Doping and Surface Modification Enhance the Applicability of Nanostructured Fullerene–MWCNT Hybrid Draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 as High Efficient Cathode Material for Lithium-Ion Batteries

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Abstract
Development of high performance cathode materials, layer-structured ternary LiNi_{x}Co_{y}M_{1−x−y}O_2 cathode materials have attracted much attention owing to their larger capacity and higher energy density. Persistent efforts have been devoted to tackling certain issues like low electronic conductivity and poor structural stability. Dual strategy of Mg doping and surface modification of the cathode material was adopted to improve the performance of the battery. Fullerene–Multi-Walled Carbon Nanotube (MWCNT) hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 nanocomposite was synthesized by a simple chemical route. The fullerene–MWCNT hybrid modifies the surface of pristine LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 thereby improves the electrochemical performance and maintains the structural stability of the cathode material. Pristine LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT nanocomposite were studied using various advanced characterization techniques such as X-ray diffraction (XRD), Micro-Raman spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), X-ray Photoelectron Spectroscopy (XPS), and High-Resolution Transmission Electron Microscopy (HRTEM). It is found that LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 particles retain their structural integrity after being enveloped with a fullerene–MWCNT hybrid. The electrochemical performance was investigated with cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) test and electrochemical impedance spectroscopy (EIS). As prepared LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2, when deployed in the form of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT composite exhibits a high specific capacity of 208 mAh g⁻¹. Fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 nanocomposite provides an effective Li⁺ and electron channel that significantly increased the Li-ion diffusion coefficient and reduced the charge transfer resistance. Besides, the lithium diffusion coefficient increased from 5.13 × 10⁻¹³ (Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2) to 8.313 × 10⁻¹³ cm² s⁻¹ due to the improved kinetics of Li insertion/extraction process in Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + fullerene–MWCNT cell.

Keywords Lithium-ion · A layered cathode · Mg · Fullerene–MWCNT hybrid · Charge transfer resistance · Diffusion coefficient

1 Introduction
Lithium-ion batteries (LIBs) with transitional metal oxide as cathode materials recently play a significant role in energy storage systems for portable electronic devices [1]. There have been several investigations into ground-breaking novel nano-architectures to enhance the efficiency and lifetime of the LIB [2]. Various carbonaceous materials have been tested as electrodes for battery applications. However, to improve the electrochemical performance of layered cathode material, two strategies were often employed (i) partially replacing foreign atoms, such as Cr, Mg, Al, and F, in an attempt to improve structural stability and (ii) surface coating with a thin layer of metal oxide to suppress the lateral effects. In general, the incorporation of carbonaceous materials into transition metal oxide cathode materials to form a conductive network has become a favorable strategy for
achieving better cycling performance and rate capability [3]. Owing to their unique physicochemical properties, the nanocarbon materials with different geometrical orientations (e.g., graphene, carbon nanotubes (CNTs), and fullerenes) have gained a lot of applications in lithium-ion batteries as the carbon materials provide enough space for storing lithium ions. The excellent conductivity of the nano carbon material provides excellent lithium storage capacities and rate performances.

Carbon nanotubes are carbon allotropes with a cylindrical shape at the nanoscale level [4]. The structural, electrical, mechanical, and magnetic properties of CNTs, made it a possible candidate for industrial and large-scale applications [4, 5]. Exceedingly, CNTs have been employed as conductive nanostructured carbon matrices to boost the specific power, rate capability, and cycling stability of the cathode materials [3]. Other important features that make doped CNTs to be used in lithium-ion batteries are high chemical resistance and low flammability [2]. The electrochemically reversible penetration of Li-ions in SWCNTs and MWCNTs has been extensively studied. Lithium ions diffuse to stable sites on either the outer or the inner surface of a single layer of CNT graphene.

Among various strategies, the bandgap approach has led several research groups, and in particular, Koh et al. [6] reported that the new hybridized SWCNT/C$_{60}$ improves the passage of electrons to particle boundaries. Carbon-based materials are promising candidates for constructing 3D conductive networks, which boost active material utilization at high rates during the electrochemical reaction through electrical and ionic pathways [7]. Moreover, as reported in the literature the Li$_2$Mn$_{2.9}$Ni$_{0.9}$Co$_{0.2}$O$_8$-MWCNT exhibited remarkable interesting properties such as high specific capacity, sufficient rate performance, significant Coulombic efficiency, and improved cycling stability compared with pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ [8].

