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Carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles as a novel anode material for high energy density lithium-ion batteries†

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Lithium-ion batteries (LIBs) have gained considerable attention from the scientific community due to their outstanding properties, such as high energy density, low self-discharge, and environmental sustainability. Among the prominent candidates for anode materials in next-generation LIBs are the spinel ferrites, represented by the  $MFe_2O_4$  series, which offer exceptional theoretical capacities, excellent reversibility, cost-effectiveness, and eco-friendliness. In the scope of this study, Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe1.7Mn0.3O4 nanoparticles were synthesized using a sol-gel synthesis method and subsequently coated with a carbon layer to further enhance their electrochemical performance. TEM images confirmed the presence of the carbon coating layer on the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite. The analysis of the measured X-ray diffraction (XRD) and Raman spectroscopy results confirmed the formation of nanocrystalline  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  before coating and amorphous carbon in the  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4/C$ after the coating. The Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> anode material exhibited a much higher specific capacity than the traditional graphite material, with initial discharge/charge capacities of 1275 and 874 mA h  $q^{-1}$ , respectively, at a 100 mA  $q^{-1}$  current density and a first coulombic efficiency of 68.54%. The long-term cycling test showed a slight capacity fading, retaining approximately 85% of its initial capacity after 75 cycles. Notably, the carbon-coating layer greatly enhanced the stability and slightly increased the capacity of the as-prepared Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>. The first discharge/charge capacities of Ni<sub>0.5</sub>Mg<sub>0.5</sub>- $Fe_{1.7}Mn_{0.3}O_4/C$  at 100 mA  $g^{-1}$  current density reached 1032 and 723 mA h  $q^{-1}$ , respectively, and a first coulombic efficiency of 70.06%, with an increase of discharge/charge capacities to 826.6 and 806.2 mA h  $g^{-1}$ , respectively, after 75 cycles (with a capacity retention of 89.7%), and a high-rate capability of 372 mA h  $g^{-1}$  at 2C. Additionally, a full cell was designed using a Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C anode and an NMC811 cathode. The output voltage was about 2.8 V, with a high initial specific capacity of 755 mA h g<sup>-1</sup> at 0.125C, a high rate-capability of 448 mA h g<sup>-1</sup> at 2C, and a high-capacity retention of 91% after 30 cycles at 2C. The carbon coating layer on Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles played a crucial role in the excellent electrochemical performance, providing conducting, buffering, and protective effects.

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## 1. Introduction

Lithium-ion batteries (LIBs) have shown great promise as an energy storage solution, finding extensive use across various domains encompassing portable devices, electric vehicles, and grid-scale energy systems.<sup>1</sup> Their exceptional attributes, such as high energy density and prolonged cycle life, make them particularly appealing.<sup>2</sup> LIBs consist of crucial constituents, namely the cathode, anode, electrolyte, and separator. Their effectiveness is contingent on the chemical composition of their diverse constituents and the morphology of their electrode materials.<sup>3</sup> Hence, there is a need to develop new efficient

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and cost-effective electrode materials to meet the growing demand for renewable energy, portable electronic devices, electric transportation, and large-scale energy storage in smart grids.4,5 Due to its cost-effectiveness, reliable reversibility concerning lithium-ion insertion/extraction, and plentiful availability, graphite is extensively utilized as the active anode material in commercial lithium-ion batteries (LIBs). Nevertheless, graphite is hindered by its low theoretical capacity of merely 372 mA h  $g^{-1}$ , which falls short of meeting the demands of extensive utilization in the green energy storage network.<sup>6-8</sup> Furthermore, the utilization of graphite in battery systems gives rise to safety considerations owing to its relatively low working voltage, which is less than 0.2 V when compared to the Li/Li<sup>+</sup> standard, and this can lead to the formation of lithium dendrites.<sup>9,10</sup> Silicon-based materials have emerged as a promising alternative to graphite for battery systems due to their large capacities. However, significant volume changes during the lithiation-delithiation process present a major obstacle to their practical application.11

To overcome the shortcomings associated with graphite and silicon-based anodes, spinel  $Li_4Ti_5O_{12}$  is another anode material that has been used for LIBs. Its discharge potential is about 1.5 V, which makes it safer than the commonly used graphite anode because the problem of lithium plating can be largely avoided.<sup>12</sup> The  $Li_4Ti_5O_{12}$  demonstrates outstanding stability and specific capacity at high current densities. However, its theoretical capacity is limited to 175 mA h g<sup>-1</sup>.<sup>13</sup> As a result, more research is necessary to develop new anode materials that offer improved safety, low cost, high theoretical capacity, and easy synthesis processes.

