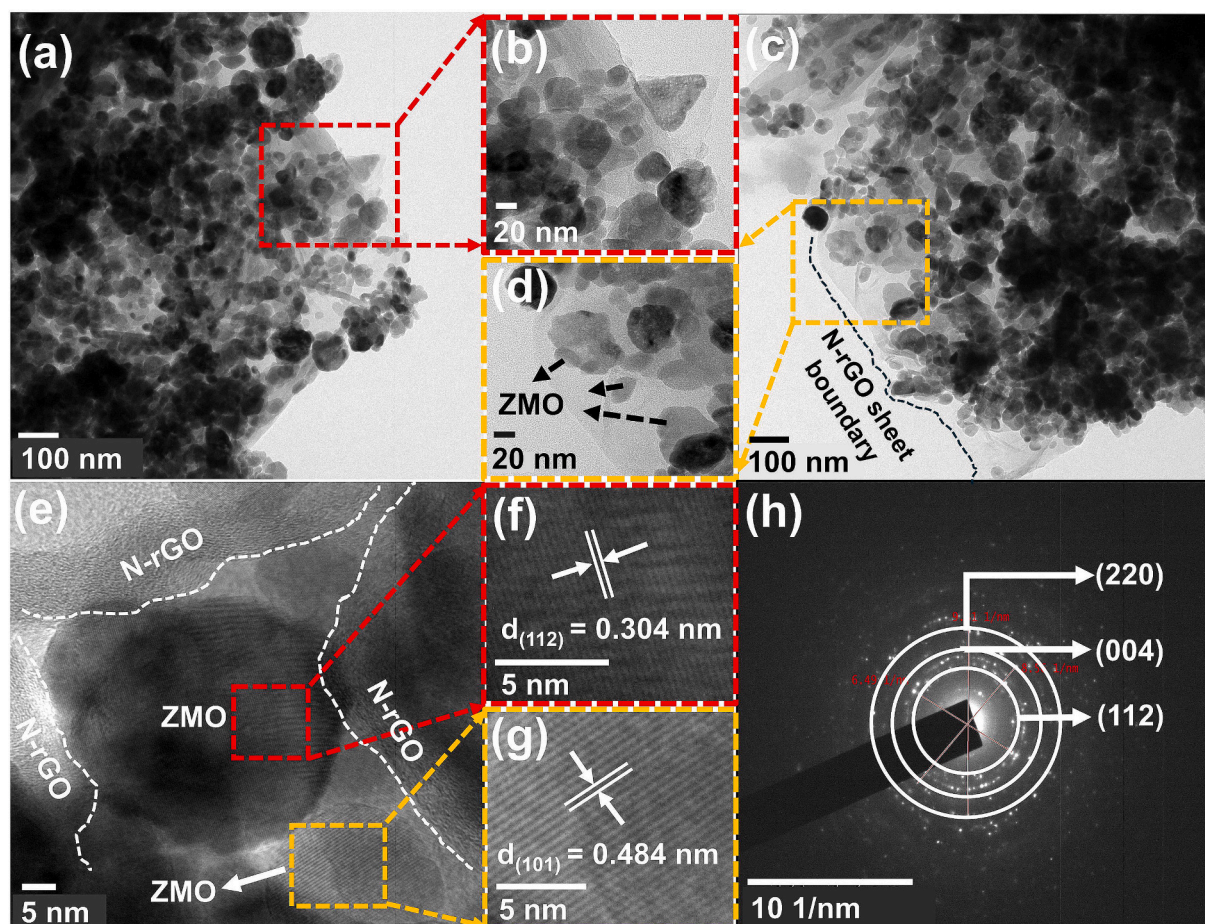


Fig. 7. (a-d) TEM, (e-g) HRTEM images at different magnifications, and (h) SAED pattern of ZMO-30 nanocomposite.

saturation was observed at high P/P_0 values, which is characteristic of H3-type hysteresis rather than H1 or H2 types. The presence of such H3 hysteresis loops indicates a mesoporous structure with slit-shaped pores, typically formed by the aggregation of nanoparticles or by stacked layered materials, which form plate-like edges [60–63].

For pristine ZMO, the observed H3-type hysteresis, as shown in Fig. 8 (a), originates from slit-shaped mesopores formed between aggregated ZnMn_2O_4 nanoparticles, where irregular particle packing and face-to-face contacts generate plate-like edges and interparticle voids [60], as observed in the FESEM images. For the ZMO-20 and ZMO-30 nanocomposites, the slit-shaped pores may arise not only from interparticle spaces between ZnMn_2O_4 nanoparticles but also from the interfacial gaps between ZnMn_2O_4 nanoparticles and stacked N-rGO sheets [64,65], as well as between adjacent N-rGO layers. Further, as shown in Figs. 8(a-c), a notable increase in nitrogen uptake was observed over the entire relative pressure range for the ZMO-20 and ZMO-30 composites, particularly at high P/P_0 values approaching unity, indicating their enhanced textural properties when compared to ZMO [64–66].

Fig. 8(d) shows pore-size distribution curves calculated from the desorption branch of ZMO, ZMO-20, and ZMO-30, obtained using the Barrett-Joyner-Halenda (BJH) method. As shown in Fig. 8(d), all samples exhibit predominantly mesoporous characteristics, with most probable pore sizes in the range of ~ 40 – 53 nm. However, the presence of larger pores extending up to ~ 100 – 130 nm indicates a combined mesoporous–macroporous structure.

Table 1 summarizes the quantitative textural parameters extracted from the BET and BJH analyses of the obtained nitrogen adsorption-desorption isotherms. The specific surface area, external surface area, and total pore volume were derived from the nitrogen adsorption

isotherms, shown in Figs. 8(a-c), whereas the most probable pore width was obtained from pore-size distribution curves shown in Fig. 8(d).

As summarized in Table 1, the specific surface area of ZMO, ZMO-20, and ZMO-30 increases from $9.53 \text{ m}^2 \text{ g}^{-1}$ for ZMO to $13.08 \text{ m}^2 \text{ g}^{-1}$ for ZMO-20 and further to $15.32 \text{ m}^2 \text{ g}^{-1}$ for ZMO-30. A similar increasing trend is observed for the external specific surface area, which rises from $9.72 \text{ m}^2 \text{ g}^{-1}$ to $14.57 \text{ m}^2 \text{ g}^{-1}$ and then to $16.27 \text{ m}^2 \text{ g}^{-1}$ with increasing N-rGO content.

Based on these observations, it is clear that the increase in Specific surface area, as well as external specific surface area, with increasing N-rGO content is attributed to the structural role of N-rGO within the composite architecture. The two-dimensional nature of N-rGO sheets enables them to act as an effective dispersing matrix, effectively suppressing the agglomeration [64,65,67] of ZnMn_2O_4 nanoparticles and thereby exposing a larger fraction of their surface, as observed in TEM and HRTEM images, which leads to higher nitrogen adsorption. In addition, the total pore volume increases gradually from $0.0439 \text{ cm}^3 \text{ g}^{-1}$ for ZMO to $0.0813 \text{ cm}^3 \text{ g}^{-1}$ for ZMO-20 and $0.0888 \text{ cm}^3 \text{ g}^{-1}$ for ZMO-30, confirming the formation of a more open and accessible pore network upon increased N-rGO incorporation. The BJH pore size distribution curves shown in Fig. 8(d) reveal a gradual shift of the dominant peak toward smaller pore widths, with the most probable pore size decreasing from 52.63 nm for ZMO to 41.78 nm for ZMO-20 and 40.22 nm for ZMO-30, indicating a refinement of the mesoporous structure. In conclusion, the BET and BJH analyses revealed that N-rGO incorporation into nanosized ZnMn_2O_4 , achieved through the one-pot synthesis, effectively mitigated agglomeration and promoted interconnected slit-shaped mesopores, leading to simultaneous increases in surface area and pore volume, accompanied by a slight decrease in the dominant pore width.

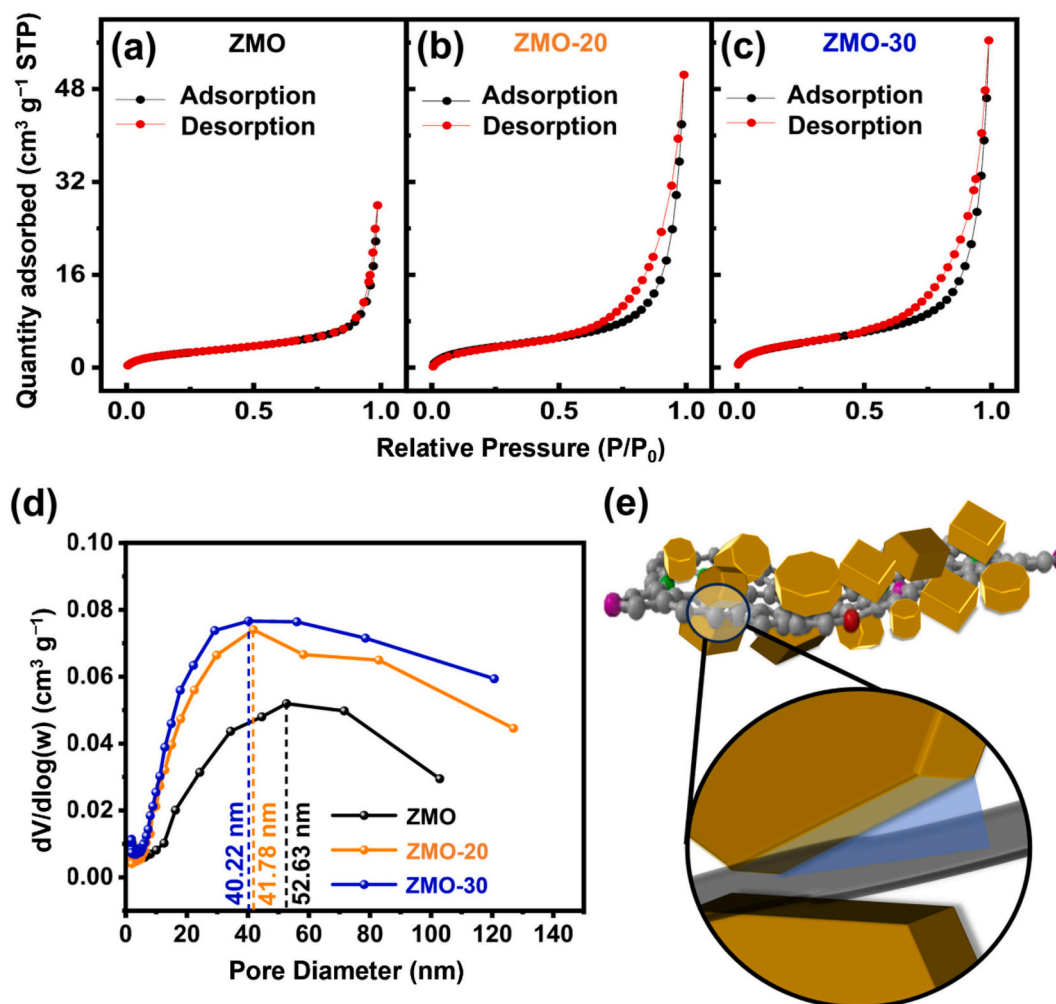


Fig. 8. Nitrogen adsorption–desorption isotherms of (a) pristine ZMO, and nanocomposites (b) ZMO-20, (c) ZMO-30, (d) pore-size distribution curves of ZMO, ZMO-20, and ZMO-30, (e) Schematic representation of slit-shaped pores of nanocomposites.

