

Research Article

Boosting LiMn₂O₄ Diffusion Coefficients and Stability via Fe/Mg Doping and MWCNT Synergistically Modulating Microstructure

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The dissolution of manganese and its deposition on the anode surface cause poor cycling stability in lithium-ion batteries. To alleviate these issues, this study probes the electrochemical activity of highly crystalline and cation-adjusted lithium manganese oxide (LMO) carbon spinel composite obtained via a modified sol-gel synthesis procedure. The pristine LMO cathode was functionalized with a Fe and Mg alloy and fused with purified multiwalled carbon nanotubes (MWCNTs) to form a catalytically stabilized LiMn_{1.98}Fe_{0.01}Mg_{0.01}O₄/MWCNT (LMO-FeMg/MWCNT) framework. High-resolution SEM analysis showed well-dispersed particles in the nanometer size range. The electrochemical characteristics of the novel composite materials yielded favourable electrochemical results with diffusion coefficients of $1.91 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ and $5.83 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for LMO-FeMg and LMO-FeMg/MWCNT, respectively. This improvement was supported by impedance studies which showed a considerable R_{ct} reduction of 0.27 Ω and 0.71 Ω . The cation stabilized system outperformed the pristine LMO material with specific capacities around 145 mAh·g⁻¹, due to an enhancement in electrochemical activity and structural stability.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are focal electrical power components for next-generation energy applications. For energy-intensive applications, the electrochemical rechargeable cells should provide high energy density, good structural stability upon cycling, high-rate capability, and sufficient safety. In this context, the positive electrode (cathode) materials have to satisfy and maintain the abovementioned requirements. However, the advancements made to the current cathode materials used in lithium-ion batteries are not progressing, due to the high cost and sustainability issues associated with the use of cobalt or nickel elements. Lithium manganese oxides (LMOs) are one of the most promising alternative cathode materials for Li-ion batteries as they can reversibly (de)intercalate lithium at high potential differences compared to a carbon anode and are cheap and environmentally benign [1]. However, Mn³⁺ dissolution occurs at temperatures higher than 55°C after repeated cycling. This

results in subsequent capacity decay and structural instability due to a Jahn–Teller (JT) distortion of the high-spin Mn^{3+} at a deep state of discharge (SOD) [2]. Despite LiMn₂O₄ being a semiconductor with a mixed ionic (10^{-4} S·cm⁻¹) and electronic (2×10^{-6} S·cm⁻¹) conductivities, upgrading the electrochemical properties via modification is considered as beneficial.

Scientists have thus employed different techniques in order to negate these downfalls towards improving the electrochemistry and stability of LMO spinels in LIBs. Although surface coating is a promising strategy for improving the structural stability of LMO, the commonly used coating process is tedious and complicated. Elemental doping into the spinel microstructure has proved to be useful in most cases. Exotic metals such as Na, Mg, In, Sn, Au, and Sb are often used as dopants in lithium-ion batteries as they serve as stabilizing agents within the lattice which not only improve the durability of the battery but also catalyse its electrontransferkinetics [3, 4]. Billaud et al. employed a coprecipitation doping technique in order to mitigate the irregular conductivity and concluded that substitution at two distinct sites gives rise to impressive ion conductivity as well as improved electrochemical performance [5]. In a recent study by Lee et al. [6], Fe allowed for increased Li⁺ ion diffusivity as a result of enlarged Li layer spacing and increased oxygen vacancy in a Fe-doped LiMn₂O₄ truncated octahedral system. Li et al. found that Fe-doped Ni hydroxide powders experienced an enhanced lithium-ion storage capacity with improved cycling stability and rate capability [7]. A similar study claimed that the replacement of Mn by Fe can effectively activate the redox reactions and improve the ionicelectronic conductivities through increasing the lower oxidation state transition metal ions [8]. The nontransition metal, manganese has also been shown to provide additional storage capacity and suppress capacity fading by increasing the average valence state of Mn which improves the diffusion kinetics during Li insertion/extraction. Additionally, the electron-transfer pathway is ensured by carbonaceous additive, as it facilitates good contact bridges between particles and overcomes interparticle resistance [9]. Carbon materials can provide excellent conducting support for the LiMn₂O₄ electrode, suppress aggregation of nanoparticles, and minimize structural degradation due to volume changes induced by lithium insertion/extraction [4].

This work reports on the synergistic effect of codoping low valent Fe and Mg ions into the spinel lattice of LMO and its infusion with MWCNT, in order to improve the ion transport kinetics and stability within the cathode system. A low-temperature and short-time processing at high temperatures is employed to prevent oxygen deficiency at the surface of $LiMn_2O_4$. We uncover the dynamics of cation modification within the spinel LMO matrix and determine the effects of MWCNT on further boosting the electrochemical performance and durability of the intercalating material.

2. Experimental Setup

2.1. Chemicals. Manganese acetate tetrahydrate ($C_4H_{14}MnO_8$, Aldrich), sodium borohydrate (NaBH₄, Fluka), potassium permanganate (KMnO₄, Aldrich), graphite (Aldrich), N-meth yl-2-pyrrolidone (NMP, Fluka), hydrogen fluoride (HF, Aldrich), iron acetate ($C_{14}H_{27}Fe_3O_{18}$, Aldrich), magnesium acetate (Mg(CH₃COO)₂, Aldrich), and lithium hydroxide (LiOH) were used as received. The cyclic voltammetry of the composite material was probed by using a 3-electrode system in 1 M LiPF₆ in 2 : 1 (v/v) ethylene carbonate/ethylene carbonate/ diethyl carbonate. NMP served as the binding agent and facilitated the adhesion of the active material onto the glassy carbon electrode (GCE). A silver-silver chloride (Ag/AgCl) electrode was used as the reference electrode and a platinum wire as the counter electrode.