Tsuyohiko Fujigaya reported that among the inorganic and polymeric materials, single-walled carbon nanotubes (SWCNT) are particularly attractive in the thermoelectric conversion technology due to their non-toxicity, material abundance, solution processability and excellent electrical conductivity [9]. Papageorgiou stated that the two dimensional nature of graphene related materials display a larger surface to volume ratio, which leads to the formation of larger interfaces and production of stronger composites [10]. Samad et al. highlighted the unique characteristics of CNT such as (i) high surface area (1315 m$^2$ g$^{-1}$) (ii) less impurity (iii) high electrical conductivity (iv) free from deep crack and (v) high catalytic activity due to excellent interaction between catalytic metals and CNT supports, which makes CNT a best catalyst material for energy conversion fuel cell [11–13].

Zhang et al. reported that the carbon surface-treated C-LMNC electrode material for lithium-ion batteries exhibited better cyclic behaviour, lower irreversible capacity loss and acceptable rate discharge capacities [14].

Ma et al. showed that the graphene oxide-coated SnO$_2$-Li$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (GO-SnO$_2$-NCM) cathode material synthesized via a facile wet chemical method exhibited excellent cycling performance, with 91% capacity retention at 1C after 100 cycles, which was higher than 74% for the pristine NCM at the same cycle [15].

Our work broadens the scope of cathodic materials based on LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$. In fact, Zhang [16] have shown that the layered cathodic material like LiNi$_{0.65}$Mg$_{0.05}$Co$_{0.3}$O$_2$, synthesized by the sol–gel method delivered an initial discharge capacity of 178 mAh g$^{-1}$ due to fewer cations mixtures. Xiang et al. [17] stated that the Mg-doped LiNi$_{0.1}$Co$_{0.2}$O$_2$ electrode delivered an initial discharge capacity of 188 mAh g$^{-1}$ and retained good cycling behavior. Cho and Park [18] suggested that the LiNi$_{0.74}$Co$_{0.2}$Mg$_{0.06}$O$_2$ electrodes delivered a discharge capacity of 158 mAh g$^{-1}$ with improved thermal stability.

Therefore, the electrochemically inactive doping element Mg in LiNi$_{x}$Co$_{y}$O$_{z}$, elevates the capacity of the cathodic material and retains high structural stability. The stability of cathode materials is enhanced by the promotion of lithium-ion transport due to the increased lithium slab gap by the Mg effect [14]. In addition, Mg$^{2+}$ ions migrate to the interslab sites that were originally occupied by lithium ions, act as pillars, and sustain the delithiation structures, suppressing the cationic migration [19]. Many techniques have been explored to maintain the surface integrity of the cathode material, in which surface alteration is one of the simplest and most realistic methods that can effectively overwhelm the growth of solid electrolyte interphase level.

In this study, to explore the constructive outcomes such as improved cycling and electrochemical performance of the cathode material, LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cathode material was synthesized by self-sustaining combustion route and LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT nanocomposite was synthesized by a simple chemical route. The novelty of the work lies in the addition of nickel to a very small percentage of the composite cathode, with Mg as a dopant, and the incorporation of fullerene–MWCNT hybrid into the layered cathode material. The partial substitution of cobalt with magnesium had a positive effect, minimized cation mixing, and favored the formation of layered cathode structures.

To the best of our knowledge, the influence of fullerene–MWCNT hybrid modification on the characteristics of the LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ with a very low content of nickel has not been reported yet. In this regard, the current piece of work assumes significant importance, as one of the early works demonstrates that for the first time
the suitability of the fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ particles to construct a 3D conductive network.

The structural and electrochemical behavior studies of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocompositewere investigated and discussed in detail. In this work, the beneficial aspects of fullerene–MWCNT as a conductive additive in LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and the synergy between LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and fullerene–MWCNT hybrid materials are explored for their enhanced electrochemical properties.

2 Experimental

2.1 Preparation of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/Fullerene–MWCNT Nanocomposite

Fullerene–MWCNT powder (ground core, 7–12 nm OD, 0.5–10 μm long, Alfa Aesar) was used as a precursor. Figure 1 clearly explains the various processes involved in the synthesis of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT nanocomposite cathode material. Initially, 0.025 g of fullerene–MWCNT and 0.5 g of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanopowder were ground for 30 min in a mortar with a pestle. The blend was dispersed by ultra-sonication with 15 ml of ethanol. The solution was vigorously stirred for 4 h at 50 °C. Finally, the resultant mixture was dried overnight in an oven.
at 80 °C to obtain the fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} nanocomposite as reported earlier by Jan et al. [3].