Table 1

Quantitative textural parameters obtained from BET and BJH analyses of the obtained nitrogen adsorption–desorption isotherms of ZMO, ZMO-20, and ZMO-30.

Parameter	ZMO	ZMO-20	ZMO-30
Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	9.53	13.08	15.32
External Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	9.72	14.57	16.27
Total Specific Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	0.0439	0.0813	0.0888
Most Probable Pore Width (nm)	52.63	41.78	40.22

The as-prepared nanocomposites are expected to facilitate electrolyte penetration, enhance ionic transport, and accommodate volume changes during cycling, thereby improving electrochemical performance.

3.2. Electrochemical performance of pristine ZMO, ZMO-20, and ZMO-30 nanocomposites

3.2.1. Cyclic voltammetry

Figs. 9(a), (c), and (e) show the cyclic voltammograms obtained for the newly fabricated cells using the as-prepared ZMO, ZMO-20, and ZMO-30 as the anode materials, respectively. The magnified views of the boxed potential window regions for each CV curve are displayed on the right in Figs. 9(b), (d), and (f).

Fig. 9(a) shows the CV curves obtained for the first three cycles for

pristine ZMO. During the first cathodic scan, the CV curve exhibited two broad reduction peaks at 1.23 V and 0.70 V, followed by a sharp, intense peak at 0.17 V. The broad peaks at 1.23 V and 0.70 V correspond to the reduction of Mn^{3+} to Mn^{2+} in ZnMn_2O_4 , followed by electrolyte decomposition that leads to the formation of the Solid Electrolyte Interface (SEI) layer [13,14,18,68]. The sharp cathodic peak at 0.17 V attributes the conversion reaction of Zn^{2+} and Mn^{2+} to their metallic Zn^0 and Mn^0 , accompanied by the formation of a Li_2O matrix and Li-Zn alloy, as described by Eq. (1) [13,14]. Furthermore, during the first anodic scan, two oxidation peaks were observed at 1.24 V and 1.62 V, corresponding to the oxidation of Mn^0 to Mn^{2+} and Zn^0 to Zn^{2+} , respectively. In the second cycle, the reduction peak at 1.23 V vanishes, but the SEI peak at 0.70 V persists in the subsequent cycles with a minor shift, indicating continued SEI evolution in the second and third cycles, as clearly shown in Fig. 9(b). The cathodic scan for the second cycle thus exhibits only a single reduction peak at 0.47 V, which is associated with the reversible reduction of Zn^{2+} and Mn^{2+} to metallic Zn^0 and Mn^0 as represented in Eq. (2) [13,14,18,68]. During the second anodic scan, the two oxidation peaks were observed at the same potential as in the previous cycle. In the third cycle, similar peaks were observed with slight variation in peak positions. The cathodic peak shifted to 0.46 V, accompanied by a slight decrease in peak current, as shown in Fig. 9(b), suggesting a gradual increase in electrochemical polarization [13,68,69].

The complete reaction mechanisms can be described as follows [14,18].

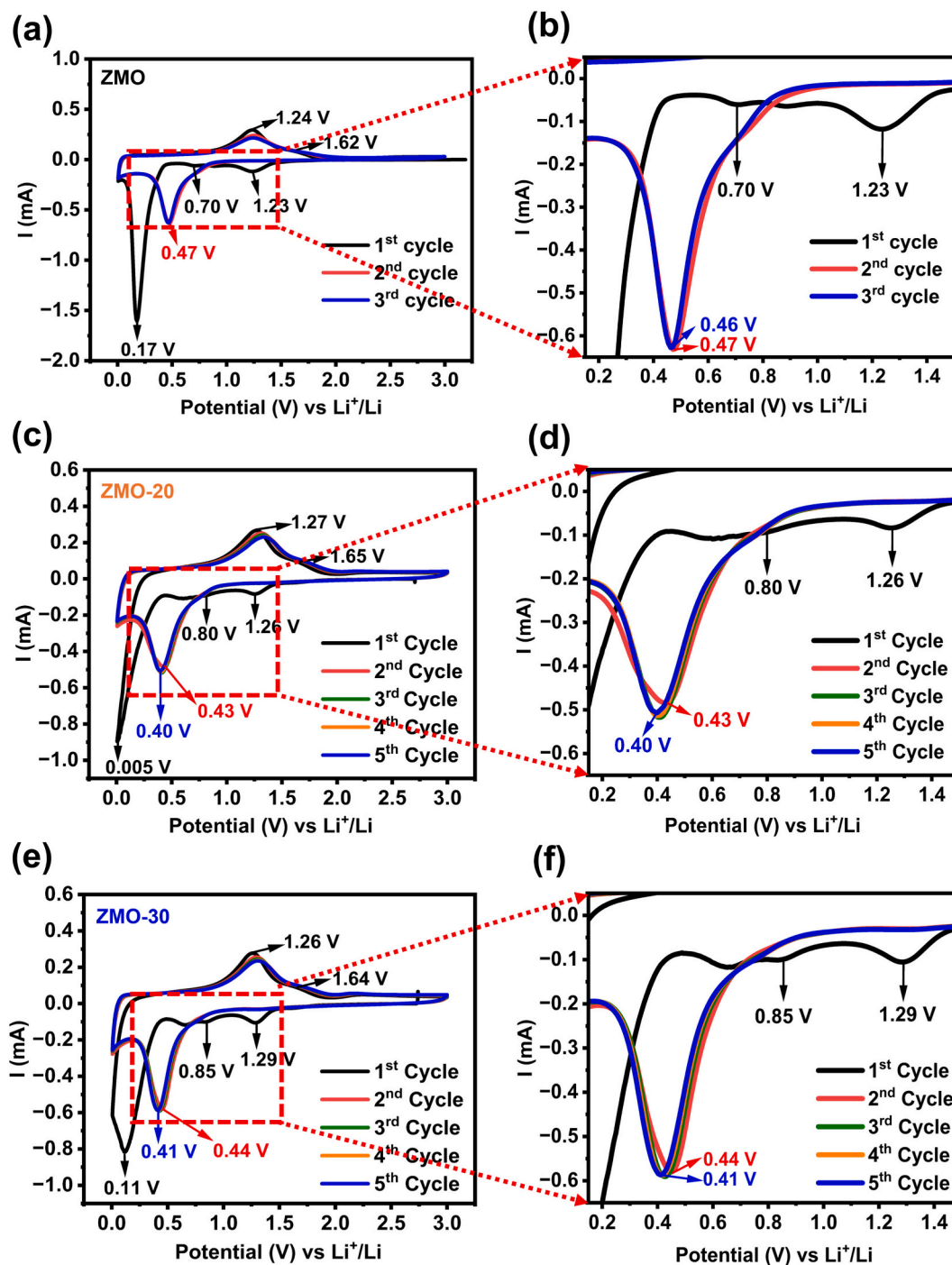
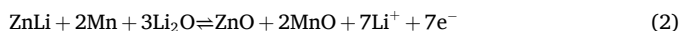
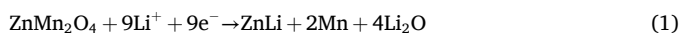


Fig. 9. Cyclic voltammograms of all the newly fabricated Li half cells recorded in the potential window of 0.01–3.0 V (vs. Li^+/Li) at a scan rate of 0.1 mV s^{-1} using as-prepared; (a) ZMO, (c) ZMO-20, (e) ZMO-30, and the corresponding magnified views of the boxed region in the respective CV curves.



Similar redox features were also observed for the fabricated Li-ion half-cell using nanocomposite ZMO-20, as shown in Fig. 9(c), with slight shifts in peak positions. During the first cathodic scan, the three peaks appear at 1.26 V, 0.80 V, and 0.005 V. The peak at 1.26 V corresponds to the Mn^{3+} to Mn^{2+} reduction, while the broad feature starting at 0.80 V is attributed to SEI formation. The low-potential peak near 0.005 V is associated with $\text{Zn}^{2+}/\text{Mn}^{2+}$ to metallic Zn^0/Mn^0 , accompanied by the formation of a Li_2O matrix and Li-Zn alloy [14].

Likewise, the anodic scan peaks observed at 1.27 V and 1.65 V are assigned to oxidation of Mn^0 to Mn^{2+} and Zn^0 to Zn^{2+} , respectively [14]. In the second cycle, the cathodic peak at 1.26 V vanishes, and the SEI peak at 0.80 V is less prominent, indicating a more stabilized SEI layer in the first cycle compared to pure ZMO, as clearly shown in Fig. 9(d). The observed intense cathodic peak at 0.43 V in the second cycle corresponds to the reduction of Zn^{2+} and Mn^{2+} to their metallic states, represented by Eq. (2) [14]. In the consecutive cycles, the SEI peaks were not observed, and the cathodic peak current increased from the second to the third cycle, followed by a marginal decrease up to the fifth cycle, as shown in Fig. 9(d). The cathodic and anodic peaks corresponding to the third, fourth, and fifth cycles exhibit good overlap with only minor

shifts, indicating good reversibility of the electrochemical reaction represented by Eq. (2), as shown in Fig. 9(c) and (d).