2.2. Purification of MWCNT. MWCNTs were baked to 300° C in a muffle furnace for 1 h before treatment with 1 M HNO₃ solution to remove impurities. The suspension was placed under ultrasonication for 2 h. After settling at the bottom of the flask, the suspension was centrifuged and washed with distilled water before drying at 60°C overnight.

2.3. Synthesis of Cathode Materials

2.3.1. (i) Pristine LiMn₂O₄ (LMO), (ii) LMO/MWCNT, (iii) LMO-FeMg, and (iv) LMO-FeMg/MWCNT. The spinel (i) LiMn₂O₄ (LMO) was prepared by dissolving LiOH and C₄H₁₄MnO₈ in deionized water with a stoichiometry/molar ratio of Li/Mn = 1:2. The solution was mixed well and evaporated at 120°C for 12 h to obtain the precursor powder. The precursor was further heated at 400°C for 1 h, followed by calcination at 800°C for 20 h in a muffle furnace to form the LMO spinel. (ii) LMO/MWCNT was obtained after calcination of LMO with purified MWCNT at 600°C [10]. The molar ratio of LMO was controlled to be 4:1. The cation-modified (iii) LMO-FeMg cathode material was prepared by dissolving stoichiometric amounts of LiOH, C₄H₁₄MnO₈, C₁₄H₂₇Fe₃O₁₈, and Mg(CH₃COO)₂ with a molar ratio of Li/Mn/Fe/Mg = 1: 1.98:0.:0.1 in deionized water, followed by a gentle stirring at 120°C, over 12 h. It was then heated at 400°C for 1 h to complete the evaporation and calcined at 800°C for 20 h in a muffle furnace to form FeMg-doped LMO crystalline powders. (iv) The LMO-FeMg/MWCNT composite was prepared by simply mixing the AS-prepared LMO-FeMg with purified MWCNT in a mass ratio of 4:1 (LMO-FeMg/ MWCNT) in 100 ml methanol and subjected to sonication for 3 h. The LMO-FeMg/MWCNT suspension was washed and dried before calcination at 600°C.

The cycling stability test was performed by using a coin cell. The cathode was prepared by mixing LMO, polyvinylidene fluoride (PVDF), and carbon black in a mass ratio of 92:6:2 in N-methyl-2-pyrrolidone (NMP) at 500 rpm for 24 h. The ink was then coated onto an aluminum foil substrate by the doctor blade method. The coating thickness was $60 \,\mu\text{m}$. The coated foil was then dried at 120°C overnight before being punched into 16 mm diameter circles. The anode was composed of a 90:6:2: 2 mixture of graphite, water-processable binder materials carboxymethylcellulose (CMC), styrene-butadiene rubber (SBR), and carbon black in water. Carbon black is a fundamental component as it increases the electrical conductivity of the system, prevents agglomeration of anode materials during cycling, and maintains stability [11]. The separator used was Celgard polypropylene film. The punched electrodes were assembled into 2032 coin cells in a dry room with a humidity of 1.0% h.r. The electrolyte used was 1 M LiPF_6 in 2:1 (v/v) ethylene carbonate/diethyl carbonate.

3. Results and Discussion

3.1. Structural Characterization. The X-ray diffraction overlay patterns in Figure 1 represent the pristine LMO, LMO-FeMg, and LMO-FeMg/MWCNT materials. The diffraction patterns were taken at room temperature in the range of 5 < 2 theta $<75^{\circ}$ using step size and measurement time of 0.027° and 1 sec/step, respectively. The patterns have been indexed to the Fd-3m phase (JCPDS no. 01-083-0358; space group Fd-3m, a = 8.19190 Å, and a unit cell volume of 543.66 Å³) suggestive of high purity and crystalline samples. Figure 1(d) inset represents the crystal structure of the cation-doped LMO through the polyhedral model. The polyhedral LMO structure shows the Fd-3m geometry of the spinel with



FIGURE 1: XRD overlays of (a) LMO, (b) LMO-FeMg, (c) LMO-FeMg/MWCNT (inset: MWCNT), and (d) FWHM fitted (111) plane and polyhedral structure of LMO-FeMg/MWCNT.

purple polyhedra representing the substitution and partial reduction of manganese. The average crystallite size of 44 nm was determined from the Scherrer equation as follows:

$$D = \frac{K\lambda}{\beta\cos\theta},\tag{1}$$

where *D* is the crystallite size (nm), λ is the diffraction wavelength (Å), β is the full width at half maximum (FWHM) value, and θ is the diffraction peak position. The values are given in Table 1. The particle size contributes to enhancing the electrochemical performance (especially improving rate capability).

To evaluate the effect of the doping ions on the crystalline lattice of the obtained spinel, the lattice parameter a was calculated from the XRD data by the least-squares method.

The *a* value of 8.246 Å for the pure spinel was obtained which is in close agreement with that of the stoichiometric $LiMn_2O_4$ spinel. The values for the doped samples were 8.244 and 8.243 Å, respectively, which are indicative of an effective doping since this process is associated with the substitution of Mn^{3+} ions in the octahedral 16d sites by cations of smaller ionic radius. This effect is further demonstrated through the charge and discharge tests.

Figure 2 shows the surface morphology of the doped LMO-FeMg spinel, where the material consists of closepacked octahedrally shaped particles. It is evident that the FeMg cations are well incorporated within the LMO particles, with the brighter contrast being the Fe and Mg atoms. Figure 2(b) shows the LMO-FeMg particles being intertwined within the MWCNT matrix. The strands have a uniform diameter of ± 50 nm which is well in agreement with the TEM

Peak position 2θ (°)	FWHM-β (°)	D (nm)
18.67	0.143	56.3
36.22	0.216	38.69
44.05	0.283	30.28
64.11	0.377	28.86
Average crysta	44	

TABLE 1: Average crystallite size determined from 2θ positions.