Spinel ferrite oxides, including  $ZnFe_2O_4$ ,<sup>14</sup>  $CoFe_2O_4$ ,<sup>15</sup>  $NiFe_2O_4$ ,<sup>16</sup>  $CuFe_2O_4$ ,<sup>17</sup>  $MgFe_2O_4$ ,<sup>18</sup> *etc.*, have gained considerable interest as potential anode materials for use in lithium-ion batteries (LIBs). This is largely because they have significantly higher theoretical capacities compared to graphite and  $Li_4Ti_5O_{12}$  anode materials.<sup>19,20</sup>

For instance, CaFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, and CuFe<sub>2</sub>O<sub>4</sub> exhibited higher specific capacities than the traditional graphite (372 mA h g<sup>-1</sup>).  $ZnFe_2O_4$  can also be considered as a good anode material candidate owing to its elevated theoretical specific capacity of around 1000 mA h g<sup>-1</sup>.<sup>21</sup>

However, the main problems of spinel oxide anode materials are their low electrical conductivity and considerable volume expansion.<sup>22</sup> To overcome these issues, carbon coating has been reported as a suitable coating material that can effectively enhance the capacity retention and cycling stability of spinel materials.<sup>17</sup> Moreover, it participates in reducing the volume change during the discharging/charging operations and facilitates the Li-ion diffusion into the metal oxide structure.<sup>13</sup>

For example, Jin *et al.* have successfully prepared  $\text{CuFe}_2\text{O}_4/\text{C}$  hollow spheres through a hydrothermal growth method based on polymers, followed by calcination. After the 70th cycle at a current density of 100 mA cm<sup>-2</sup>, the anodic material demonstrated a specific capacity of 550 mA h g<sup>-1</sup>, which is significantly greater than the initial specific capacity of the CuFe<sub>2</sub>O<sub>4</sub> hollow spheres (~120 mA h g<sup>-1</sup>).<sup>23</sup> In addition, Deng *et al.* 

reported a significant enhancement in the electrochemical properties of  $ZnFe_2O_4/C$  hollow spheres. They found that the  $ZnFe_2O_4$  sample modified with carbon exhibited a specific capacity of 841 mA h g<sup>-1</sup> after 30 cycles, along with a high-rate capability.<sup>24</sup>

To our knowledge, no studies have reported on the electrochemical performances of nanocrystalline Ni0.5Mg0.5Fe1.7Mn0.3O4 as anode materials for LIBs. This study details the preparation of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles, aiming to explore their potential as LIB anodes. We enhanced the cycling stability and rate capability of Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> anode through carbon coating. The nanocrystalline powders were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. The anode materials' performance for LIBs was evaluated using electrochemical tests in a lithium half-cell, including cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) tests. Additionally, the carbon-coated Ni0.5Mg0.5-Fe1.7Mn0.3O4/C anode's performance for LIBs was specifically evaluated in the full-cell configuration.

### 2. Experimental

# 2.1. Synthesis of $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$ and $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4/C$ samples

The synthesis of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel material was conducted utilizing the sol–gel method, as detailed in a prior study.<sup>25</sup> A solution was prepared by dissolving Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, and MnCl<sub>2</sub>·4H<sub>2</sub>O in distilled water, maintaining a molar ratio of Ni:Mg:Fe:Mn = 0.5:0.5:1.7:0.3. Citric acid, acting as a complexing agent, was subsequently introduced to this mixture. This combined solution was then heated to 90 °C with continuous stirring until it transformed into a viscous gel. The gel underwent a drying process at a temperature of 160 °C for a duration of 12 hours, resulting in the formation of a xerogel. Subsequently, the xerogel underwent calcination in an ambient air environment within a temperature range of 250–800 °C. Prior to each calcination phase, the sample was subjected to intermediate grindings.

In this synthesis process, the reagents reacted to produce the  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  spinel oxide, as depicted by the subsequent chemical equation:

$$0.5 \text{ Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 0.5 \text{ Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 1.7 \text{ FeCl}_3 \cdot 6\text{H}_2\text{O} + 0.3 \text{ MnCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4 + 2.85 \text{ Cl}_2\uparrow + 2 \text{ NO}_2\uparrow + 17.4 \text{ H}_2\text{O}\uparrow$$

Carbon coating was performed by mixing the as-synthesized  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  material with sucrose powder as the carbon source ( $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$ :glucose = 95:5, which was the percentage) using acetone solution. Subsequently, the composite underwent a calcination process at a temperature of

600  $^{\circ}$ C for a duration of 5 hours, while being exposed to an argon environment to get the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C sample.

#### 2.2. Material characterization

The sample was characterized using X-ray diffraction (XRD) analysis with a "BRUKER D8 ADVANCE" diffractometer, equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.54056$  Å). The diffraction data was collected within the 10 to 100 degrees  $(2\theta)$ angular range, using a step size of 0.01 degrees and a count time of 10 seconds per step. To investigate the morphology and particle size of the sample, scanning electron microscopy (SEM) was performed using a JEOL JSM-IT500HRL instrument. The chemical compositions of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material were examined using energy-dispersive spectroscopy (EDS). Transmission Electron Microscopy (TEM) using the TECNAI G2/FEI model was used to study the microstructure of both uncoated and carbon-coated samples and to assess the state of the carbon coating layer. Energy dispersive spectroscopy (EDS) was used to analyze the surface composition and elemental content of the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C sample. Raman spectroscopy analysis was conducted to identify the vibrational bands present in the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> sample, and to investigate the presence of carbon in the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C material. This analysis was carried out with a spectrometer (Horiba) and an excitation wavelength of 532 cm<sup>-1</sup>, using the spectral range of 100–2000 cm<sup>-1</sup>.