For the fabricated Li-ion half-cell using ZMO-30 nanocomposite as the anode material, the CV curves exhibit a broad peak at 1.30 V during the first cathodic scan, which corresponds to the reduction of Mn^{3+} to Mn^{2+} in ZnMn_2O_4 , while the broad feature at 0.85 V is associated with SEI formation. The low-potential peak near 0.11 V can be assigned to the reduction of $\text{Zn}^{2+}/\text{Mn}^{2+}$ to metallic states, accompanied by the formation of a Li_2O matrix and Li–Zn alloy, as also observed for pure ZMO and nanocomposite ZMO-20 [14]. During the anodic scan, the oxidation peaks at 1.26 V and 1.64 V correspond to oxidation of Mn^0 to Mn^{2+} and Zn^0 to Zn^{2+} , respectively [14]. In the second cycle, the cathodic peak observed at 1.30 V completely disappears, as shown in Fig. 9(e), indicating the completion of the irreversible reduction of Mn^{3+} to Mn^{2+} and the SEI peak observed at 0.85 V is completely suppressed, indicating an

enhanced SEI stabilization achieved in the first cycle, compared to both ZMO and ZMO-20, as clearly shown in Fig. 9(f). The prominent cathodic peak observed at 0.44 V in the second cycle corresponds to the reduction of Zn^{2+} and Mn^{2+} to their metallic states, as shown in Eq. (2). As shown in Figs. 9(d) and (f), the reversible cathodic peaks exhibited higher peak currents for ZMO-30 than for ZMO-20. This observation clearly indicates that increasing the GO content enabled a larger fraction of ZnMn_2O_4 nanoparticles to participate effectively in the reversible conversion reaction, described in Eq. (1). In subsequent cycles, the peak current increases marginally up to the third cycle and then slightly decreases, similar to the behavior observed for ZMO-20. Furthermore, the CV curves of ZMO-30 exhibit much better overlap of the cathodic and anodic peaks, as shown in Figs. 9(e) and (f), indicating superior reversibility of the conversion reactions and a more stable current response.

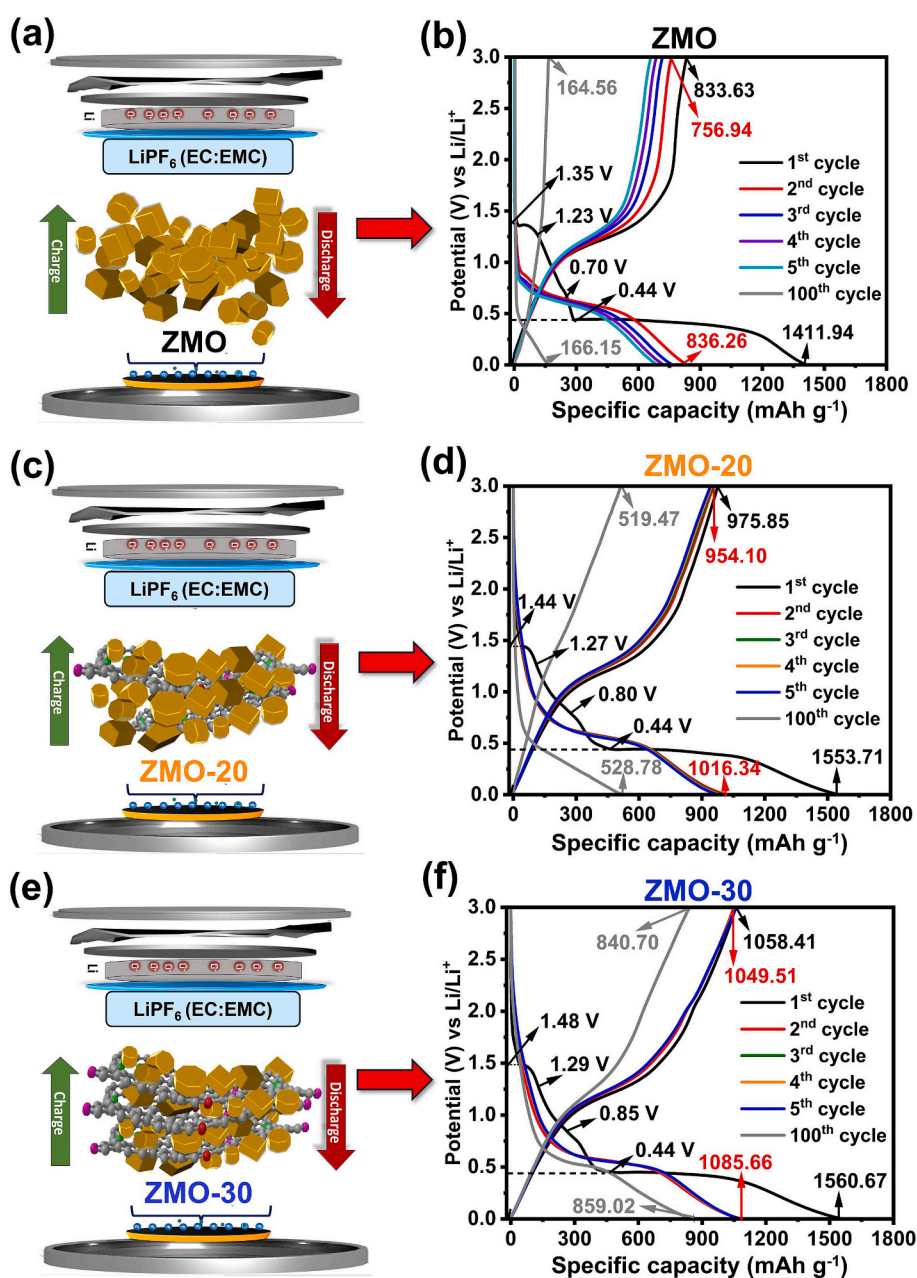


Fig. 10. Schematic illustration of the various parts of the fabricated Li-ion half-cell using (a) pristine ZMO, (c) ZMO-20, and (e) ZMO-30 as the anode materials, along with their respective galvanostatic charge–discharge profiles for the first five cycles and the 100th cycle, shown in (b) pristine ZMO, (d) ZMO-20, and (f) ZMO-30 at a current density of 100 mA g⁻¹.

With increasing GO content, the Mn^{3+} to Mn^{2+} cathodic reduction peak observed in the first cycles depicts a slight positive shift toward higher potentials, as shown in Figs. 9(a), (c), and (e). Additionally, the cathodic SEI peak appearing at 0.70 V in the first cycle for pure ZMO also exhibits a slight positive shift and displays a much broader dual peak behavior as GO content is increased from 20% to 30%, as illustrated in Figs. 9(b), (d), and (f). The positive shift of these cathodic features reflects a change in the dominant electrode surface, which governs the electrolyte reduction. The SEI formation could be preferentially occurring on the graphene surface at higher potentials, rather than directly on the ZnMn_2O_4 surface [70]. For the nanocomposites ZMO-20 and ZMO-30, the reversible cathodic reduction peak exhibits a slight negative shift, as shown in Figs. 9(b), (d), and (f). This negative shift of the cathodic peak may be attributed to the reduced polarization and improved charge-transfer kinetics induced by the conductive N-rGO framework, consistent with the enhanced conversion reaction kinetics reported for graphene-modified metal oxide anodes [71,72].

Hence, the newly fabricated half-cells using the nanocomposite anodes of ZMO-20 and ZMO-30 exhibited better redox behavior by promoting graphene-dominated interfacial reactions, enabling earlier SEI formation, reduced polarization, enhanced conversion kinetics, and improved electrochemical reversibility compared with the pure ZMO sample.

3.2.2. Galvanostatic charge–discharge

Figs. 10(a), (c), and (e) show the schematic illustration of the fabricated Li-half cell with as-prepared pure ZMO, ZMO-20, and ZMO-30 as the anode materials, respectively. Figs. 10(b), (d), and (f) show the corresponding galvanostatic charge–discharge (GCD) curves for the first five cycles and the 100th cycle, allowing a direct comparison of electrochemical behavior under identical testing conditions.

As shown in Fig. 10(b), the two prominent discharge plateaus were observed in the voltage range 1.36 V–0.01 V during the first discharge for pure ZMO, and the overall specific discharge capacity delivered was $1411.94 \text{ mAh g}^{-1}$. The first discharge plateau, starting at $\sim 1.36 \text{ V}$, is attributed to the reduction of Mn^{3+} to Mn^{2+} . Subsequently, a broad cathodic feature was observed at 0.70 V, corresponding to the formation of the solid electrolyte interphase (SEI) layer [13]. The second, longer, and broader discharge plateau, starting at $\sim 0.44 \text{ V}$, corresponds to a complete, irreversible chemical reaction of ZnMn_2O_4 , as represented by Eq. (1), supported by the CV peak that begins at 0.44 V in the first cathodic scan. Based on this irreversible reaction, the theoretical capacity of pristine ZnMn_2O_4 for the initial lithiation in the first discharge is $\sim 1008 \text{ mAh g}^{-1}$ [68]. The extra-specific discharge capacity observed beyond this theoretical capacity is primarily associated with the reduction of Mn^{3+} to Mn^{2+} and the subsequent formation of the SEI [13,18]. The first charging of the fabricated cell with pure ZMO is based on the reversible chemical reaction as shown in Eq. (2). Based on this reaction, the theoretical specific charge capacity of pristine ZnMn_2O_4 is $\sim 784 \text{ mAh g}^{-1}$. In the first charge cycle, the specific charge capacity decreased to $833.63 \text{ mAh g}^{-1}$, shown in Fig. 10(b), and it is still higher than the theoretical capacity ($\sim 784 \text{ mAh g}^{-1}$). This excess capacity observed may be due to additional lithium storage arising from interfacial or pseudocapacitive effects, and it is in good agreement with the surface/space-charge storage mechanism reported for transition-metal-oxide as anodes [68,73]. More importantly, the first specific charge capacity is significantly lower than the corresponding first specific discharge capacity, indicating irreversible Li^+ consumption during the initial lithiation process. The relatively low initial Coulombic efficiency is primarily attributed to electrolyte decomposition and solid electrolyte interphase (SEI) formation, together with the limited reversibility of Li_2O generated during the conversion reaction, irreversible lithium trapping, and other irreversible side reactions commonly observed in conversion-type transition-metal oxide anodes [74]. Consequently, the initial Coulombic efficiency of the ZMO electrode is 59.06%.