Particle size reduction has a limitation as extremely small particles show negative effect in performance. More critically, independent of the particle size distribution, the existence of coarse particles are found to promote lithium plating, which lowers cell performance and threatens the safety of battery operation. This is the average crystallite size of 44 nm. The particle size contributes to enhancing the electrochemical performance (especially improving rate capability).



FIGURE 2: HRSEM of (a) LMO-FeMg and (b) LMO-FeMg/MWCNT with insets showing the corresponding energy dispersive X-ray spectra (EDS).

analysis (see following). The inclusion of the MWCNT gives the material a fluffier appearance with an increased surface area which serves as an ideal medium for Li-ion extraction and intercalation. The composite facilitates electronic contact between the $\text{LiMn}_{1.98}\text{Fe}_{0.01}\text{Mg}_{0.01}\text{O}_4$ electrode and the current collector through an overlap of the electrochemically active energies of the conductive MWCNT. This multidimensional aspect is viable as Li-ion diffusion through the electrolyte is enhanced [12].

The energy dispersive spectrum shows the elemental composition obtained from HRSEM analysis for LMO-FeMg and LMO-FeMg/MWCNT. While EDS does not detect elemental Li and Mg in the composite, it was evident from XRD analysis which deduced the spinel crystal structure. Additionally, increased carbon levels were detected which reflect the successful infusion with MWCNT. The average Fe content in the sample was calculated to be 1.08% and a small amount of 0.25% for Mg was detected, respectively. In the LMO-FeMg/MWCNT sample, the average Fe content was found to be 0.73% and the Mg amounted to be 0.85%. The dopant concentrations are close to 1% as expected.

From Figure 3(a), well-defined lattice fringes are observable and are roughly spaced at 0.42 nm apart, which are indicative of the crystallinity of the LMO-FeMg material. The inset shows the particles at higher magnification, where the particle shapes appear to be octahedrally shaped, which is well in agreement with the HRSEM. In Figure 3(b), the particles grow well within the nanotube network with the SAED image confirming the deduced crystal orientation in Figure 3(c) and average particle size in Figure 3(d) ranging between 100 and 140 nm which is slightly smaller than conventionally doped Li-Mn-O particles. No defect was observed at the interface between the host spinel and layered surface phase, which provides an efficient path for the ionic and electronic mobility [13].

Figure 4 shows the FTIR spectra of LMO, LMO-FeMg, and LMO-FeMg/MWCNT in the wavenumber range of 0-4000 cm⁻¹ at room temperature. The distinct absorption bands observed at 507.1 and 612.3 cm⁻¹ are characteristic of LMO spinels and are assigned to the stretching vibration of the MO₆ octahedra. These distinctive symmetrical bands are a direct result of the Mn ion being split into two octahedrons, namely, $[{\rm Mn}^{3+}O_6]$ and $[{\rm Mn}^{4+}O_6].$ There is a small shift of two peaks towards the higher wavenumbers at 509.1 and 614.3 cm^{-1} . This slight shift could be attributed to the presence of Fe and Mg dopants [14]. The octahedral site preferences of the codoped cations are clearly demonstrated by these findings. Specific interactions such as Mg-O/Mn-O interactions cause peak shifts in the FTIR spectra, with higher wavenumbers and higher Mn-O bond strengths [15]. The results show that doping enhances the Mn-O bond, further enhancing the stability of the spinel structure. The occurrence and intensity of the absorption band at

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FIGURE 3: HRSEM image of (a) LMO-FeMg, (b) LMO-FeMg/MWCNT, (c) SAED image, and (d) average particle diameter of LMO-FeMg/MW CNT.



FIGURE 4: FTIR overlays of (a) LMO, (b) LMO-FeMg, and (c) LMO-FeMg/MWCNT.

 1217 cm^{-1} are due to the stretching vibration of epoxy C-O which indicates the presence of MWCNT.

The normalized Raman spectrographs of LMO, LMO-FeMg, and LMO-FeMg/MWCNT in the spectral regions of 400-800 and $1400-1700 \text{ cm}^{-1}$ are shown in Figure 5. The strong band in (a) is representative of the A_{1g} Raman vibrational mode of LMO which is indicative of the MnO₆ octahedrons and the LiO₄ tetrahedrons combined [16]. A slight blue shift of about 10 cm⁻¹ is observed between the cation-doped and pristine materials. This is indicative of the Fe and Mg dopants which substitute with Mn atoms in the spinel. The shoulder at 580 cm⁻¹ can be ascribed to the F_{2q} mode which becomes a noticeably broader A_{1q} band as a result of bond length variations which were introduced by the dopants. This could be due to the increase of Mn⁴⁺ in the LMO crystallite [17]. An intense D band and less intense G band shown in (d) can be ascribed to the MWCNT-coated spinel [18], which indicates that the MWCNT in LMO-FeMg composites has fewer surface defects. Therefore, spinel rigidity and improved Li diffusion pathways are maintained.

To further probe the modified materials and interfaces, X-ray photoelectron spectroscopy (XPS) was used to provide quantitative chemical insights. XPS spectra were measured at room temperature in an ultra-high vacuum (UHV) chamber at a base pressure of 2×10^{-10} mbar. The measurement chamber was equipped with a SPECS XR 50M monochromatised X-ray source with an Al anode (Al K α excitation line, or $h\nu = 1486.71$ eV) and a SPECS PHOIBOS 150 hemispherical electron energy analyser. A flood gun set was used to operate at the following parameters: electron energy of 2.0 eV and electron flux of $25 \,\mu$ A. The overall energy resolution of the combined analyser + photon source system was set to 1.0 eV for the survey scans and to 0.8 eV for all the other high-resolution core-level spectra.