2.2 Instruments Used for Structural Characterization

The structural properties were studied by X-ray diffractometer (XRD, Shimadzu XRD-6000) and the morphological properties of as-prepared samples were analyzed by field-emission scanning electron microscopy (FESEM, JSM-6700F 15 kV), and high-resolution transmission electron microscopy (HRTEM, JEOL 2010 200 kV). Micro-Raman scattering measurements were conducted using a DXR Raman Microscope (Thermo Fisher Scientific Inc.) and the source of excitation used was an argon-ion laser operating at 514 nm with a laser incident power of 0.3 mW. For quantitative chemical insights, the as-synthesized particles were characterized by X-ray photoelectron spectroscopy (XPS).

2.3 Fabrication of Electrode and Electrochemical Measurements

The synthesized LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}/fullerene–MWCNT composite material, acetylene black and polyvinylidene fluoride (PVDF) in the proportion of 80:10:10 in N-Methyl-2-Pyrrolidone (NMP) were added together and mixed thoroughly to obtain the slurry. The slurry was carefully coated onto an aluminium foil by the doctor-blade technique and dried at 70 °C to remove water content. The 2032-type coin cells with the coated material as cathode, lithium metal as an anode, and Celgard 2325 membrane as the separator were assembled. In a similar way, the 2032-type coin cells with LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} coated material as the cathode, lithium metal as an anode, and Celgard 2325 membrane as the separator were also assembled. The separator was wetted with the electrolyte 1M LiPF_{6} in EC: DEC; 1:1(v/v).

Between a potential window 2.5–4.5V, the cycling profile for the prepared coin cells was studied at room temperature. The voltammograms were analysed using the SP150 (Bio-logic) electrochemical impedance analyser at 0.1 mV s^{-1}. Electrochemical Impedance Spectroscopy (EIS) for coin cells was recorded between 200 kHz and 100 mHz frequency.

3 Results and Discussion

3.1 XRD Analysis

Figure 2 shows the XRD pattern of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}, fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}, and fullerene–MWCNT hybrid. From Fig. 2a and b, the R3m space group related patterns of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} and fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} nanocomposite were confirmed by the existence of diffraction peak at 2θ = 38° and 46°. A well-layered nanostructure was observed from the distinct splitting of 006/102 and 108/110 doublet peaks [20].

The XRD pattern of the fullerene–MWCNT hybrid, shown in Fig. 2c which displayed two peaks located at 2θ = 25.74° & 42.87° can be ascribed to the hexagonal graphite crystal planes of (002) and (001) respectively. Also, the XRD pattern of fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} nanocomposite does not reveal the diffraction peaks of graphene or graphite is likely due to the extremely crystalline phase of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} nanocomposite [5].

The physical mixing of fullerene–MWCNT hybrid in LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} has been reported to have an insignificant effect on the properties of MWCNTs relative to the covalent hybrid structure. The XRD results show that the surface modification with fullerene–MWCNT hybrid does not affect the crystal structure and preserves the structural stability of the electrode component.

3.2 FESEM Analysis

The surface morphology patterns of pristine LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}, fullerene–MWCNT hybrid, and fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} nanocomposite electrode were examined by FESEM as shown in Fig. 3 respectively. Incidentally, Fig. 3a shows the formation of cubic shaped like nanoparticles of pristine LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} which is also confirmed from the high-resolution TEM images as shown in Fig. 5a. The FESEM images as shown in Fig. 3b of fullerene–MWCNT hybrid show small spherical shaped like fullerene nanoparticles with an average particle size of 22 nm and MWCNT length of 1.06 µm as shown in histograms of particle size and MWCNT length distribution in Fig. 3c and d. The well-connected MWCNT conductive networks adhered to the surface nanocluster particles improved the electrochemical recombination effect of the cathodic ions [21].
in clusters were separated by the presence of fullerene and MWCNTs (Fig. 3e). The LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocubes accommodated into the holes of fullerenes are further wrapped by MWCNT as shown in Fig. 3f.