During the second discharge cycle, the specific capacity was 836.26

mAh g^{-1} , and the observed slight increase in capacity may be due to the continuous evolution of SEI, as confirmed by the CV results, which showed that the SEI peak persisted across consecutive cycles, and with surface-controlled pseudocapacitive Li^+ ion storage on the nano-structured electrode [68,73]. During the second charge cycle, the specific capacity further decreased to $756.94 \text{ mAh g}^{-1}$. This decline may be attributed to irreversible lithium consumption during SEI layer formation, consistent with the CV results. In addition, structural changes may occur, leading to partial loss of electrical contact between particles, which likely originates during the preceding discharge process [13,68,75]. The coulombic efficiency increased to 91.02% during the second cycle, indicating that Li insertion and extraction became much more reversible after the irreversible conversion reaction. In subsequent cycles, the specific charge and discharge curves showed less overlap, and the capacity gradually decreased, indicating the same irreversible process. At the 100th cycle, the specific discharge capacity was found to be $166.15 \text{ mAh g}^{-1}$, and the specific charge capacity was about $164.56 \text{ mAh g}^{-1}$, as shown in Fig. 10(b).

As shown in Fig. 10(d), the fabricated Li-ion half-cell with ZMO-20 nanocomposite electrode also exhibits two characteristic discharge plateaus within a slightly higher potential window of 1.44–0.01 V, which are consistent with the conversion mechanism as described for the pure ZMO electrode. Compared with the pure ZMO electrode, the high-voltage plateau is shifted to a slightly higher potential, indicating improved interfacial effects arising from N-rGO. The lithium storage behavior of graphene-based nanocomposites involves multiple surface and defect-driven processes. As a result, it remains challenging to precisely and comprehensively illustrate their lithium storage mechanisms [76]. Therefore, the theoretical capacity of ZnMn_2O_4 /N-rGO nanocomposites cannot be accurately determined or commented on. The first specific discharge capacity of ZMO-20 was found to be $1553.73 \text{ mAh g}^{-1}$, which is higher than that of the pure ZMO electrode, indicating increased charge storage ability with the addition of 20% GO-driven N-rGO. During charging, the specific charge capacity obtained was found to be $975.85 \text{ mAh g}^{-1}$, which is also higher than that of pure ZMO, as shown in Fig. 10(d). Accordingly, the coulombic efficiency of the first cycle for ZMO-20 nanocomposite was found to be 62.8%, which is slightly higher than that of pristine ZMO (59.06%), suggesting partial suppression of irreversible Li^+ consumption due to improved interfacial stability provided by the N-rGO framework.

In the second cycle, the discharge and charge capacity of ZMO-20 were observed as $1016.34 \text{ mAh g}^{-1}$ and $954.10 \text{ mAh g}^{-1}$, respectively, which is much higher than that of the theoretical capacity of pristine ZnMn_2O_4 . During the subsequent third, fourth, and fifth cycles, the cell with the ZMO-20 electrode showed higher capacity and greater capacity retention than pure ZMO, as shown in Fig. 10(d). The enhanced capacity in each cycle relative to pristine ZMO correlates well with the nanocomposite's improved textural properties, as discussed in the BET analysis section. Further, XPS analysis confirms the presence of abundant pyridinic and pyrrolic nitrogen species, which can introduce defect-rich active sites and promote interfacial and surface-controlled lithium storage, as discussed in the XPS analysis section. In conclusion, the synergistic effect of increased surface accessibility and nitrogen-induced interfacial activity may have contributed to the additional capacity beyond the theoretical limit of ZnMn_2O_4 . Also, the better capacity retention compared to pure ZMO can be attributed to the graphene sheets' effective mitigation of volume expansion [14]. However, at the 100th cycle, the specific capacity reduced to $528.24 \text{ mAh g}^{-1}$, and the charge capacity was found to be $519.47 \text{ mAh g}^{-1}$, which is much higher than that of pure ZMO. Hence, the cell with the nanocomposite ZMO-20 electrode exhibits improved electrochemical performance compared to the pure ZMO electrode.

The fabricated Li-ion half-cell with the ZMO-30 electrode also exhibits two well-defined discharge plateaus observed in the first discharge within the potential window of 1.48–0.01 V, similar to those of pure ZMO and ZMO-20, as shown in Fig. 10(f). The further positive shift

of the high-voltage plateau to 1.48 V indicates a stronger influence of graphene-dominated interfacial reactions and preferential SEI formation on the N-rGO surface, as discussed in the CV analysis. The first specific discharge and charge capacities of the nanocomposite ZMO-30 electrode reached 1560.67 mAh g⁻¹ and 1058.41 mAh g⁻¹, respectively. Hence, both specific discharge and charge capacities were increased with increasing GO content. The coulombic efficiency also further increased to 67.82%, which is higher than that of pure ZMO and the ZMO-20 nanocomposite. The progressive increase in the coulombic efficiency with increasing N-rGO content may be attributed to the beneficial role of the conductive N-rGO framework, which enhances electrical conductivity, accommodates the volume changes associated with lithiation/delithiation, and mitigates electrode pulverization while promoting rapid SEI stabilization and suppressing parasitic reactions during cycling, consistent with previous reports on graphene-based anodes [55,77]. The initial coulombic efficiencies obtained in the present study (59.06% for ZMO, 62.8% for ZMO-20, and 67.82% for ZMO-30) are comparable with those reported for representative ZnMn₂O₄/graphene-based composite anodes, including graphene-wrapped porous ZnMn₂O₄ (69.6%) [14], graphene-wrapped ZnMn₂O₄ hollow microspheres (71.1%) [19], and ZnMn₂O₄/rGO-carbon nanofibres (60.6%) [21]. Furthermore, the improved capacity can be correlated with the optimized structural and interfacial characteristics of the nanocomposite, as evidenced by BET and XPS analyses, which collectively contribute to enhanced charge-transfer kinetics and lithium storage behavior.

In the second cycle, discharge and charge capacities were estimated at 1085.66 mAh g⁻¹ and 1049.51 mAh g⁻¹, respectively, yielding a CE efficiency of 96.67%. During the subsequent third, fourth, and fifth cycles, the charge/discharge curves are well overlapped, indicating excellent capacity retention, as shown in Fig. 10(f). After the 100th cycle, the observed specific discharge and charge capacities were 859.02 and 840.70 mAh g⁻¹, respectively, indicating enhanced capacity retention for the ZMO-30 nanocomposite electrode. All the galvanostatic charge-discharge results for pure and nanocomposite electrodes are consistent with the CV results.

3.2.3. Cycling performance and rate capability

Fig. 11 shows the cyclic performance, including the evolution of specific discharge capacity and coulombic efficiency for pure ZMO and the nanocomposites ZMO-20 and ZMO-30 over the first 100 cycles at a current density of 100 mA g⁻¹ with specific discharge capacities obtained at the 2nd, 50th, and 100th cycles. Among newly prepared electrodes, ZMO-30 showed superior stability in discharge capacity for ~60 cycles, indicating a significantly improved electrochemical durability. After the 100th cycle, the discharge capacities of the newly fabricated cells with ZMO, ZMO-20, and ZMO-30 are 166.15 mAh g⁻¹,

528.78 mAh g⁻¹, and 859.02 mAh g⁻¹, respectively, showing improved cyclic stability and an excellent capacity boost with increasing GO content. Following cycling performance analysis, SEM images of the cycled electrodes after 100 charge-discharge cycles (Fig. S2) revealed that the ZMO-30 electrode retained a comparatively smoother and more compact surface morphology than ZMO-20, indicating improved structural integrity during prolonged cycling. Furthermore, the cyclic performance of the newly developed ZMO-30 nanocomposite, synthesized via a one-pot hydrothermal route, was compared with that of previously reported pristine ZnMn₂O₄ nanostructures, as shown in Table 2.

As shown in Table 2, the ZMO-30 nanocomposite demonstrates superior electrochemical performance compared to most previously reported pristine ZnMn₂O₄ nanostructures under similar current-rate conditions. This improvement highlights the effectiveness of N-rGO incorporation and the one-pot hydrothermal synthesis strategy in enhancing conductivity, structural stability, and overall lithium storage behavior.

After evaluating the cyclic performance, the rate capability of the fabricated Li-ion half-cells with ZMO, ZMO-20, and ZMO-30 electrodes was systematically investigated at varying current densities. Fig. 12 shows the rate performance of Li-ion half-cells fabricated using ZMO, ZMO-20, and ZMO-30 electrodes at varying current densities. The cells were sequentially cycled at 100, 200, 500 mA g⁻¹, 1 A g⁻¹, and 2 A g⁻¹, followed by a return to 100 mA g⁻¹ to assess capacity recovery. The ZMO-30 nanocomposite exhibits superior rate performance and improved capacity retention with increasing current density compared to ZMO-20 and pure ZMO. Even at 2 A g⁻¹, ZMO-30 delivers a high reversible capacity of 610.41 mAh g⁻¹ at the 42nd cycle. Upon returning to 100 mA g⁻¹, the ZMO-30 nanocomposite electrode recovers a substantial fraction of the initial capacity, indicating excellent structural robustness and reversibility.

A comparison with previously reported ZnMn₂O₄/rGO-based nanocomposites under similar high current densities is presented in Table 3, which suggests improved high-rate capability for the present ZnMn₂O₄/N-rGO (ZMO-30) nanocomposite. The enhanced rate performance compared to previously reported rGO-based composites may be attributed to the combined effects of improved electronic conductivity and modified metal oxide-N-rGO interfacial interaction associated with nitrogen incorporation. While rGO provides continuous conductive pathways, nitrogen incorporation can alter the electronic structure of the carbon framework and introduce chemically active sites. In particular, graphitic-N is known to enhance electrical conductivity, whereas pyridinic-N has been reported to promote stronger metal-carbon interfacial interactions in transition-metal/N-doped carbon systems [25]. These factors may have contributed to improved electron transport and charge-transfer kinetics under high current densities [24].