The survey scan for the pristine and modified cathode materials presented in Figure 6 shows minute Na contamination in the sample, deriving from the synthesis process. The amount of Fe and Mg ions present in LMO-FeMg and LMO-FeMg/MWCNT was below the detection limit of the XPS system (approximately 1% to 5%), making these two elements not detectable. The O1 core level spectra for the samples are displayed in Figure 7. These spectra have been fitted by adding the three Voigt line-shaped singlets labelled O1, O2, and O3 in the figure, to a Shirley background. This is consistent with the literature reported for similar compounds [19]. The fitted components and the background are appended to the spectra, and the overall fit shows very good agreement with the experimental data. O1, the component at the lower binding energy (BE) side, is assigned to stoichiometric oxygen in the main matrix. Component O2 can be ascribed to oxygen vacancies and/or defects within the crystalline structure [20]. Finally, O3 is attributed to surface contaminants, i.e., oxygen that is chemisorbed on the surface of the sample. The BEs and the relative percentage areas of the three fitted components for O1s are reported in Table 2. The values in the table show that about 60% of the spectral weight of the core level in LMNO and LMO-FeMg is derived from stoichiometric oxygen, while this percentage decreases to 45% in LMO-FeMg/MWCNT because the percentage

ratio of component O3 increases tremendously with respect to the other two samples.

Figure 8 displays the fitted Mn 3s core level spectra for the three samples. The line shape of the Mn 3s core level is a good indicator of the oxidation state of Mn in a compound. In fact, it consists of two separated components resulting from the exchange interaction between the 3s core hole and the 3d unfilled shell [21]. The main peak at lower BE can be assigned to the high-spin (HS) state, or Mn (1), and its satellite at higher BE to the low-spin (LS) state, or Mn (2), due to the 3s core electron spin being coupled, respectively, parallel or antiparallel to the 3d electrons' majority spin. Each spectrum has been fitted with two singlets having a Voigt line shape and a Shirley-type background. The fitted components, the background, and the overall fit to the data have been appended to the figure. The magnitude of the exchange splitting ΔE_{3s} is proportional to 2S + 1, where S is the total spin moment of the unpaired 3d electrons in the ground state. This means that an exchange splitting, ΔE_{3s} , around 5 eV is a signature of a majority Mn^{3+} , or 3 d⁴, for Mn ions. Deviations from this value hint at changes in the 3+/4+ oxidation state ratio [22, 23]. In this study, the addition of Fe and Mg to LMO in LMO-FeMg causes ΔE_{3s} to decrease by about 0.56 eV (from 5.49 eV in LMO to 4.93 eV in LMO-FeMg). This hints at an increase in the percentage of the Mn⁴⁺ contribution in LMO-FeMg, which is supported by the change in the Mn 2p core level line shape as is shown below. The addition of MWCNT in LMO-FeMg/MWCNT causes the Mn 3s exchange splitting to increase again to 5.18 eV, showing that the amount of Mn³⁺ is increasing again with respect to that of LMO-FeMg (a fact that is again supported by the change in the Mn 2p line shape). It can therefore be inferred that the addition of FeMg and MWCNT causes changes in the oxidation state of Mn ions which can then be related to the chemical performance of the composites.

Mn 2p core level spectra are displayed in Figure 9(a). The line shape of this core level is composed of two broad peaks whose centroids are located at ~642 eV and ~654 eV BE, corresponding to Mn 2p^{3/2} and Mn 2p^{1/2}spin-orbit components, respectively. The oxidation state of Mn ions can be inferred by comparing the line shape of this core level with the relevant literature. Colour-coded arrows in the figure indicate the centroid of the main Mn³⁺/Mn⁴⁺ features. The line shape of the Mn 2p core level of LMO is in very good agreement with that of Mn₂O₃ [24], showing a majority 3+ oxidation state of Mn ions in this composite. The addition of FeMg causes a change in the line shape: the spectral weight of the low BE shoulder (which is the defining feature of a 3+ oxidation state) evidently decreases, confirming the shift towards a majority 4+ oxidation state in LMO-FeMg, as already discussed for the Mn 3s core level. The further addition of MWCNT sees an increase in the intensity of the 3+ shoulder, confirming that the oxidation state changes to be more similar to that of the LMO composite.

Finally, Figure 9(b) shows the C 1s core level spectrum for LMO-FeMg/MWCNT. The spectrum has been fitted with 4 components, representing the carbon bonds with its ligands, consistent with respect to the relevant literature [25, 26]. C1 and C2 are ascribed to double and single carbon-to-carbon chemical bonds and are the most intense features in the spectrum.



FIGURE 5: Raman overlay of (a) LMO, (b) LMO-FeMg, (c) LMO-FeMg/MWCNT, and (d) LMO-FeMg/MWCNT at higher spectral shifts.



FIGURE 6: Wide survey scans for LMO, LMO-FeMg, and LMO-FeMg/MWCNT.