### 3.3 FTIR Analysis

The formation of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ was further confirmed by FT-IR analysis. Figure 4a shows the mode of vibrations of synthesized pristine layered nanostructure of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cathode material in the region between 500 and 1400 cm$^{-1}$. The peak at 1139 cm$^{-1}$ is common for all Co oxide anchored species. The peaks between 800 and 1050 cm$^{-1}$ are due to the stretching vibrations of terminal M=O and below 800 cm$^{-1}$ (734 cm$^{-1}$) is due to bridged M–O–M stretching vibration [22–24]. In the spectrum (Fig. 4b) of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$, the peaks at 556, 594 and 1120 cm$^{-1}$ could be related to the F$_{1u}$ mode of active vibrations of the fullerene regime [25]. The FTIR analysis confirms the presence of fullerene–MWCNT hybrid in the synthesized composite of cathode material.

### 3.4 HRTEM Analysis

The microstructure of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT hybrid nanocomposite were investigated by high-resolution TEM (HRTEM). Figure 5a shows that pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ presented a nanocube like structure arranged one over the other. Figure 5b represents the HRTEM image of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite which shows that individual LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocubes are well dispersed, bonded with the spherical fullerenes, and enveloped by the transparent backbones of MWCNTs. The LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ particles were separated by the multi-walled carbon nanotubes and thereby agglomeration of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ particles was barred. During the composite formation, MWCNTs were broken and they infringe into the particles of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$. The
Fig. 3 FESEM images of a LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}, b fullerene–MWCNT hybrid c Histogram of the particle size distribution in fullerene–MWCNT hybrid d Histogram of the MWCNT length distribution in fullerene–MWCNT hybrid e, f fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} at different dimensions
broken ends of the nanotubes are extruded but not totally isolated from the composites of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and are still connected with the composites. Such findings confirm that the MWCNTs are well embedded into the fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite. In addition, the micro-Raman shows that the composite forms a dense covering layer showing defects on the walls and edges of the carbon nanotubes [26]. Figure 5c and d shows histogram plots of length and diameter distribution of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite. From the histogram plots Fig. 5c it was noted that the MWCNTs have an average length of 266 nm with an average MWCNT diameter of 6.5 nm as shown in Fig. 5d in the composite. The histogram plot in Fig. 5e had recorded an average particle size of 12 nm.

The well-defined diffraction spots from the selected area electron diffraction pattern (SAED) as shown in Fig. 5f confirm the crystalline nature of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite. From SAED, the observed interplanar spacing \( d \) is about 0.465 nm for fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite which matches quite well with the \( d \)-spacing of (003) planes as reported in XRD Sect. 3.1.

From the data, it can be argued that high-resolution transmission electron microscopy images of the pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanoparticles, shown in Fig. 5g reveal the crystalline nature of the mixtures. The \( d \)-spacing of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanoparticle (0.471 nm) obtained from the HRTEM image exactly matched with the most intense lines of (003) plane from the X-ray diffraction pattern as reported in Sect. 3.1.

The HRTEM image of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ nanocomposite shown in Fig. 5h discloses well-defined lattice fringes with a separation of 0.471 nm corresponding to (003) plane of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and another separation of 0.344 nm corresponding to the graphitic crystalline planes of (002) respectively.

Minimizing the particle size to about 12 nm effectively decreases the length of the diffusion path of the charging species and favors high rate capability [27].

### 3.5 Micro-Raman Spectral Analysis

Micro-Raman spectra of pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$, fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and fullerene–MWCNT hybrid are shown in Fig. 6. According to the theoretical factor-group study, there are two Raman active modes of \( E_g \) and \( A_{1g} \) for the layered metal oxides with the \( R3m \) as a space group [28]. The LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ Raman spectrum (Fig. 6a) shows bands of \( E_g \) and \( A_{1g} \) at 540.78 cm$^{-1}$ and 649.63 cm$^{-1}$.

In the Raman spectrum of the fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ composite shown in Fig. 6b, aside from the two Raman bands assigned to the pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$, all the characteristic bands of the fullerene–MWCNT hybrid were retained without any shift. This shows the intercalative mode of interaction between pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ powders and the hybrid.

Slight downshifts in the intensity of \( E_g \) and \( A_{1g} \) bands (489.36 cm$^{-1}$ and 587.44 cm$^{-1}$) were observed for the composite when compared to the bands of pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ in Fig. 6a. This is due to the conformational changes that occurred within LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ during composite formation.