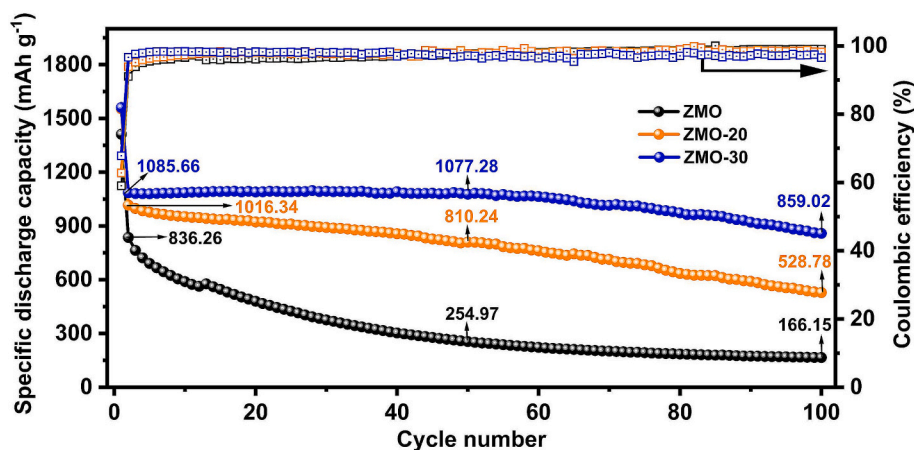


Fig. 11. Cyclic performance and coulombic efficiency comparison of all the fabricated Li half cells with pure ZMO, and nanocomposites ZMO-20 and ZMO-30 as anode materials at a current density of 100 mA g⁻¹.

Table 2

A comparison of the electrochemical cyclic performance of the newly developed nanocomposite ZMO-30 electrode with previously reported pristine ZnMn_2O_4 nano and microstructures cycled at 100 mA g^{-1} current rate.

Material	Synthesis method	Current density (mA g^{-1})	Cycle number	Final capacity (mAh g^{-1})	Ref.
ZnMn_2O_4 nanocrystals	Polymer pyrolysis	100	50	569	[78]
ZnMn_2O_4 nanowires	Solid-state reaction	100	40	650	[79]
ZnMn_2O_4 nanoparticles	One-pot Hydrothermal	100	90	716	[80]
ZnMn_2O_4 mesoscale tubular arrays	Reactive template + calcination	100	100	784.3	[81]
ZnMn_2O_4 flowerlike microspheres	Solvothermal + calcination	100	120	662	[82]
ZnMn_2O_4 porous nanospheres	Microemulsion	100	120	810	[28]
ZnMn_2O_4 crumbled nanosheets	Electrospinning	100	500	461	[83]
ZnMn_2O_4 porous rugby balls	Hydrothermal + calcination	100	100	614	[84]
ZnMn_2O_4 nano-peanuts	Solvothermal + calcination	100	200	812	[85]
$\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ (ZMO-30)	One-pot hydrothermal	100	100	859.02	Present work

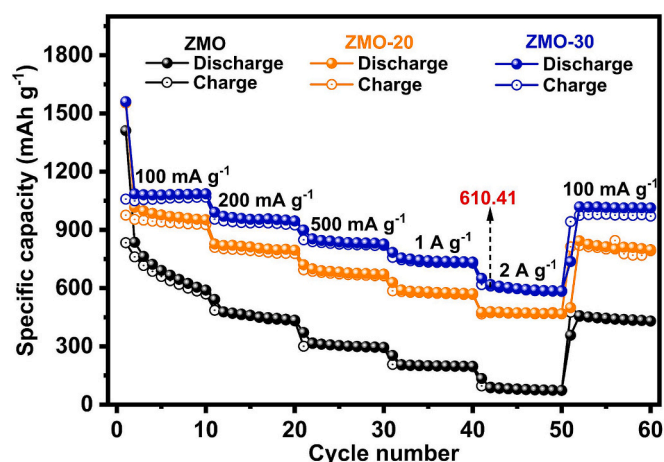


Fig. 12. Rate performance comparison of the fabricated Li half cells with pure ZMO and nanocomposites ZMO-20 and ZMO-30 as anode materials at different current densities.

Table 3

Comparative summary of electrochemical performance at high current densities of previously reported ZnMn_2O_4 /graphene-based nanocomposites and the present work.

Material	Architecture	Current density (A g^{-1})	Capacity (mAh g^{-1})	Reference
$\text{rGO}/\text{ZnMn}_2\text{O}_4$ porous nanorods	Graphene-wrapped Porous nanorods	2.0	~440	[86]
$\text{rGO}/\text{ZnMn}_2\text{O}_4$ porous nanospheres	Graphene-wrapped Porous nanospheres	1.2	560.8	[14]
$\text{rGO}/\text{ZnMn}_2\text{O}_4$ hollow porous microspheres	Graphene-wrapped Hollow microspheres	2.0	~280	[19]
$\text{ZnMn}_2\text{O}_4/\text{rGO}/\text{CNFs}$	Graphene-wrapped ZnMn_2O_4 /carbon nanofibers	2.0	~659	[87]
$\text{ZnMn}_2\text{O}_4/\text{rGO}/\text{CNT composite}$	CNT/rGO 3D conductive network	2.0	~481	[21]
$\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ (ZMO-30)	N-rGO coupled ZnMn_2O_4 nanocomposite	2.0	610.41	This work

Consequently, the $\text{ZnMn}_2\text{O}_4/\text{N-rGO}$ (ZMO-30) nanocomposite exhibits enhanced rate performance compared to rGO-based counterparts.

In addition to the intrinsic material characteristics discussed, electrode loading is also an important factor influencing electrode architecture, electrolyte accessibility, transport characteristics, and

consequently the measured electrochemical performance [88]. Therefore, the slight difference in active material loading between the ZMO-20 (0.48 mg cm^{-2}) and ZMO-30 (0.46 mg cm^{-2}) electrodes should also be considered when interpreting the electrochemical results. Nevertheless, based on the combined BET, XPS, FESEM, HRTEM, and electrochemical analyses, the improved electrochemical performance of the ZMO-30 nanocomposite is associated with synergistic effects arising from optimized textural properties, a modified nitrogen bonding configuration, and an improved metal oxide–N-rGO interfacial architecture enabled by the higher GO-derived N-rGO framework. The increased surface area and pore structure facilitate greater electrolyte accessibility and Li^+ transport, while XPS analysis reveals a more balanced distribution of pyridinic and pyrrolic nitrogen species, with a higher contribution of graphitic nitrogen compared to ZMO-20. Such a nitrogen configuration is known to promote faster interfacial reaction kinetics and improved electrochemical stability [89], while the increased graphitic-N content enhances the electrical conductivity of the carbon framework, enabling efficient charge transport during cycling [23]. As a consequence, a larger fraction of ZnMn_2O_4 participates in the reversible conversion reaction, $\text{Zn}^{2+}/\text{Mn}^{2+} \leftrightarrow \text{Zn}^0/\text{Mn}^0$, as evidenced by the higher cathodic peak current in CV and the improved reversible capacity of ZMO-30. In addition, defect-rich pyridinic and pyrrolic nitrogen sites contribute to surface-controlled lithium storage, while the flexible N-rGO support network accommodates volume changes during cycling, thereby enhancing structural stability [23]. Overall, the improved electrochemical performance of the ZMO-30 electrode arises from the combined effects of enhanced charge transport, increased active sites, and improved structural integrity.

3.2.4. Electrochemical impedance spectroscopy

To further substantiate the enhanced electrochemical performance and to elucidate the role of N-rGO in governing electrochemical kinetics, electrochemical impedance spectroscopy (EIS) measurements were carried out on ZMO-20 and ZMO-30 electrodes. The spectra were recorded prior to cycling to analyze the intrinsic charge-transfer behavior of the electrodes.

Fig. 13(a) shows the electrochemical impedance spectra of the fabricated Li-ion half-cells using ZMO-20 and ZMO-30 nanocomposites as anode materials before cycling at room temperature. As observed, the Nyquist plots of the nanocomposite electrodes display a depressed semicircle in the high- to mid-frequency region, followed by an inclined line in the low-frequency region. The as-obtained electrochemical impedance spectra were fitted using Biologic EC-Lab software, and the electrical behavior of the electrochemical cell was evaluated using an equivalent circuit model [90] as illustrated in the inset of Fig. 13(a). The corresponding electrical and diffusion parameters were extracted from the fitting. The χ^2 value of the fitting was in the range of 10^{-2} , indicating a good fit. The high-frequency intercept on the real axis corresponds to the ohmic resistance of the cell, which is mainly associated with the electrolyte resistance represented as R_e , while the semicircle is

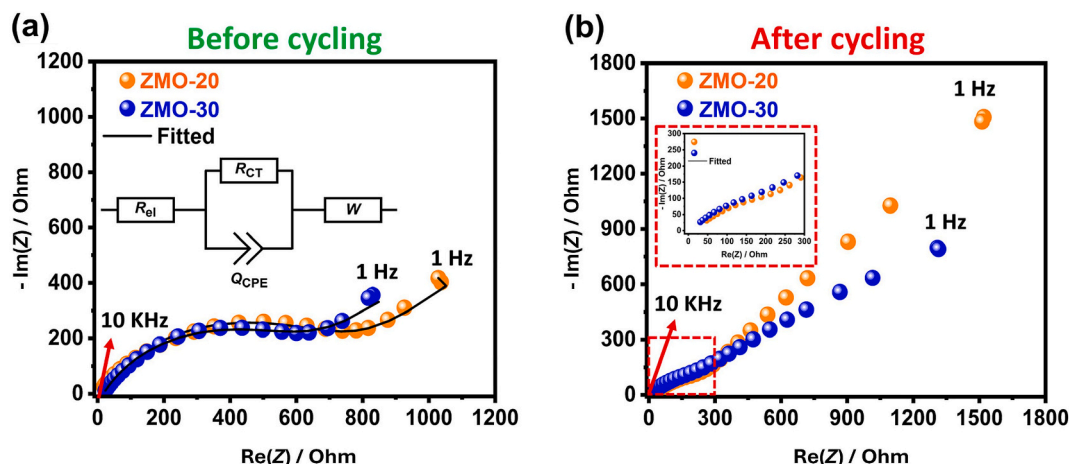


Fig. 13. Electrochemical impedance spectra (Nyquist plots) of ZMO-20 and ZMO-30 nanocomposite cells measured at room temperature (a) before cycling, with an inset showing the equivalent circuit used for fitting, and (b) after 100 cycles, with an inset displaying a magnified view of the high-frequency region highlighted by the red box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

associated with the charge-transfer process occurring at the electrode-electrolyte interface, represented by the charge-transfer resistance, R_{CT} , in parallel with a constant phase element represented as Q_{CPE} [14,90,91]. The constant phase element (Q_{CPE}) introduced is used to describe the non-ideal capacitive behavior of the double layer, which originates from surface roughness and heterogeneity [91]. The small inclined line observed in the low-frequency region is associated with the Warburg diffusion element (W), indicating diffusion-controlled lithium-ion transport within the electrode [91]. The extracted R_{el} , R_{CT} , and χ^2 values obtained from the fitting are summarized in Table 4 and form the basis of the following discussion.