#### 2.3. Electrochemical measurements

The working electrodes for electrochemical tests were prepared by combining 70 wt% of the active material, 20 wt% of carbon black as a conductive agent, and 10 wt% of CarboxyMethyl Cellulose (CMC) as a binder. The resulting mixture was dispersed in double-distilled water and agitated for 6 hours to form a viscous slurry. The doctor-blade technique was employed to uniformly apply the slurry onto a copper foil current collector with a thickness of 0.1 mm, where the mass loading was 1.3–1.5 mg cm $^{-2}$ . The loaded copper foil was then dried overnight at 65 °C to remove the solvent (water). It was cut into disks of 11 mm diameter and left to further dry out overnight in a vacuum oven at 100 °C to eliminate all remaining solvent. The electrochemical tests of the fabricated materials were carried out using CR2032 button cells in a half-cell setup. The half-cells containing uncoated and carbon-coated materials were assembled under controlled conditions within an argon-filled glove box (Jacomex, France) at ambient temperature, while ensuring that water and oxygen levels remained below 0.5 ppm. The electrodes used in the setup comprised of a Li metal disc with an 8 mm diameter serving as the counter and reference electrodes. A Whatman separator was employed to segregate the negative and positive electrodes. The electrolyte adopted was a 2.0 M LiPF<sub>6</sub> solution dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC), mixed in a 1:1 proportion. Each coin cell contained 120 µL of this electrolyte.

The galvanostatic discharge/charge and long-term cycling tests on the newly investigated uncoated and coated spinel oxide were carried out at a current density of 100 mA  $g^{-1}$ 

 $(100 \text{ mA g}^{-1} = 0.125 \text{C})$  over the 0.01–3.00 V voltage range. Rate capability analysis was conducted at various C-rates, including 0.03C, 0.06C, 0.125C, 0.25C, 0.625C, 1.25C and 2C. Cyclic voltammetry curves of uncoated electrode Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> were obtained by varying the potential between 0.01 V and 3.0 V and utilizing a scan rate of 1 mV  $s^{-1}$ . Electrochemical impedance spectra (EIS) were characterized over a frequency range of 100 kHz to 0.01 Hz. The electrochemical testing of the full cell was carried out at a current density of 100 mA g<sup>-1</sup>, within a voltage range of 1-4 V. For this, we used an NMC811 electrode, sourced from Argonne National Laboratory, as the positive electrode, and our synthesized carbon-coated spinel oxide Ni0.5Mg0.5Fe1.7Mn0.3O4/C as the negative electrode. The full cell, comprising NMC811 vs. Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C, was assembled using the same procedure as for the half-cells of Ni0.5Mg0.5Fe1.7Mn0.3O4 and Ni0.5Mg0.5-Fe1.7Mn0.3O4/C negative electrodes. However, in the full-cell configuration, the NMC811 electrode was used instead of the lithium metal disc. The N/P (negative/positive) mass ratio was maintained at approximately 0.84. A discharge/charge rate of 0.125C and 2C was applied, corresponding to a specific current of 100 mA  $g^{-1}$  and 1600 mA  $g^{-1}$  for the negative electrode material. All potentials were referenced to the Li/Li<sup>+</sup> electrode. It should be noted that discharging and charging were regarded as lithiation and delithiation processes in this study. All electrochemical tests were conducted at ambient temperature utilizing a multi-channel potentiostat (MPG-2, Bio-Logic).

## 3. Results and discussion

The crystal structure of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel oxide and the incorporation of carbon were characterized using X-ray diffraction (XRD) and Raman spectroscopy techniques. Fig. 1 displays the X-ray diffraction pattern acquired at ambient temperature for the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> powder that underwent thermal treatment at a temperature of 800 °C,



Fig. 1 Room temperature XRD patterns of the synthesized  $\rm Ni_{0.5}Mg_{0.5}-Fe_{1.7}Mn_{0.3}O_4$  and  $\rm Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4/C$  materials.

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and carbon coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C powder. The X-ray diffraction (XRD) peaks observed in the diffraction pattern of uncoated material Ni0.5Mg0.5Fe1.7Mn0.3O4 have been successfully identified and assigned to the cubic spinel structure with  $Fd\bar{3}m$  (no. 227) as the corresponding space group.<sup>26</sup> No additional peaks corresponding to other phases were observed in the X-ray diffraction (XRD) pattern, indicating that the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> compound synthesized and subjected to thermal treatment at 800 °C is a pure single-phase spinel material. This outcome can be attributed to the chelation of citric acid molecules with the cations (Ni<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, and Mn<sup>2+</sup>) during the synthesis process, which effectively hinders the formation of impurities. The obtained sample of  $Ni_{0.5}Mg_{0.5}$ Fe1.7Mn0.3O4 exhibits a notable level of crystallinity, which is supported by the clear existence of distinct X-ray diffraction (XRD) peaks characterized by narrow full width at half maximum (FWHM) values.<sup>27</sup> The determined crystallite size of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material is 38 nm. The X-ray powder diffraction patterns of the sample Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> were analyzed using High-Score software, as depicted in Fig. 1. The analysis of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> combination demonstrated that all the diffraction peaks could be accurately identified as originating from the single-phase cubic spinel MgFe<sub>2</sub>O<sub>4</sub>. The space group  $Fd\bar{3}m$  was utilized for indexing, with reference to the standard JCPDS card (no. 88-1936) and a lattice parameter of a = 8.3827 Å. The obtained outcome was compared to the pure MgFe<sub>2</sub>O<sub>4</sub>.<sup>28</sup>

The X-ray diffraction (XRD) pattern of the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite did not reveal any diffraction peaks for carbon, indicating that the carbon produced from glucose decomposition may be amorphous.<sup>29</sup> In addition, there is no apparent difference between the XRD patterns of uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C materials. Therefore, the XRD results confirm the formation of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite.