3.2. Electrochemical Measurements. The electrochemical performance of the LMO-FeMg and LMO-FeMg/MWCNT composite materials was probed using a 3-electrode system in 1 M LiPF₆ in 2:1 (v/v) ethylene carbonate/ethylene carbonate/diethyl carbonate. Galvanostatic charge/discharge and cyclability analysis was conducted on a BTS battery analyser workstation. Electrochemical measurements (CV and EIS) were conducted to probe the redox activity of LMO-FeMg/MWCNT resulting from the synergy of a chemical interaction. The cyclic voltammogram of LMO-FeMg shown in Figure 10(a) displays multiple redox peaks in the voltage range of -0.5-0.5 at a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$. The redox couples at -0.25/-0.19 V and 0.28/ 0.19 V can be ascribed to Mn^{3+/4+} transitions upon Li-ion insertion and extraction reactions taking place across the electrode surface. The broader peak pair in the -0.46/0.5 V

region is obtained due to the partial substitution of Fe and Mg atoms and can be ascribed as $Fe^{2+/3+}$ transitions which contribute towards the improved current densities. The voltage gap between the reduction and oxidation peaks is attributed to the electrode polarization, closely correlating with the active material's conductivity. Changing the scan rate affects the CV features including the current as is observed for LMO-FeMg at varying scan rates (5–60 mV·s⁻¹) in Figure 10(b). The inset shows the plot of anodic and cathodic peak currents (i_{pa} and i_{pc}) against the square root of the scan rate $(v^{1/2})$. The plot shows a linear dependence between i_p and $v^{1/2}$ at almost all scan rates, and the peak currents (i_p) are proportional to the square root of the scan rate $(\nu^{1/2})$, i.e., $i_{p}\alpha v^{1/2}$ at different scan rates. This indicates that the electrode reaction is a diffusion-controlled process. The system displays better performance at a slower scan rate; however,



FIGURE 7: O 1s core level spectra and fit results for LMO, LMO-FeMg, and LMO-FeMg/MWCNT.

TABLE 2: BEs (in eV), FWHM (in eV), and relative percentage areas (in %) of the three components of the O 1s core level.

	O1 (eV)	O2 (eV)	O3 (eV)	O1 area (%)	O2 area (%)	O3 area (%)
LMO	530.03	531.52	533.5	60	31.4	8.6
LMO-FeMg	530.02	531.45	533.12	62.6	20.2	17.2
LMO-FeMg/MWCNT	529.88	531.45	533.2	45.2	25.5	29.3

as the rate increased the reversibility was maintained in accordance with equation (1) and illustrated good comprehensive stability with a stable increasing current density.

$$\mathbf{I}_{\mathbf{p}\mathbf{a}} = -\mathbf{I}_{\mathbf{p}\mathbf{c}},$$
$$-\frac{I_{pa}}{I_{pc}} = \frac{10 \text{ mA}}{7 \text{ mA}} = 1.4 \text{ mA},$$
(2)

$$\therefore -\frac{I_{pa}}{I_{pc}} \approx 1 \dots \text{ chemically reversible.}$$

After the addition of MWCNT, the electrochemical behaviour of LMO-FeMg/MWCNT was probed by using similar parameters as for LMO-FeMg, for comparison. The cyclic voltammogram of LMO-FeMg/MWCNT shown in Figure 11(a) is obtained at a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$. Four distinct oxidation peaks were observed, with the peaks at -0.44 and -0.19 V being attributed to the Mn³/Mn⁴⁺ redox

couple and the peaks at 0.22 and 0.36 V attributed to the Fe^{3+}/Fe^{4+} transitions [27]. The current density of the LMO-FeMg/MWCNT sample was significantly enhanced compared to LMO-FeMg, which suggests that the nanotubes facilitate the ease of movement of electrons within the 3D framework and the reduction of the polarization loss.

The scan rate-dependent study of the LMO-FeMg/ MWCNT composite is shown in Figure 12(b), where two broad oxidation peaks were observed that shift to higher voltage regions as the scan rate increases. The Ragone plot of peak current vs scan rate (inset) shows that the redox reaction taking place on the electrode surface is indeed a diffusion-controlled process in which Li-ions migrate between the electrode interface and electrolyte. MWCNTs facilitate the interaction with LMO-FeMg particles to form a 3D network that promotes lithium-ion transport. The charge/discharge redox reactions during the charge and discharge processes are represented in the following equations:



FIGURE 8: Mn 3s core level spectra and fit results for LMO, LMO-FeMg, and LMO-FeMg/MWCNT.



FIGURE 9: Mn 2p core level spectra (a) for LMO, LMO-FeMg, and LMO-FeMg/MWCNT and (b) the C 1s core level spectrum for LMO-FeMg/MWCNT.



FIGURE 10: (a) Cyclic voltammogram of LMO-FeMg at $1 \text{ mV} \cdot \text{s}^{-1}$ and (b) scan rate-dependent study peak current as a function of root of scan rate (inset).



FIGURE 11: Cyclic voltammogram of (a) LMO-FeMg/MWCNT at a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$ and (b) scan rate profile between 5 and 60 mV \cdot \text{s}^{-1} vs. and the peak current as a function of root scan rate (inset) in 1 M LiPF_{6} .

Charge reaction:

$$LiMn_{1.98}Fe_{0.01}Mg_{0.01}O_4 \longrightarrow Li_{1-x}Mn_{1.98}Fe_{0.01}Mg_{0.01}O_4 + xLi^+ + xe^-.$$
 (3)

Discharge reaction:

$$Li_{1-x}Mn_{1.98}Fe_{0.01}Mg_{0.01}O_4 + xLi^+ + xe^- \longrightarrow LiMn_{1.98}Fe_{0.01}Mg_{0.01}O_4.$$
(4)



FIGURE 12: EIS overlay of (a) LMO, (b) LMO-FeMg, and (c) LMO-FeMg/MWCNT with the corresponding impedance fitted data.

Additionally, it is widely known that the diffusion of Liions is the rate-determining step for Li-ion batteries [28]. Due to the combined synergistic effect of Fe and Mg, the composite offers increased Li⁺ ion diffusivity resulting from the increased oxygen vacancy as the path of Li⁺ ion and additional storage capacity, mainly due to the high theoretical volumetric capacity of metallic magnesium. A diffusion coefficient of 5.83×10^{-10} cm²·s⁻¹ was obtained for LMO-FeMg and 1.91×10^{-9} cm²·s⁻¹ for LMO-FeMg/MWCNT, by using the following equation, where I_p , n, A, D_{Li}^+ , and $v^{1/2}$ are the peak current, number of electrons, area of the electrode, diffusion coefficient, and scan rate, respectively.