The ZMO-20 electrode exhibits an electrolyte resistance (R_{el}) of $6.2 \pm 0.6 \, \Omega$ and a charge-transfer resistance (R_{CT}) of $696.5 \pm 1.0 \, \Omega$. In comparison, the ZMO-30 electrode shows a higher electrolyte resistance (R_{el}) value of $14.6 \pm 0.6 \, \Omega$. The slight increase in R_{el} may be associated with differences in initial electrolyte wetting or early-stage interphase formation, as these processes are known to strongly influence initial impedance characteristics in lithium-ion cells [92]. More importantly, the ZMO-30 electrode exhibited a much lower charge-transfer resistance (R_{CT}) of $553.9 \pm 3.0 \, \Omega$, suggesting comparatively improved interfacial charge-transfer kinetics. The improved kinetics can be attributed to increased interfacial interactions between $ZnMn_2O_4$ and the conductive N-rGO framework, which facilitates efficient electron transport and electrochemical utilization of the active material. The combined BET, XPS, and electrochemical analyses consistently indicate that increasing GO content enhances interfacial charge-transfer kinetics and electrochemical utilization. Similarly, Fig. 13(b) shows the electrochemical impedance spectra obtained for the ZMO-20 and ZMO-30 electrodes after 100 cycles at room temperature. As observed in Fig. 13(b), the impedance spectra do not exhibit well-defined multiple semicircles, making the reliable determination of the charge-transfer resistance and the SEI-layer resistance via equivalent-circuit fitting challenging.

To further evaluate the Li-ion diffusion behavior of the two electrodes, the low-frequency region of the electrochemical impedance spectra of the ZMO-20 and ZMO-30 electrodes was analyzed before cycling, and after 100 cycles, using the semi-infinite diffusion model.

Table 4

Electrolyte resistance (R_{el}), charge-transfer resistance (R_{CT}), and χ^2 values obtained from EIS fitting of ZMO-20 and ZMO-30 electrodes before cycling.

Composite	Electrolyte resistance, R_{el} (Ω)	Charge-transfer resistance, R_{CT} (Ω)	χ^2 value
ZMO-20	6.2 ± 0.6	696.5 ± 1.0	4.62×10^{-2}
ZMO-30	14.6 ± 0.6	553.9 ± 3.0	1.46×10^{-2}

According to this model, the real part of impedance, $Re(Z)$, in the diffusion-controlled regime follows the relation [93],

$$Re(Z) = R_{el} + R_{CT} + \sigma \omega^{-1/2} \quad (3)$$

This relation implies that the slope of the linear fit of $Re(Z)$ versus $\omega^{-1/2}$ plots is the Warburg coefficient (σ) [90].

Fig. 14(a) and (b) show the $Re(Z)$ versus $\omega^{-1/2}$ plots of ZMO-20 and ZMO-30 electrodes and their corresponding linear fits obtained before cycling and after 100 cycles, respectively. As shown in Fig. 14, all $Re(Z)$ versus $\omega^{-1/2}$ plots were highly linear, with adjusted R^2 values exceeding 0.99, confirming the validity of the diffusion-controlled regime. The Warburg coefficients (σ) obtained from slopes of the linear fit for ZMO-20 and ZMO-30 electrodes before cycling and after 100 charge-discharge cycles are listed in Table 5.

As shown in Table 5, the Warburg coefficient (σ) of ZMO-20 and ZMO-30 obtained before cycling was 993 ± 32 and $867 \pm 50 \, \Omega \, s^{1/2}$, respectively. The lower Warburg coefficient observed for ZMO-30 indicates a reduced Li-ion diffusion resistance with increased GO content. Overall, the reduced charge-transfer resistance (R_{CT}) and lower Warburg coefficient (σ) values observed for the ZMO-30 electrode indicate improved charge transport and Li⁺ diffusion behavior. This enhancement can be correlated with the improved structural and interfacial characteristics arising from the higher GO content. The stronger interfacial interaction between $ZnMn_2O_4$ and N-rGO in ZMO-30 facilitates efficient electron transport and ion diffusion around the $ZnMn_2O_4$ nanoparticles, thereby reducing charge-transfer resistance. In addition, the Warburg coefficient (σ) values of ZMO-20 and ZMO-30 after 100 cycles are 3529 ± 25 and $2895 \pm 51 \, \Omega \, s^{1/2}$, respectively. The increase in σ after cycling indicates enhanced diffusion resistance due to repeated lithiation and delithiation [90]. However, the comparatively lower σ value for ZMO-30 suggests better preservation of lithium-ion diffusion pathways. This improved diffusion stability can be attributed to the N-rGO framework, which helps maintain continuous electron and ion transport networks and mitigates transport degradation during prolonged cycling.

Figs. 15(a) and (b) show schematic illustrations of the lithium-storage mechanism and interfacial charge-transfer behavior in the ZMO-30 nanocomposite electrode during electrochemical cycling.

As illustrated in Fig. 15(a), $ZnMn_2O_4$ nanoparticles are uniformly anchored onto the conductive N-rGO framework, forming an interconnected metal oxide-N-rGO architecture with intimate interfacial contact, consistent with the HRTEM observations. During discharge (lithiation), Li⁺ ions migrate from the lithium electrode through the electrolyte toward the ZMO-30 active material, where the

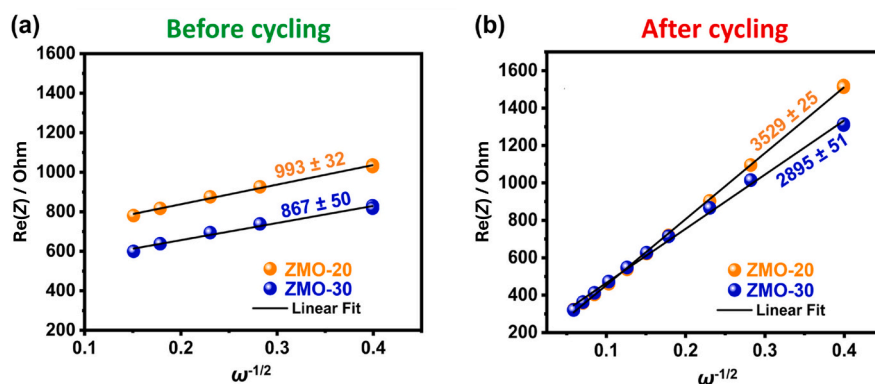


Fig. 14. $\text{Re}(Z)$ versus $\omega^{-1/2}$ plots of ZMO-20 and ZMO-30 electrodes and their corresponding linear fits: (a) before cycling and (b) after 100 cycles.

Table 5

Warburg coefficients (σ) derived from low-frequency EIS analysis for ZMO-20 and ZMO-30 electrodes before cycling and after 100 charge–discharge cycles.

Composite	$\sigma_{\text{Before cycling}} (\Omega \text{ s}^{1/2})$	$\sigma_{\text{After 100 cycles}} (\Omega \text{ s}^{1/2})$
ZMO-20	993 ± 32	3529 ± 25
ZMO-30	867 ± 50	2895 ± 51

interconnected interface provides shortened ion-diffusion pathways. Simultaneously, electrons are efficiently transported through the conductive N-rGO framework and current collector, facilitating reversible electrochemical conversion reactions. During charging (delithiation), Li^+ ions reverse-migrate from the ZMO-30 nanocomposite electrode back toward the lithium electrode. Fig. 15(b) schematically illustrates the local interfacial charge-transfer process at the ZnMn_2O_4 /N-rGO interface, where the conductive N-rGO framework promotes efficient electron transport and facilitates Li^+ diffusion around the ZnMn_2O_4 nanoparticles. The enhanced electrochemical performance of the ZMO-30 nanocomposite is therefore attributed to the synergistic effects of the optimized textural properties, modified nitrogen bonding configuration, improved ZnMn_2O_4 –N-rGO interfacial architecture, enhanced electronic conductivity, and stable ion-transport pathways provided by the interconnected N-rGO framework, rather than solely to the modest increase in surface area and pore volume.

4. Conclusion

In this work, pristine ZnMn_2O_4 (ZMO) nanoparticles and ZnMn_2O_4 /N-rGO nanocomposites with different GO loadings (ZMO-20 and ZMO-30) were successfully synthesized via a one-pot hydrothermal method, enabling effective integration of ZnMn_2O_4 nanoparticles with the N-rGO graphene framework. Structural and spectroscopic analyses confirmed

the formation of phase-pure ZnMn_2O_4 and the successful incorporation of nitrogen-doped reduced graphene oxide, with a redistribution of nitrogen bonding configurations observed at higher GO content. Microscopic studies revealed improved dispersion of ZnMn_2O_4 nanoparticles within the N-rGO framework, indicating enhanced interfacial contact and composite integration in the ZMO-30 nanocomposite.