To conduct a more comprehensive examination of the structural characteristics, the X-ray diffraction (XRD) pattern of the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel ferrite was subjected to refinement using the Rietveld method. Nevertheless, the process of structural refinement was conducted using the cubic structure and the  $Fd\bar{3}m$  space group. Fig. 2(a) presents the Rietveld refinement plot for the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1 7</sub>Mn<sub>0 3</sub>O<sub>4</sub> spinel. The red circles represent the experimental X-ray diffraction (XRD) pattern, the black solid lines depict the theoretical XRD pattern, and the blue solid line corresponds to the difference curves. The vertical green bars indicate the positions of various Bragg reflections. Fig. 2(a) presented in this study demonstrates a strong correspondence between the observed X-ray diffraction (XRD) pattern and the calculated XRD pattern. This agreement provides evidence of the successful structural refinement achieved for the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel ferrite. Furthermore, the evaluation of the quality of structural refinement was performed by considering several R-factors, such as the weighted profile factor  $(R_{wp})$ , profile factor  $(R_p)$ , expected factor  $(R_{exp})$ , and Chisquared value ( $\chi^2$ ). Table S1 (ESI<sup>†</sup>) summarizes the findings



Fig. 2 (a) Rietveld analysis of the X-ray diffraction patterns for the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material calcined at 800 °C. (b) Crystal structure of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel with the cubic  $Fd\bar{3}m$  structure, red balls represent the oxygen anions whereas the green-brown and blue-pink balls show the tetrahedral and octahedral sites, respectively.

from the powder X-ray diffraction analysis of the produced Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel oxide using Rietveld refinement. The results include structural parameters, Chi-squared factor ( $\chi^2$ ), and various reliability *R*-factors. Based on the obtained *R*-factors values, it can be concluded that the synthesized Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel oxide crystallizes in the cubic *Fd*3*m* structure, characterized by a lattice parameter of *a* = 8.36215 Å.

Fig. 2(b) illustrates the crystal structure of the  $Ni_{0.5}Mg_{0.5}$ -Fe<sub>1 7</sub>Mn<sub>0 3</sub>O<sub>4</sub> sample, which exhibits cubic  $Fd\bar{3}m$  symmetry. The analysis demonstrates that the synthesized material exhibits a crystal structure that is characterized by the connectivity of tetrahedra and octahedra sites, which are composed of oxygen anions. Based on the established framework, it becomes apparent that there are three distinct and easily discernible classifications of sites, denoted as 8a, 16d, and 32e sites. Notably, the 8a and 16d sites can be correlated with the tetrahedral and octahedral sites, respectively. The cations Ni<sup>2+</sup> and Mg<sup>2+</sup> are present in a ratio of 1/8 within the tetrahedral sites formed by the anions  $O^{2-}$ . Conversely, the cations  $Fe^{3+}/Mn^{3+}$  are situated in half of the octahedral sites formed by the anions  $O^{2-}$ . Furthermore, it should be noted that all the sites in the 32e structure are currently occupied by the  $O^{2-}$  anions. Hence, it is evident within the provided crystal structure that a substantial fraction of the tetrahedral sites (7/8) and half of the octahedral sites are vacant, thereby providing vacancies for the incorporation of lithium ions in the lacunae of the unit cell.



Fig. 3 Raman scattering curves collected at room temperature of the uncoated  $\rm Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  and carbon-coated  $\rm Ni_{0.5}Mg_{0.5}Fe_{1.7}-Mn_{0.3}O_4/C$  samples.

To further investigate the crystal structure of the synthesized  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  material and to confirm the presence of a carbon layer in the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles, Raman scattering spectroscopy was employed. Fig. 3 shows the Raman spectra of the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C materials. The Raman spectra of the coated material exhibit two distinct peaks at wavenumbers of approximately 1328.21 and 1582.06 cm<sup>-1</sup>, which correspond to the typical D and G bands for carbon, respectively.<sup>30,31</sup> The D band is associated with the A<sub>1g</sub> phonon of sp<sup>3</sup> carbon atoms at the edge and disordered carbon, while the G band is ascribed to the in-plane vibration of sp<sup>2</sup> carbon atoms in carbon atomic rings or long-chain carbon. The  $I_{\rm D}/I_{\rm G}$ ratio is a common evaluation value for carbon materials, indicating the degree of disorder and its association with electronic conductivity.<sup>32,33</sup> The calculated  $I_D/I_G$  value of 0.97 suggests a significant degree of disorder within the carbon structure of the as-prepared Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite, indicating amorphous carbon and agreeing with the XRD results.

The Raman spectra of the uncoated  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  material exhibited six peaks between 100 and 700 cm<sup>-1</sup>, which is also observed in the carbon-coated material.