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_{Li+} v^{1/2}.$$
 (5)

The diffusion coefficient of Li^+ in the LMO-FeMg/ MWCNT electrode is an order of magnitude larger than that in the LMO-FeMg electrode. This confirms the notion that carbon nanotubes not only reinforce the structural stability of the LMO cathode material to mitigate Mn dissolution but also improve its electrochemical properties [29].

Electrochemical impedance spectroscopy (EIS) was performed to investigate charge-transfer activity as well as interfacial properties of the electrodes. The EIS measurements were recorded at a potential of 3 V at a frequency range of 10^5 – 10^{-2} Hz [30]. The Nyquist plots of (a) LMO, (b) LMO-FeMg, and (c) LMO-FeMg/MWCNT are shown in Figure 12. The kinetic difference of the electrodes was extracted by modeling AC impedance spectra based on the Randles equivalent circuit shown in the inset of the spectrograph. Equivalent circuits consist of the Randles circuit, solution resistance, R_{sol} ; charge-transfer resistance, R_{ct} ; double-layer capacity, C_{dl} ; and reflective finite Warburg impedance, W. Each plot presents a single semicircle at high frequency that is well defined and an inclined line at low-frequency attributed to Warburg impedance related to Li+ diffusion in the bulk of electrode. The decreased impedance in the Fe- and Mg-doped materials as compared to pristine LMO correlates well with

the diffusion coefficient obtained from cyclic voltammetry. The LMO-FeMg/MWCNT displayed the lowest charge-transfer resistance resulting from catalysed redox kinetics within the composite framework. The data points of the semicircle at low-frequency regions give the intercept correlating with $R_s + R_{ct}$ from the R_{ct} values, which were extrapolated by subtracting the value of R_s [31].

The cycling performance of (i) LMO, (ii) LMO-FeMg, and (iii) LMO-FeMg/MWCNT after 100 cycles is shown in Figure 13(a). The pristine LMO displays a typical cyclic channel after 100 cycles with a significant capacity drop and capability retention of only 69%.

The specific capacitance (C_s) of cathode materials electrodes was calculated by using the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V},\tag{6}$$

where C_s (*F*/*g*) is the specific capacitance, *I*(*A*/*g*) stands for current density, *m* (g) is the coated mass of the active material, *V* is the total volume (cm³), and *s* stands for discharging time, **t**, respectively.

The LMO-FeMg material delivered an initial specific capacity of about 145 mAh·g⁻¹ with a moderate capacity fade after consecutive cycling. The improved cycling capacities of LMO-FeMg can be a result of dopant substitution of Mn within the spinel which significantly reduces Mn^{3+} disproportionation reactions as well as the J–T effects [32]. This is an interesting advancement, as it signifies the role of cations in improving the chemical interactions and charge diffusion. With the functionalization of the LMO-FeMg with MWCNT, the carbon composite cathode delivered an initial specific capacity of about 138 mAh·g⁻¹. However, the structure appears more stable displaying improved capacity retention over time.

The charge-discharge capabilities of LMO-FeMg/ MWCNT are shown in Figure 13(b). Two distinct voltage plateaus are observed at 4.0 and 3.2 V, which indicates the



FIGURE 13: (a) Cycling performance of (i) LMO, (ii) LMO-FeMg, and (iii) LMO-FeMg/MWCNT at 1C rate. Charge-discharge capacities of (b) LMO-FeMg/MWCNT after 1st, 50th, and 100th cycle/s at 2.4–4.0 V.



FIGURE 14: Cycling performance of LMO-FeMg/MWCNT at various c-rates.

Li-ion transitions taking place between λ -MnO₂ and LMO. The lithium ions were inserted into the tetrahedral sites at the 4 V plateau with 0 < $x \le 1$. The remaining lithium ions were inserted into the octahedral sites at the 3 V plateau with 0 < $x \le 2$. It is to be noted that cycles 50–100 have a specific discharge capacity of 100 mAh·g⁻¹. The 1st, 50th, and 100th cycles of LMO-FeMg/MWCNT show an initial dischargespecific capacity of 142 mAh·g⁻¹ with the 50th and 100th cycles in the vicinity of 120 mAh·g⁻¹, which can be attributed to the synergy between the composite materials.

The rate performance of the cathode materials was further analysed with the discharge capacity of LMO-FeMg and LMO-FeMg/MWCNT at c-rates ranging from 0.5 to 7 C after 30 cycles with 1C being taken as 100% discharge capacity as shown in Figure 14.

A relatively high discharge capacity between 140 and $145 \text{ mAh} \cdot \text{g}^{-1}$ was obtained at 0.5C for LMO-FeMg/ MWCNT. It can be seen that the discharge capacity of LMO-FeMg lessens slightly to $137 \text{ mAh} \cdot \text{g}^{-1}$ after 30 cycles. Both materials obtain a capacity retention of 97% at room temperature which indicates that the composite material is both durable and operable at high currents. The LMO-FeMg/MWCNT demonstrates good reversibility at varying c-rates as well as a reduction in capacity loss in comparison with the pristine LMO as the discharge capacity remains above 105 mAh·g⁻¹ even at 7C [33]. This capacity retention after deep current cycling is higher than that of LMO-FeMg which was about 140 mAh·g⁻¹ at 0.5C (inset). This implies that the network of carbon nanotubes and Fe and Mg cations enhances the capacity retention of the LMO spinel [34–36].