Electrochemical investigations demonstrated that the ZnMn_2O_4 /N-rGO nanocomposites exhibit significantly improved lithium-ion storage performance compared to pristine ZnMn_2O_4 , with the ZMO-30 electrode delivering a high reversible capacity of $859.02 \text{ mAh g}^{-1}$ after 100 cycles at 100 mA g^{-1} , along with enhanced rate capability. The improved performance can be attributed to enhanced interfacial interactions, improved electronic conductivity, and reduced charge-transfer and ion-diffusion resistances, as supported by CV, GCD, and EIS analyses. Overall, this study highlights the effectiveness of controlled N-rGO incorporation in improving the electrochemical performance and cycling stability of ZnMn_2O_4 -based anode materials, demonstrating its potential for high-performance lithium-ion battery applications. Further optimization of interfacial engineering strategies and structural design could enable even higher long-term cycling stability and rate performance in ZnMn_2O_4 -based anodes.

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. **Prasad Gonugunta:** Writing – review & editing, Supervision, Resources, Data curation. **Thamayanthi Panneerselvam:** Resources. **R. Murugan:** Resources. **Gangineni Ramesh Babu:** Writing – review & editing, Supervision. **Ruud Hendrikx:** Data curation. **Peyman Taheri:** Writing – review & editing, Resources. **Arjan**

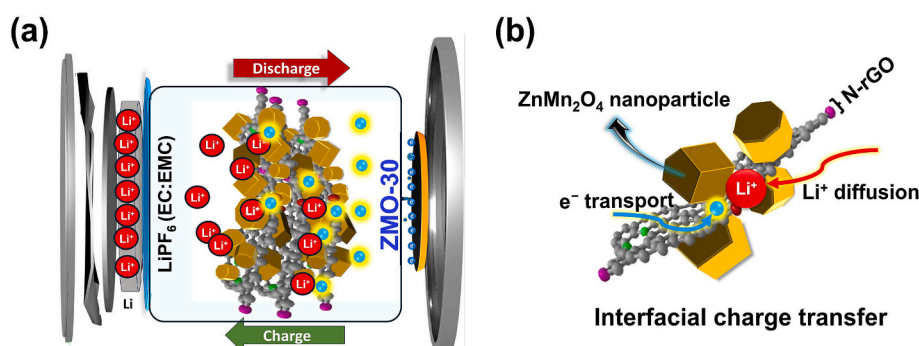


Fig. 15. Schematic illustrations highlighting (a) the charge–discharge process along with Li-ion and electron transport pathways in the ZMO-30 nanocomposite electrode, and (b) the interfacial charge-transfer process occurring at the ZnMn_2O_4 /N-rGO interface.

Mol: Writing – review & editing, Resources. **N. Satyanarayana:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Formal analysis. **Prasaanth Ravi Anusuyadevi:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Formal analysis, Data curation, Conceptualization.

Fundings

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 A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2026.120415>.

Data availability

The data will be made available upon request.

References

- [1] D. Kasprzak, C.C. Mayorga-Martinez, M. Pumera, Sustainable and flexible energy storage devices: a review, *Energy Fuel* 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] S. Zhao, X. Zhang, Y. Kong, Y. An, C. Li, Y. Xu, X. Sun, K. Wang, Y. Ma, Embedded CoSe₂ nanocrystals in hollow carbon nanobox walls with interfacial coupling for high-performance lithium storage, *Journal of Energy, Chemistry* 113 (2026) 255–265, <https://doi.org/10.1016/j.jelechem.2025.09.024>.
- [4] Y. Li, J. Yang, T. Su, K. Zhang, Y. Li, M. Manawan, D. Ma, C. Yang, Z. Liu, Z. Shi, C. P. de León Albarrán, Y.W. Zhang, J.H. Pan, Strain and doping engineering unlocking power density and cyclability of microspherical TiNb₂O₇ anodes of lithium-ion batteries, *Journal of Energy, Chemistry* 108 (2025) 827–837, <https://doi.org/10.1016/j.jelechem.2025.04.035>.
- [5] 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/natrevmats.2016.13>.
- [6] J.-M. Tarascon, M. Armand, Issues and Challenges Facing Rechargeable lithium Batteries, *www.nature.com*, 2001.
- [7] 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>.
- [8] 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>.
- [9] 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>.
- [10] 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>.
- [11] Y. Zhu, X. Liao, H. Qiu, S. An, Y. Zhang, W. He, Mixed metals oxides with strong synergetic electrochemistry as battery-type electrodes for ultrafast energy storage, *J. Alloys Compd.* 848 (2020), <https://doi.org/10.1016/j.jallcom.2020.156395>.
- [12] S. Yuvaraj, R.K. Selvan, Y.S. Lee, An overview of AB₂O₄- and A₂BO₄-structured negative electrodes for advanced Li-ion batteries, *RSC Adv.* 6 (2016) 21448–21474, <https://doi.org/10.1039/c5ra23503k>.
- [13] B. Chandran, R.S. Babu, P. Goungunta, O. Padmaraj, T. Panneerselvam, R. Murugan, G.R. Babu, R. Hendrikx, P. Taheri, A. Mol, N. Satyanarayana, P. R. Anusuyadevi, Self-adaptive ZnMn₂O₄/α-MnO₂ 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>.
- [14] D. Cai, D. Wang, H. Huang, X. Duan, B. Liu, L. Wang, Y. Liu, Q. Li, T. Wang, Rational synthesis of ZnMn₂O₄ 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>.
- [15] Z. Bai, N. Fan, C. Sun, Z. Ju, C. Guo, J. Yang, Y. Qian, Facile synthesis of loaf-like ZnMn₂O₄ nanorods and their excellent performance in Li-ion batteries, *Nanoscale* 5 (2013) 2442–2447, <https://doi.org/10.1039/c3nr33211j>.
- [16] G. Zhang, L. Yu, H. Bin Wu, H.E. Hoster, X.W. Lou, Formation of ZnMn₂O₄ 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] L. Luo, H. Qiao, K. Chen, Y. Fei, Q. Wei, Fabrication of electrospun ZnMn₂O₄ nanofibers as anode material for lithium-ion batteries, *Electrochim. Acta* 177 (2015) 283–289, <https://doi.org/10.1016/j.electacta.2015.01.100>.
- [18] P. Zhou, L. Zhong, Z. Liu, M. Liu, T. Zhou, Y. Zhao, X. Lai, J. Bi, D. Gao, Porous ZnMn₂O₄ 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>.
- [19] T. Zhang, H. Yue, H. Qiu, K. Zhu, L. Zhang, Y. Wei, F. Du, G. Chen, D. Zhang, Synthesis of graphene-wrapped ZnMn₂O₄ hollow microspheres as high performance anode materials for lithium ion batteries, *RSC Adv.* 5 (2015) 99107–99114, <https://doi.org/10.1039/c5ra16667e>.
- [20] Z. Zhang, J. Zhao, J. Zhou, Y. Zhao, X. Tang, S. Zhou, Interfacial engineering of metal oxide/graphene nanoscrolls with remarkable performance for lithium ion batteries, *Energy Storage Mater.* 8 (2017) 35–41, <https://doi.org/10.1016/j.ensm.2017.03.003>.
- [21] 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 ZnMn₂O₄ as a high-stability anode for lithium-ion batteries, *Electrochim. Acta* 338 (2020), <https://doi.org/10.1016/j.electacta.2020.135853>.
- [22] 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>.
- [23] 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>.
- [24] 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. Hydrog. Energy* 46 (2021) 11865–11877, <https://doi.org/10.1016/j.ijhydene.2021.01.099>.
- [25] 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 Co₃P and N-doped carbon to effectively facilitate oxygen reduction, *ACS Sustain. Chem. Eng.* 11 (2023) 5238–5249, <https://doi.org/10.1021/acssuschemeng.2c07734>.
- [26] Z. Zhao, J. Chen, H. Zhou, B. Hu, C. Meng, A. Yuan, Y. Qiao, Engineering Mn-N sites on nitrogen-doped carbon spheres as efficient bifunctional electrocatalysts for zinc-air batteries, *metals, Advances* 40 (2026) 62–70, <https://doi.org/10.1016/j.metadv.2025.12.006>.
- [27] X. Liang, J. Zhong, Y. Shi, J. Guo, G. Huang, C. Hong, Y. Zhao, Hydrothermal synthesis of highly nitrogen-doped few-layer graphene via solid-gas reaction, *Mater. Res. Bull.* 61 (2015) 252–258, <https://doi.org/10.1016/j.materresbull.2014.09.088>.
- [28] X. Chen, Y. Zhang, H. Lin, P. Xia, X. Cai, X. Li, X. Li, W. Li, Porous ZnMn₂O₄ 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>.
- [29] 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 ZnMn₂O₄ through a charge compensation mechanism using the substitution of Al³⁺ for Zn²⁺, *RSC Adv.* 8 (2018) 7361–7368, <https://doi.org/10.1039/c8ra00310f>.
- [30] L. Malavasi, P. Galinetto, M.C. Mozzati, C.B. Azzoni, G. Flor, Raman spectroscopy of AMn₂O₄ (a = Mn, Mg and Zn) spinels, *Phys. Chem. Chem. Phys.* 4 (2002) 3876–3880, <https://doi.org/10.1039/b203520k>.
- [31] H. Li, B. Song, W.J. Wang, X.L. Chen, Facile synthesis, thermal, magnetic, Raman characterizations of spinel structure ZnMn₂O₄, *Mater. Chem. Phys.* 130 (2011) 39–44, <https://doi.org/10.1016/j.matchemphys.2011.04.072>.
- [32] Q. Sun, M. Bijelić, A.B. Djurišić, C. Suchowski, X. Liu, M. Xie, A.M.C. Ng, H. Kong Li, K. Shih, S. Burazer, Z. Skoko, I. Djerdj, J. Popović, Graphene-oxide-wrapped ZnMn₂O₄ as a high performance lithium-ion battery anode, *Nanotechnology* 28 (2017), <https://doi.org/10.1088/1361-6528/aa8a5b>.