It's pertinent to remember that, in the group theory analysis, the AB<sub>2</sub>O<sub>4</sub>-type spinels exhibiting cubic  $Fd\bar{3}m$  symmetry are predicted to have five active Raman modes, which may be defined as A<sub>1g</sub>, E<sub>g</sub>, and  $3T_{2g}$ .<sup>34</sup> The Raman scattering spectra of the produced material, obtained at room temperature, are depicted in Fig. 3. The remarkable crystallinity of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> sample is confirmed by the Raman spectra presented in Fig. 3. A total of six distinct Raman bands were detected at the respective wavenumbers of 189, 323, 473, 523, 650, and 691 cm<sup>-1</sup>. The detected Raman bands, have distinct characteristics that align with the crystal structure of MgFe<sub>2</sub>O<sub>4</sub>, namely the cubic spinel configuration. This crystal structure is commonly associated with the  $Fd\bar{3}m$  space group.<sup>35</sup> Based on prior research, it has been shown that the Raman bands detected at a wavenumber of 189 cm<sup>-1</sup> can be attributed to the T2g(3) mode, which signifies the vibrations of the localized lattice within the octahedral sub-lattice.<sup>28</sup> Nevertheless, it has been observed that two separate Raman bands have been found within the frequency range of  $300-500 \text{ cm}^{-1}$ . The bands seen in this study are associated with the Eg and T2g(2) vibrational modes. Specifically, these bands are allocated to the symmetric and asymmetric bending vibrations of the A/B-O tetrahedron.<sup>23</sup> In contrast, the three Raman peaks detected at elevated wavenumbers, namely at 523, 650, and 691 cm<sup>-1</sup>, are ascribed to the asymmetric and symmetric stretching vibrations of oxygen atoms that are linked to metal ions situated within tetrahedral sites. The vibrational modes are designated as T2g(1) for asymmetric stretching vibrations and A1g for symmetric stretching vibrations, respectively. The Raman bands observed at a frequency greater than 600 cm<sup>-1</sup> are attributed to the vibrational modes of the A-site. The A1g mode exhibits a distinct separation into two distinct modes at about 650 and 691 cm<sup>-1</sup>, which can be attributed to the presence of various ions, specifically Mg<sup>2+</sup> and Ni<sup>2+</sup>, within the tetrahedral site.<sup>36</sup> This observation confirms the presence of a pure cubic spinel phase in the material that was synthesized.

The size and morphology of particles significantly impact the material's electrochemical performance. Creating active materials at the nanoscale is a highly efficient approach to enhancing electrode kinetics. Nanoparticles provide a larger contact area between the electrode and electrolyte, shorten the pathway for Li+ ion diffusion and electron movement, and increase the number of electrochemically active sites.<sup>37</sup>

The morphology of the as-prepared  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$ sample was investigated by SEM analysis, as illustrated in Fig. 4(a)–(c). The prepared material demonstrates the presence of spherical particles, with an average diameter of around 217 nm. Besides, EDS elemental mapping of  $Ni_{0.5}Mg_{0.5}$ -Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> is illustrated in Fig. 4(d)–(h) in which the signals corresponding to O, Mg, Ni, Fe, and Mn elements are detected with well-distributed elements and concentrated on the particles without obvious element segregation. Elemental analysis of the synthesized material was conducted using EDS spectroscopy.



Fig. 4 (a)–(c) SEM images of  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  material. (d)–(h) EDS mapping images of the O, Ni, Mg, Fe, and Mn elements for  $Ni_{0.5}Mg_{0.5}$ -Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material.

The surface elemental composition of the  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$ material was determined using EDX analysis. Fig. S1, which can be found in the ESI,† provides evidence of the presence of nickel (Ni), magnesium (Mg), iron (Fe), manganese (Mn), and oxygen (O) in the as-synthesized sample, thereby confirming its purity.

TEM analysis was used to observe the inner microstructure of the uncoated and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> materials. The images are presented in Fig. 5 and Fig. S2 (ESI<sup>+</sup>). Fig. S2 (ESI<sup>†</sup>) shows that there is no carbon layer on the surface of the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles. However, Fig. 5(a)-(e) reveal amorphous carbon coating layers on the surface of the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles. The homogeneity of various elements in the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C powder was examined through high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along with corresponding elemental mapping technique. The images produced by HAADF-STEM and energy-dispersive spectroscopy (EDS) mapping of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C, are presented in Fig. 5(f)-(l). These images reveal a consistent distribution of C, O, Ni, Mg, Fe, and Mn elements within the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles.

The electrochemical performance of  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$ and  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4/C$  were evaluated by cyclic voltammetry and galvanostatic charge/discharge experiments at various current densities. These tests were conducted at room temperature, within a potential range ranging from 0.01 V to 3.0 V. Fig. 6 illustrates the cyclic voltammetry profile of the  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  electrode within the voltage range of 0.01-3.0 V, with a scan rate of 1 mV s<sup>-1</sup>. The initial cycle of the  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  sample exhibits notable distinctions compared to subsequent cycles. This disparity can be attributed to the cathodic lithiation process during the first cycle, wherein two cathodic peaks are observed. A pronounced reduction peak is observed at a potential of 0.01 V (*versus* Li<sup>+</sup>/Li), which is succeeded by a subsequent reduction peak occurring at 0.74 V (*versus* Li<sup>+</sup>/Li). These peaks are likely a result of the



Fig. 5 (a)–(e) TEM images of carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C, (f) STEM image, and (g)–(l) corresponding elemental mapping images of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C sample.