4. Conclusion

The novel LMO-FeMg and LMO-FeMg/MWCNT composite cathode materials were obtained via the sol-gel method and compared with one another as well as with the pristine LMO cathode material. The formation of the crystalline LMO-FeMg/ MWCNT composite and its physical and electrochemical properties were probed using microscopic and spectroscopic analyses. HRSEM analysis showed octahedrally shaped particles with an average diameter of 140 nm being well dispersed and reinforced within the LMO-FeMg/MWCNT framework. The modified cathode yielded favourable electrochemical results with diffusion coefficients of 1.91×10^{-9} cm² · s^{-1} and $5.83 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$. This improvement was also observed in the impedance studies where considerable R_{ct} reductions of 0.27Ω and 0.71Ω for LMO-FeMg and LMO-FeMg/MWCNT were obtained. The FeMg-doped LMO and FeMg/MWCNT within a coin cell setup outperformed that containing the pristine LMO material with specific capacities around $145 \text{ mAh} \cdot \text{g}^{-1}$ compared to about $107 \text{ mAh} \cdot \text{g}^{-1}$ for LMO. The composite cathode delivered enhanced electrontransfer kinetics due to the higher surface area and stability provided by the MWCNTs which also facilitates good dispersion of LMO-FeMg as observed by HRSEM. The good cycling performance of the LMO-FeMg/MWCNT cathode is attributed to the reduction of the polarization loss for this peculiar doped-cation-to-Mn ratio.

Data Availability

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

SW, TJ, and NR conceptualized the study. NR proposed the methodology. SW, DC, and EC investigated the study. NR wrote the original draft. SW and EC reviewed and edited the manuscript. NR, EC, and BPD edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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References

- [1] F. P. Nkosi, C. J. Jafta, M. Kebede, L. Le Roux, M. K. Mathe, and K. I. Ozoemena, "Microwave-assisted optimization of the manganese redox states for enhanced capacity and capacity retention of $LiAl_xMn_{2-x}O_4$ (x = 0 and 0.3) spinel materials," *RSC Advances*, vol. 5, no. 41, pp. 32256–32262, 2015.
- [2] X. Li, Y. Xu, and C. Wang, "Suppression of Jahn-Teller distortion of spinel LiMn2O4 cathode," *Journal of Alloys and Compounds*, vol. 479, no. 1-2, pp. 310–313, 2009.
- [3] F. Wen, C. Zhu, L. Li, G. Zeng, J. Duan, and Z. Chen, "Enhanced pseudocapacitive behaviors of Sb-based anodes for lithium ion batteries via dual modification approach of Fe

doping combined with double carbon coatings," *Journal of Alloys and Compounds*, vol. 889, Article ID 161658, 2021.

- [4] N. Ross, N. W. Hlongwa, C. O. Ikpo, M. M. Ndipingwi, P. G. L. Baker, and E. Iwuoha, "Iron-gold coated-LiMn_{2-X}O₄ nanowire high power cathode system probed by spectroscopic and microstructural analysis," *Journal of Nano Research*, vol. 44, pp. 10–20, 2016.
- [5] J. Billaud, D. Sheptyakov, S. Sallard et al., "Li/Fe substitution in Li-rich Ni, Co, Mn oxides for enhanced electrochemical performance as cathode materials," *Journal of Materials Chemistry A*, vol. 7, no. 25, pp. 15215–15224, 2019.
- [6] S.-N. Lee, D.-H. Park, J.-H. Kim et al., "Enhanced cycling performance of Fe-doped LiMn₂O₄ truncated octahedral cathodes for Li-ion batteries," *Chemelectrochem*, vol. 9, no. 11, 2022.
- [7] Y. Li, R. Huang, G. Pan, J. Yao, and Z. Zou, "High-tap-densityFedoped nickel hydroxide with enhanced lithium storage performance," ACS Omega, vol. 4, no. 4, pp. 7759–7765, 2019.
- [8] D. Mao, X. Tan, Z. Fan et al., "Unveiling the roles of trace Fe and F Co-doped into high-Ni Li-rich layered oxides in performance improvement," ACS Applied Materials and Interfaces, vol. 15, no. 8, pp. 10774–10784, 2023.
- [9] S. M. Abbas, A. M. Hashem, A. E. Abdel-Ghany et al., "Agmodified LiMn2O4 cathode for lithium-ion batteries: coating functionalization," *Energies*, vol. 13, no. 19, p. 5194, 2020.
- [10] H. Xiaa, Z. Luo, and J. Xie, "Nanostructured LiMn₂O₄ and their composites as high-performance cathodes for lithiumion batteries," *Progress in Natural Science: Materials International*, vol. 22, 2012.
- [11] W. Tang, Y. Hou, F. Wang, L. Liu, Y. Wu, and K. Zhu, "Li Mn_2O_4 nanotube as cathode material of second-level charge capability for aqueous rechargeable batteries," *Nano Letters*, vol. 13, no. 5, pp. 2036–2040, 2013.
- [12] Y. Yu, J. Guo, M. Xiang et al., "Enhancing the durable performance of LiMn2O4 at high-rate and elevated temperature by nickel-magnesium dual doping," *Scientific Reports*, vol. 9, no. 1, Article ID 16864, 2019.
- [13] L. Li, Y. Deng, K. Hu et al., "Nanostructure designing and hybridizing of high-capacity silicon-based anode for lithiumion batteries," *Progress in Natural Science: Materials International*, vol. 33, no. 1, pp. 16–36, 2023.
- [14] H. M. Zhou, Y. H. Zhu, J. Li, W. J. Sun, and Z. Z. Liu, "Electrochemical performance of Al2O3 pre-coated spinel LiMn2O4," *Rare Metals*, vol. 38, no. 2, pp. 128–135, 2019.
- [15] M. Lee, S. Lee, P. Oh, Y. Kim, and J. Cho, "High performance LiMn₂O₄ cathode materials grown with epitaxial layered nanostructure for Li-ion batteries," *Nano Letters*, vol. 14, no. 2, pp. 993–999, 2014.
- [16] S. Laha, S. Natarajan, J. Gopalakrishnan et al., "Oxygenparticipated electrochemistry of new lithium-rich layered oxides Li3MRuO5 (M=Mn, Fe)," *Physical Chemistry Chemical Physics*, vol. 17, no. 5, pp. 3749–3760, 2015.
- [17] T. Singh and A. Kumar, "Fluorescence behavior and specific interactions of an ionic liquid in ethylene glycol derivatives," *Journal of Physical Chemistry B*, vol. 112, no. 13, pp. 4079– 4086, 2008.
- [18] S. Willenberg and N. Ross, "Enhanced electrochemistry of carbon supported functionalized nanocomposite cathode for aqueous lithium-ion batteries," *Electroanalysis*, vol. 32, no. 12, pp. 2976–2981, 2020.
- [19] S. Pavithra, P. Sivaraj, P. Arjunan et al., "Surface modification and electrochemical performance of Al2O3 coated and Nidoped spinel LiMn2O4 for aqueous rechargeable battery applications," *Surface Engineering and Applied Electrochemistry*, vol. 56, no. 4, pp. 432–439, 2020.