- [33] 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>.
- [34] 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>.
- [35] 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>.
- [36] N.M.S. Hidayah, W.W. Liu, C.W. Lai, N.Z. Noriman, C.S. Khe, U. Hashim, H.C. Lee, Comparison on Graphite, Graphene Oxide and Reduced Graphene Oxide: Synthesis and Characterization, in: *AIP Conf. Proc.*, American Institute of Physics Inc., 2017, <https://doi.org/10.1063/1.5005764>.
- [37] 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>.
- [38] 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>.
- [39] 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>.
- [40] 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>.
- [41] M. Qiu, Z. Chen, Z. Yang, W. Li, Y. Tian, W. Zhang, Y. Xu, H. Cheng, ZnMn_2O_4 nanorods: An effective Fenton-like heterogeneous catalyst with t2g3eg1 electronic configuration, *Catal. Sci. Technol.* 8 (2018) 2557–2566, <https://doi.org/10.1039/c8cy00436f>.
- [42] Y. Wang, S. Xu, Y. Zhang, L. Hou, C. Yuan, Facile construction of porous ZnMn_2O_4 hollow Micro-rods as advanced anode material for Lithium ion batteries, *Nanomaterials* 13 (2023), <https://doi.org/10.3390/nano13030512>.
- [43] 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>.
- [44] A.E. Hughes, C.D. Easton, P.R. Anusuyadevi, T.J. Raebler, 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>.
- [45] 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>.
- [46] 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>.
- [47] 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>.
- [48] 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>.
- [49] H.J. Lee, J.S. Kim, K.Y. Lee, K.H. Park, J.S. Bae, M. Mubarak, H. Lee, Elucidation of an intrinsic parameter for evaluating the electrical quality of graphene flakes, *Sci. Rep.* 9 (2019), <https://doi.org/10.1038/s41598-018-37010-x>.
- [50] 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>.
- [51] Carbon, XPS Periodic Table - IN. <https://www.thermofisher.com/in/en/home/materials-science/learning-center/periodic-table/non-metal/carbon.html>, 2026 (accessed December 12, 2025).
- [52] M.S. Ratsoma, H. Mathebulu, 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>.
- [53] 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: *AICChE Annual Meeting, Conference Proceedings*, American Institute of Chemical Engineers, 2019, <https://doi.org/10.1039/x0xx00000x>.
- [54] 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>.
- [55] 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>.
- [56] 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/acsaami.6b15872>.
- [57] 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>.
- [58] 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>.
- [59] J. Zhao, F. Wang, P. Su, M. Li, J. Chen, Q. Yang, C. Li, Spinel ZnMn_2O_4 nanoplate assemblies fabricated via “escape-by-crafty-scheme” strategy, *J. Mater. Chem.* 22 (2012) 13328–13333, <https://doi.org/10.1039/c2jm32261g>.
- [60] Y. Yamaguchi, R. Aono, E. Hayashi, K. Kamata, M. Hara, Template-free synthesis of mesoporous $\beta\text{-MnO}_2$ nanoparticles: structure, formation mechanism, and catalytic properties, *ACS Appl. Mater. Interfaces* 12 (2020) 36004–36013, <https://doi.org/10.1021/acsaami.0c08043>.
- [61] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report), *Pure Appl. Chem.* 87 (2015) 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.
- [62] B.D. Zdravkov, J.J. Čermák, M. Šefara, J. Janků, Pore classification in the characterization of porous materials: a perspective, *Cent. Eur. J. Chem.* 5 (2007) 385–395, <https://doi.org/10.2478/s11532-007-0017-9>.
- [63] K. Sing, Reporting Physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *Pure Appl. Chem. - Pure Appl. Chem.* 54 (1982) 2201–2218, <https://doi.org/10.1351/pac198254112201>.
- [64] S. Jabeen, A. Ahmad, A. Kumar, S.A. Alsali, J. Makasana, S. Ballal, R.S.K. Sharma, P.K. Pathak, R.R. Chaudhary, V. Mishra, Preparation of nano-composite of CoCr_2O_4 with rGO by solvothermal method for water splitting, *Diam. Relat. Mater.* 154 (2025), <https://doi.org/10.1016/j.diamond.2025.112167>.
- [65] F. Khurshid, M. Jeyavelan, M.S.L. Hudson, S. Nagarajan, Ag-doped ZnO nanorods embedded reduced graphene oxide nanocomposite for photo-electrochemical applications, *R. Soc. Open Sci.* 6 (2019), <https://doi.org/10.1098/rsos.181764>.
- [66] K. Sing, The Use of Nitrogen Adsorption for the Characterisation of Porous Materials. www.elsevier.nl/locate/colsurfa, 2001.
- [67] N.S. Alsaifi, A. Amari, K.M. Katubi, F.M. Alzahrani, F. Ben Rebah, M.A. Tahoon, The synthesis of magnetic nitrogen-doped graphene oxide nanocomposite for the removal of reactive Orange 12 dye, *Adsorpt. Sci. Technol.* 2022 (2022), <https://doi.org/10.1155/2022/9417542>.
- [68] 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>.
- [69] 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>.
- [70] X. Liu, D. Chao, Q. Zhang, H. Liu, H. Hu, J. Zhao, Y. Li, Y. Huang, J. Lin, Z.X. Shen, The roles of lithium-philic giant nitrogen-doped graphene in protecting micron-sized silicon anode from fading, *Sci. Rep.* 5 (2015), <https://doi.org/10.1038/srep15665>.
- [71] 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/acsaami.8b00353>.
- [72] 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 lithium modulation of zinc manganite vertical graphene arrays, *Mater. Adv.* 2 (2021) 6694–6702, <https://doi.org/10.1039/d1ma00727k>.
- [73] 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>.
- [74] X. Li, X. Sun, X. Hu, F. Fan, S. Cai, C. Zheng, G.D. Stucky, Review on comprehending and enhancing the initial coulombic efficiency of anode materials in lithium-ion/sodium-ion batteries, *Nano Energy* 77 (2020), <https://doi.org/10.1016/j.nanoen.2020.105143>.
- [75] C. Liu, T. Zhang, L. Cao, K. Luo, High-capacity anode material for Lithium-ion batteries with a Core-Shell NiFe_2O_4 /reduced graphene oxide Heterostructure, *ACS Omega* 6 (2021) 25269–25276, <https://doi.org/10.1021/acsomega.1c03050>.
- [76] Z. Liu, Y. Tian, P. Wang, G. Zhang, Applications of graphene-based composites in the anode of lithium-ion batteries, *Front. Nanotechnol.* 4 (2022), <https://doi.org/10.3389/fnano.2022.952200>.
- [77] Y. Joshi, A. Umasankaran, C. Klaassen, M. AlAmer, Y.L. Joo, Critical roles of reduced graphene oxide in the electrochemical performance of silicon/reduced graphene oxide hybrids for high rate capable lithium-ion battery anodes, *Electrochim. Acta* 404 (2022), <https://doi.org/10.1016/j.electacta.2021.139753>.
- [78] Y. Yang, Y. Zhao, L. Xiao, L. Zhang, Nanocrystalline ZnMn_2O_4 as a novel lithium-storage material, *Electrochem. Commun.* 10 (2008) 1117–1120, <https://doi.org/10.1016/j.elecom.2008.05.026>.

- [79] S.W. Kim, H.W. Lee, P. Muralidharan, D.H. Seo, W.S. Yoon, D.K. Kim, K. Kang, Electrochemical performance and ex situ analysis of ZnMn_2O_4 nanowires as anode materials for lithium rechargeable batteries, *Nano Res.* 4 (2011) 505–510, <https://doi.org/10.1007/s12274-011-0106-0>.
- [80] F.M. Courtel, Y. Abu-Lebdeh, I.J. Davidson, ZnMn_2O_4 nanoparticles synthesized by a hydrothermal method as an anode material for Li-ion batteries, *Electrochim. Acta* 71 (2012) 123–127, <https://doi.org/10.1016/j.electacta.2012.03.108>.
- [81] J.G. Kim, S.H. Lee, Y. Kim, W.B. Kim, Fabrication of free-standing ZnMn_2O_4 mesoscale tubular arrays for lithium-ion anodes with highly reversible lithium storage properties, *ACS Appl. Mater. Interfaces* 5 (2013) 11321–11328, <https://doi.org/10.1021/am403546s>.
- [82] X. Zeng, L. Shi, L. Li, J. Yang, X. Cheng, M. Gao, The preparation of flowerlike ZnMn_2O_4 microspheres assembled with porous nanosheets and their lithium battery performance as anode materials, *RSC Adv.* 5 (2015) 70379–70386, <https://doi.org/10.1039/c5ra11473j>.
- [83] S. Gu, J. Xu, B. Lu, Crumpled ZnMn_2O_4 Nanosheets for Long-term-cycling Lithium-ion battery anodes, *Energ. Technol.* 4 (2016) 1106–1111, <https://doi.org/10.1002/ente.201600087>.
- [84] N. Ren, H. Jiu, L.Y. Jiang, Q. Zhang, S. Yu, Y. Gao, Z. Gao, L. Zhang, Facile synthesis of hierarchical porous ZnMn_2O_4 rugby-balls on Ni foam for lithium-ion batteries with enhanced electrochemical properties, *J. Alloys Compd.* 740 (2018) 28–35, <https://doi.org/10.1016/j.jallcom.2017.12.362>.
- [85] 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>.
- [86] 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>.
- [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] 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>.
- [89] W. Dong, Z. Wu, X. Zhu, D. Shen, M. Zhao, F. Yang, Q. Chang, S. Tang, X. Hong, Z. Dong, S. Yang, Synergistic Pyridinic N/Pyrrolic N configurations in rGO/CNT composite sulfur hosts for high-performance lithium-sulfur batteries, *Chem. Eng. J.* 488 (2024) 150872, <https://doi.org/10.1016/j.cej.2024.150872>.
- [90] 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 panpipe-like structure as anode material for Li-ion battery, *Electrochim. Acta* 426 (2022) 140780, <https://doi.org/10.1016/j.electacta.2022.140780>.
- [91] 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>.
- [92] S.J. An, J. Li, Z. Du, C. Daniel, D.L. Wood, Fast formation cycling for lithium ion batteries, *J. Power Sources* 342 (2017) 846–852, <https://doi.org/10.1016/j.jpowsour.2017.01.011>.
- [93] R. Vedalakshmi, V. Saraswathy, H.W. Song, N. Palaniswamy, Determination of diffusion coefficient of chloride in concrete using Warburg diffusion coefficient, *Corros. Sci.* 51 (2009) 1299–1307, <https://doi.org/10.1016/j.corsci.2009.03.017>.