Fig. 6 Cyclic voltammetry profile in the voltage range of 0.01–3.0 V at a scan rate of 1 mV s<sup>-1</sup> of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> electrode.

incorporation of Li<sup>+</sup> ions into the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material through a series of multistep reactions, these reactions could be assigned to the cations reduced to metallic status (Fe<sup>3+</sup>/Fe<sup>0</sup>, Mn<sup>3+</sup>/ Mn<sup>0</sup>, and Ni<sup>2+</sup>/Ni<sup>0</sup> without Mg<sup>2+</sup> reduction to Mg<sup>0</sup> due to the high bond energy of MgO<sup>38</sup>) with the formation of SEI films and the generation of amorphous  $Li_2O$  (eqn (1)).<sup>36,39</sup> However, in this case, it can be observed that the cathodic peak at 0.01 V is indicative of the distinctive behavior associated with the insertion of Li<sup>+</sup> ions into the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material.<sup>40</sup> The initial anodic peak observed at 1.8 V can be ascribed to the oxidation processes of iron (Fe) to ferric ions ( $Fe^{3+}$ ), nickel (Ni) to nickel ions (Ni<sup>2+</sup>), and manganese (Mn) to manganese ions (Mn<sup>2+</sup>), facilitated by the creation of iron(m) oxide Fe<sub>2</sub>O<sub>3</sub> (eqn (3)), MnO (eqn (4)), and NiO (eqn (2)) phases with the decomposition of the  $Li_2O$  phase.<sup>7,25</sup> Additionally, the pronounced cathodic peak recorded at a potential of 0.01 V (vs. Li<sup>+</sup>/Li) during the initial cathodic peak could be ascribed to the formation of the solid-electrolyte interphase (SEI) layer, which arises from the decomposition of the electrolyte. This phenomenon is widely recognized for its significant contribution to the substantial reduction in capacity observed during the initial discharge cycle.<sup>41</sup> In the subsequent four CV cycles, they have similar cathodic and anodic peaks at 0.65 V and 1.9 V, respectively, The cathodic peaks for the subsequent four cycles could be linked to the reduction of NiO, Fe<sub>2</sub>O<sub>3</sub>, and MnO to Ni, Fe, and Mn, respectively. The following anodic process might be attributed to the oxidation of metallic nickel (Ni) to divalent ions (Ni<sup>2+</sup>), metallic iron (Fe) to ferric ions (Fe<sup>3+</sup>), and metallic manganese (Mn) to divalent ions (Mn<sup>2+</sup>), indicating similar kinetics during the charge and discharge of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material.

Based on the literature,  ${}^{25,26,42,43}$  and the analysis that has been previously discussed, the electrochemical reactions of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> compound can be described as follows:

![](_page_6_Figure_2.jpeg)

Fig. 7 Galvanostatic discharge/charge curves tested at a current density of 100 mA  $g^{-1}$  (100 mA  $g^{-1}$  = 0.125C) of (a) uncoated  $Ni_{0.5}Mg_{0.5}$ -  $Fe_{1.7}Mn_{0.3}O_4$  and (b) carbon-coated  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4/C$  electrodes. (c) Cycling performances of  $Ni_{0.5}Mg_{0.5}Fe_{1.7}Mn_{0.3}O_4$  and  $Ni_{0.5}Mg_{0.5}$ -  $Fe_{1.7}Mn_{0.3}O_4/C$  at a current density of 100 mA  $g^{-1}$  (100 mA  $g^{-1}$  = 0.125C).

capability in terms of Li<sup>+</sup> insertion/extraction (Fig. 8(a)). The two electrodes were cycled at different current rates of 0.03C, 0.06C, 0.125C, 0.25C, 0.625C, 1.25C and 2C, corresponding to 25, 50, 100, 200, 500, 1000 and 1600 mA g<sup>-1</sup>. The coated electrode cell delivers average charge capacities of 720, 778, 760, 731, 690, 651, and 372 mA h g<sup>-1</sup>. At the highest current density of 1600 mA g<sup>-1</sup>, Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C delivers 372 mA h g<sup>-1</sup> instead of the limited capacity of 192 mA h g<sup>-1</sup>

$$0.5Ni + 0.5Li_2O \leftrightarrow 0.5NiO + Li^+ + 1e^-$$
(2)

$$(1.7/2)$$
Fe<sub>2</sub>O<sub>3</sub> + 5.1Li<sup>+</sup> + 5.1e<sup>-</sup>  $\leftrightarrow$  1.7Fe + 2.55Li<sub>2</sub>O (3)

$$0.3MnO + 0.6Li^{+} + 0.6e^{-} \leftrightarrow 0.3Mn + 0.3Li_{2}O$$
 (4)