- [20] J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurst, and V. Meunier, "Evaluating the characteristics of multiwall carbon nanotubes," *Carbon*, vol. 49, no. 8, pp. 2581–2602, 2011.
- [21] P. Mohanty, S. Chowdhury, R. J. Choudhary et al., "Structural and magnetic properties of $(Co_{1-x}Ni_x)$ Cr_2O_4 (x= 0.5, 0.25) nanoparticles," *AIP Advances*, vol. 8, 2018.
- [22] T. H. Dolla, D. G. Billing, C. Sheppard et al., "Mn substituted Mn_xZn_{1-x}Co₂O₄ oxides synthesized by co-precipitation; effect of doping on the structural, electronic and magnetic properties," *RSC Advances*, vol. 8, no. 70, pp. 39837–39848, 2018.
- [23] C. S. Fadley and D. A. Shirley, "Multiplet splitting of metalatom electron binding energies," *Physical Review A*, vol. 2, no. 4, 1970.
- [24] E. S. Ilton, J. E. Post, P. J. Heaney, F. T. Ling, and S. N. Kerisit, "XPS determination of Mn oxidation states in Mn (hydr)oxides," *Applied Surface Science*, vol. 366, pp. 475–485, 2016.
- [25] S. Willenberg, E. Carleschi, and N. Ross, "Spectroscopic and electrochemical exploration of carbon-infused intercalationtype spinel composite for aqueous systems," *Frontiers in Chemistry*, vol. 10, Article ID 890291, 2022.
- [26] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and R. S. Smart, "Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni," *Applied Surface Science*, vol. 257, no. 7, pp. 2717–2730, 2011.
- [27] G. Greczynski and L. Hultman, "Referencing to adventitious carbon in X-ray photoelectron spectroscopy: can differential charging explain C 1s peak shifts?" *Applied Surface Science*, vol. 606, Article ID 154855, 2022.
- [28] D. J. Morgan, "Comments on the XPS analysis of carbon materials," *Chimia*, vol. 7, no. 3, p. 51, 2021.
- [29] X. Sun and L. Zhang, "Outstanding Li-storage performance of LiFePO4@MWCNTs cathode material with 3D network structure for lithium-ion batteries," *Journal of Physics and Chemistry of Solids*, vol. 116, pp. 216–221, 2018.
- [30] N. Bensalah and N. Mustafa, "In situ generated MWCNT-FeF3·0.33 H2O nanocomposites toward stable performance cathode material for lithium ion batteries," *Emergent Mater*, vol. 2, no. 1, pp. 59–66, 2019.
- [31] C. Heubner, M. Schneider, and A. Michaelis, "Diffusionlimited C-rate: a fundamental principle quantifying the intrinsic limits of Li-ion batteries," *Advanced Energy Materials*, vol. 10, no. 2, 2020.
- [32] S. Sifuba, S. Willenberg, U. Feleni, N. Ross, and E. Iwuoha, "Electrochemical analysis of architecturally enhanced LiFe0.5Mn0.5PO4 multiwalled carbon nanotube composite," *Journal of Nanotechnology*, vol. 2021, Article ID 6532348, 8 pages, 2021.
- [33] Z. Yang, Y. Wang, X. Chen, H. Wu, and Y. Zhang, "Mg²⁺ and Ti⁴⁺ Co-doped spinel LiMn₂O₄ as lithium-ion battery cathode," *ChemistrySelect*, vol. 4, no. 33, pp. 9583–9589, 2019.
- [34] J. L. Wang, Z. H. Li, J. Yang et al., "Effect of Al-doping on the electrochemical properties of a three-dimensionally porous lithium manganese oxide for lithium-ion batteries," *Electrochemistry Acta*, vol. 75, pp. 115–122, 2012.
- [35] Y. Wu, Z. Wen, H. Feng, and J. Li, "Hollow porous LiMn₂O₄ microcubes as rechargeable lithium battery cathode with high electrochemical performance," *Small*, vol. 8, no. 6, pp. 858– 862, 2012.
- [36] A. Iqbal, Y. Iqbal, A. M. Khan, and S. Ahmed, "Effect of bication (Cu-Cr) substitution on the structure and electrochemical performance of LiMn 2 O 4 spinel cathodes at low and high current rates," *Journal of Saudi Chemical Society*, vol. 22, no. 4, pp. 449–458, 2018.