The Raman spectrum of fullerene–MWCNT hybrid as shown in Fig. 6c displayed a strong G band at 1574.33 cm$^{-1}$ which arises from the tangential C–C bond stretching with sp$^2$ hybridized carbon atoms in an ordered graphitic structure and corresponds to a splitting of the \( E_g \) stretching mode of crystalline graphite. A weak D band at 1349.41 cm$^{-1}$ arises due to the disorder-induced in sp$^2$-bonded carbon. The intensity of the D-band corresponds to the open-ended sp$^2$ hybridized carbon atoms, associated with the measurement of disorders in the C–C bonds [29]. A 2D band at 2696.51 cm$^{-1}$ is the characteristic band of graphene. This observation again confirms the non-covalent interaction of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ with fullerene–MWCNT hybrid [29].
Fig. 5 HRTEM images of a LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ b Fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ c, d Histogram of MWCNT length and diameter distribution in fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ e Histogram of the particle size distribution in the composite and f SAED of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ g, h Lattice fringes of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$
3.6 X-Ray Photoelectron Spectra Analysis

To gain further insight into the oxidation state of metal elements in pristine LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2, X-ray Photoelectron Spectroscopy (XPS) measurement was performed as shown in Fig. 7. The Li 1s spectrum in Fig. 7a consists of two peaks at 68 and 59 eV assigned to Li^+ ions of the lamellar oxide. The O 1s spectrum as shown in Fig. 7b consists of two peaks at 531 eV and another at 529 eV. The peak of the Mg 2s spectrum as shown in Fig. 7c is seen at 87 eV. The Ni 2p spectrum in Fig. 7d reveals two main core peaks of Ni 2p at 854 eV (Ni 2p^{3/2}) and 871 eV (Ni 2p^{1/2}) with an associated satellite peak at 861 eV (Ni 2p^{1/2}) [30]. The Co 2p core peaks of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT composite are shown in Fig. 7e. The spectrum splits into two parts (Co 2p^{3/2} and Co 2p^{1/2}) due to spin–orbit coupling, with an intensity ratio of 2:1. The main peak of Co 2p^{3/2} for LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene-doped MWCNT composite is positioned at 780 and 778 eV respectively [30]. The Co 2p^{1/2} components are located at 795 eV and 793 eV for LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT composite respectively.

The shift towards lower binding energy indicates the Co^{2+} oxidation state. The observed C 1s peak at 283 eV in the LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT composite in Fig. 7f mainly represents graphitic carbon [30]. As reported in the literature [15] the modification of NCM with graphene oxide can lead to the transition metals changing their oxidation states and issue in low discharge capacity and poor cycling performance. In this work, the observed XPS peaks of fullerene–MWCNT hybrid draped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 nanocomposite are almost identical with those of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2, which indicates that the incorporation of fullerene–MWCNT hybrid did not affect the oxidation state of the elements by which the cathode material maintains its structural stability. This is confirmed by the high discharge capacity and good cycling performance of Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + fullerene–MWCNT cell.

3.7 Cyclic Voltammetry of Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + Fullerene–MWCNT Cells

Cyclic Voltammetry (CV) curves of pristine Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2/fullerene–MWCNT composite cells containing 1 M LiPF_6 in EC:DEC:1:1(v/v) measured between the potential range of 2.3 V and 4.5 V at a scan rate of 0.1 mV/s for the initial three cycles are shown in Fig. 8.

The CV curves for pristine Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 and Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + fullerene–MWCNT composite
The electrodes show a pair of well-defined redox peaks and exhibit excellent electrochemical activity with a completely reversible process. A slightly broad oxidation and reduction peaks occurred at 4.12 V and 3.75 V for Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 cell (Fig. 8a), whereas for Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + fullerene–MWCNT cell (Fig. 9b) the oxidation and reduction peaks occurred at 4.01 V and 3.82 V respectively corresponding to the Ni^{2+}/Ni^{4+} redox couple.

The polarization potential for the redox couple of Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 + fullerene–MWCNT composite cell was found to be 0.19 V which is very much lesser than 0.37 V of Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 cell. With the addition of the fullerene–MWCNT hybrid, the electrode polarization of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_2 has been significantly reduced resulting in an excellent electrochemical reversible process [3].
Fig. 8 Cyclic voltammograms of a Li/LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and b Li/LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ + fullerene–MWCNT composite cells containing 1 M LiPF$_6$ in EC:DEC:1:1(v/v).