To improve the cycling stability of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material, a carbon coating process was adopted. The carbon coating was demonstrated to improve the metal oxide's electrochemical stability during long-term cycling. The carbon prevents the metal oxide particle agglomeration and maintains the structure's stability. Additionally, it participates in reducing the volume change during discharge/charge processes and facilitates the Li<sup>+</sup> ion diffusion into the metal oxide's structure.<sup>28,44</sup> The charge-discharge profile of both uncoated and coated anode materials is depicted in Fig. 7(a) and (b). The data were obtained by conducting experiments within the voltage range of 0.01–3 V (vs. Li/Li<sup>+</sup>) and at a current density of 100 mA  $g^{-1}$  for LIBs. The initial discharge and charge capacities for the uncoated and coated materials were determined to be 1275/ 874 and 1032/723 mA h g<sup>-1</sup>, respectively, accompanied by initial coulombic efficiencies (ICE) of 68.54% and 70.06%, respectively. Consequently, the first coulombic efficiency of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C anode is slightly higher than that of the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> anode. This improvement may be attributed to the carbon layer, which protects the electrode materials from direct contact with the liquid electrolyte.45 In addition, it is important to note that the initial capacity reduction during the first cycle is mainly due to the formation of a solid electrolyte interphase (SEI) layer on the electrode surface, accompanied by the generation of the inactive magnesium oxide phase (MgO).<sup>46</sup> In the 75th cycle, the charge capacities of uncoated and carbon-coated anode materials were 744 mA h g<sup>-1</sup> and 806 mA h g<sup>-1</sup> respectively. From the longterm cycling, the coated material shows an increase in capacity after 75 cycles compared to the uncoated material which shows a decrease in capacity, as indicated in Fig. 7(c). Moreover, the carbon-coated material displayed a capacity retention of approximately 89.7%, while reaching nearly 100% coulombic efficiency in the 75th cycle. The details of the electrochemical properties of these two electrodes are shown in Table S2 (ESI<sup>†</sup>). The excellent cycle stability of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material after carbon coating can be attributed to the stable solid electrolyte interphase (SEI) formed between the electrode and the electrolyte. Additionally, the improvement in the cycling stability of the coated material, compared to the uncoated sample, is a result of enhanced mechanical stability and stress resistance due to volume changes during the charge/discharge process. The coating limits the material's volume expansion by limiting its capacity; indeed, the anode did not reach its maximum capacity. Consequently, the volume change during lithiation is reduced, leading to improved stability.47 As a result, both the electrochemical performance and cycling stability of the electrode are enhanced.

To better understand the advantages of carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles in lithium-based energy storage, we compared the performance of uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C rate

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![](_page_7_Figure_1.jpeg)

**Fig. 8** The stability analysis of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C for comparison: (a) their rate capability from 0.03C to 2C (100 mA g<sup>-1</sup> = 0.125C), (b) the cycling performance at 2C for 100 cycles, (c) and (d) their Nyquist plots before and after 100 cycles at 2C (100 mA g<sup>-1</sup> = 0.125C).

for Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>. More importantly, when the current density was returned to 25 mA  $g^{-1}$ , a large irreversible capacity of 818 mA h g<sup>-1</sup> was recovered, showing a strong tolerance to the rapid insertion/extraction of Li<sup>+</sup> ions. To further evaluate the long-term cycling performance at high current density, uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>, and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe1.7Mn0.3O4/C electrodes were charged and discharged for 100 cycles at 2C for comparison. As shown in Fig. 8(b), the uncoated material Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> experienced an apparent capacity fading after 50 cycles and its capacity retention reached only 18.24% after 100 cycles, while the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/ C still retained 91.17% of the initial discharge capacity after 100 cycles, reflecting the unstable structure of the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and the stable structure of the carboncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C. The details of the electrochemical properties of these two electrodes are shown in Table S2 (ESI<sup>†</sup>).

To understand the carbon coating effect in more detail, electrochemical impedance spectroscopy (EIS) tests were performed before and after 100 cycles at a high current rate of 2C (100 mA  $g^{-1} = 0.125C$ ). These tests were performed in the frequency range of 100 kHz to 0.01 Hz using cells with uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C electrodes (Fig. 8(c) and (d)). From Fig. 8(c) and (d), the observed impedance spectra showed a semicircle in the high-frequency region, corresponding to the charge transfer resistance due to the transport of lithium ions across the electrode/electrolyte interface, and an inclined straight line in the low-frequency region, corresponding to the Warburg impedance due to the diffusion of Li+ ions into the electrode materials.<sup>48</sup> Fig. 8(c) and (d) show the equivalent circuit model, consisting of the contact resistance  $(R_s)$ , surface film resistance  $(R_{\rm f})$ , charge transfer resistance  $(R_{\rm ct})$  and Warburg impedance  $(W_4)$ ; the fitting parameters are summarized in Table S3 (ESI<sup>†</sup>).<sup>49</sup> The  $R_{\text{total}}$  (where  $R_{\text{total}} = R_{\text{s}} + R_{\text{f}} + R_{\text{ct}}$ ) can be closely monitored to explore the origin of the electrochemical properties of LiB cells in practice. A small R<sub>total</sub> indicates improved cycling performance and rate capability of LiB. From the equivalent circuit model, the fitted R<sub>ct</sub> parameter for cells before cycling are 18646 and 10237  $\Omega$  for uncoated  $Ni_{0.5}Mg_{0.5}\text{-}$ Fe1.7Mn0.3O4 and carbon-coated Ni0.5Mg0.5Fe1.7Mn0.3O4/C electrodes, respectively. The lower  $R_{ct}$  value of the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C electrode suggests a higher charge diffusion efficiency in this novel nanostructure.<sup>50</sup> Meanwhile,  $R_{\rm ct}$  decreased to 2145 and 400  $\Omega$  after 100 cycles at a 2C rate for uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C electrodes, respectively. It is observed that the  $R_{\rm ct}$  values after 100 cycles were lower than those of the cell before cycling, indicating a lower charge transfer resistance, which suggests an improvement in electron transport during the repeated lithiation and delithiation processes. For  $R_{total}$ , the results indicate that the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/ C electrode has a significantly lower total resistance after cycling compared to the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> and carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C electrodes before cycling, indicating improved stability and rate capability

performance. Thus, the EIS result shows that the Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite electrode has higher electrical conductivity compared to the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> material, resulting in stable and higher reversible capacity.

The Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C carbon-coated electrode exhibits excellent cycling performance and rate capability compared to the uncoated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> electrode, which is attributed to the protective carbon coating layer which protects the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles from direct contact with the electrolyte, thereby maintaining the structural integrity of the nanoparticles during the lithiation–delithiation process. Furthermore, the carbon layers not only mitigate the volume expansion of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> nanoparticles but also maintain stable electronic conductivity during the lithiation–delithiation process impedance text ref. 51.

To evaluate the performance of the carbon-coated  $Ni_{0.5}Mg_{0.5}$ -Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C material in a complete battery system, a full cell was designed using an NMC811 cathode (Fig. 9(a) and (b)). The full cell's output voltage was 2.8 V at 0.125C current rate, within the voltage window of 1–4 V, matching the voltage difference between the NMC811 cathode and  $Ni_{0.5}Mg_{0.5}$ Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C anode. Furthermore, in Fig. 9(a), the charge/discharge cycles of the full cell at a 0.125C current rate are illustrated within the voltage range of 1–4 V. The full cell exhibited a capacity of 755 mA h g<sup>-1</sup> with a coulombic efficiency of 65% during the

![](_page_8_Figure_4.jpeg)

Fig. 9 (a) Charge/discharge cycle of the (Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C)/NMC811 full cell performed at a current density of 100 mA g<sup>-1</sup> (100 mA g<sup>-1</sup> = 0.125C) within the voltage range 1–4 V, (b) cycling performances at 2C charge/discharge rate.

![](_page_8_Figure_8.jpeg)

Fig. 10 A comparison of capacity, voltage, and energy density of anode materials for LIBs.

first cycle, based on the mass of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C anode. Subsequently, after 4 cycles, the capacity decreased to 633 mA h g<sup>-1</sup>, with an increase in the coulombic efficiency to 97%. The cycling performance of the full cell was investigated at 2C within the voltage window of 1–4 V (Fig. 9(b)). After 30 cycles, a capacity of 448 mA h g<sup>-1</sup> was achieved with a capacity retention of 91% and a coulombic efficiency of 98%. The low capacity of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C electrode in the full cell is mainly due to its low first coulombic efficiency of the Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C anode may be attributed to various factors, such as the inadequate balance between the positive and negative electrodes, electrolyte decomposition during cycling, and other factors.

Fig. 10 shows the reversible capacity, the average potential, and the estimated energy density of anode materials for lithium full cells. In this study, we demonstrate that the Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C composite material displays a reversible capacity above 800 mA h g<sup>-1</sup>. This value is notably 2–3 times greater than the reversible capacity observed in the graphite anode material,<sup>35</sup> and also shows a high specific capacity compared to the spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,<sup>52</sup> TiO<sub>2</sub>,<sup>53</sup> and Li<sub>3</sub>VO<sub>4</sub>,<sup>54</sup> anode materials. Furthermore, the energy density of spinel oxide Ni<sub>0.5</sub>Mg<sub>0.5</sub>-Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C Li-ion cell is calculated to be 360 Wh kg<sup>-1</sup> based on the capacity and the average potential of positive and negative electrodes with a relatively high operating voltage of 1.1 V *versus* Li/Li<sup>+</sup> compared to the traditional graphite.

### 4. Conclusion

In summary, Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> spinel ferrite oxide nanoparticles were prepared using a simple and efficient sol–gel synthesis method and then coated with carbon. Analysis using X-ray diffraction and Raman spectroscopy confirmed that the synthesized materials have a single cubic spinel phase with the space group  $Fd\bar{3}m$ , and also confirmed the presence of an amorphous carbon layer on Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles. Scanning electron microscopy analysis highlighted the existence of spherical nanoparticles in the synthesized substance, with a particle size of 217 nm. Further confirmation of the existence of the carbon layer was obtained through TEM analysis. The Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub> electrode was developed as an anode for lithium-ion batteries and demonstrated an initial specific capacity of over 874 mA h  $g^{-1}$ , as well as a capacity retention of approximately 85% after 75 cycles. Carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C nanoparticles exhibited excellent cycling stability as an anode for LIBs, with a capacity retention of approximately 89.7%. Furthermore, the carbon-coated Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C showed enhanced capacity, stability, and rate capability over extended cycling tests, underscoring the value of the carbon coating in improving the material's electrochemical performance. The combination of Ni<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>1.7</sub>Mn<sub>0.3</sub>O<sub>4</sub>/C material in a full-cell configuration with an NMC811 cathode demonstrated promising results, including high specific capacity, and stability after 30 cycles at 2C. These findings suggest that this material could serve as a promising candidate for next-generation anode materials in lithium-ion batteries.

## Conflicts of interest

There are no conflicts to declare.

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