Fig. 9 a Cycling profile of Li/LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cell containing 1 M LiPF$_6$ in EC:DEC:1:1(v/v) at 0.1C. b Specific capacity Vs cycle number of Li/LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cell. c Cycling profile of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT cell containing 1 M LiPF$_6$ in EC:DEC:1:1(v/v) at 0.1C at 0.1C, Inset is the 20th, 40th, 60th, 80th, and 100th cycling profile and d Specific capacity Vs cycle number of Li/LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ + fullerene–MWCNT cell.
The charge/discharge study was carried out for the assembled Li/LiNi0.1Mg0.1Co0.8O2 and Li/LiNi0.1Mg0.1Co0.8O2 + Fullerene–MWCNT cell. Figure 9a shows the typical galvanostatic charge–discharge cycling profile of Mg-doped Li/LiNi0.1Mg0.1Co0.8O2 cell containing 1 M LiPF6 in EC:DEC; 1:1 (v/v) at 0.1 C rate maintained at room temperature. A discharge capacity of 195 mAh g−1 and a charging capacity of 199 mAh g−1 at its first cycle attaining 98% of its coulombic efficiency were seen with a reduction of discharge capacity to 186 mAh g−1 at its fifth cycle resulting in a fade-in capacity of 1.8 mAh g−1 per cycle.

The rate capability of Mg-doped Li/LiNi0.1Mg0.1Co0.8O2 cell at different C-rates is shown in Fig. 9b. For the 0.2 C rate, the cell delivered a discharge capacity of 181 mAh g−1 with a charging capacity 173 mAh g−1 with 95% of coulombic efficiency. At higher C-rates the discharge capacity reduced to 152 mAh g−1 at 1 C and 147 mAh g−1 at 2 C. The discharge capacity decreased with an increase in the C-rate.

The typical galvanostatic charge/discharge cycling profile of Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell at 0.1 C rate between 2.5 and 4.5 V is depicted in Fig. 9c. The cell was found to deliver a discharge capacity of 208 mAh g−1 with a charging capacity of 211 mAh g−1 during its first cycle with 99% of Coulombic efficiency, with a decrease of the discharge capacity to 202 mAh g−1 at its 5th cycle with a fade in the capacity of 1.2 mAh g−1 per cycle. The rate capability of Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell investigated at 0.1C, 0.2C, 1C, and 2C rates as shown in Fig. 9d. It is worth pointing out that the Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell exhibited high discharge capacity and also less fade in capacity than pristine Li/LiNi0.1Mg0.1Co0.8O2.

Ma et al. reported that the nanocomposite graphene oxide- coated -SnO2-NCM electrode for lithium-ion batteries synthesised by wet chemical method delivered a discharge capacity of 197 mAh g−1 [15]. Tang et al. stated that the high power cathode LiNi0.1Mn1.5O4 nanorods wrapped with graphene nanosheets for lithium-ion batteries delivered an increased discharge capacity, facilitating the transfer of lithium ions across the active material/electrolyte interface, as well as the transfer of electrons from the current collector to the active material. This unique Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell provides a shorter lithium-ion diffusion path and good electronic conductivity, resulting in the demonstration of excellent electrochemical properties.

In addition, the factors that may have contributed to the superior electrochemical performance of the fullerene–MWCNT hybrid draped LiNi0.1Mg0.1Co0.8O2 nanocomposite electrode are improvement in the structural stability, a decrease in the disorder of metal ions in the lattice, suppression of the dissolution of transition-metal ions, and phase transitions, removal of HF from the electrolyte solution, and a reduced amount of heat production during charge–discharge processes. Also, the improved electrochemical performance of the fullerene–MWCNT hybrid draped LiNi0.1Mg0.1Co0.8O2 nanocomposite was attributed to an increase in the grain connectivity and high electronic conductivity. The good elasticity between the graphene layers of MWCNT can buffer the volume changes of the oxide materials, inhibit the agglomeration between the oxides and the powdered electrode materials, and obviously improve the cycling performance of the electrode materials.

3.9 Impedance Spectroscopy of Li/LiNi0.1Mg0.1Co0.8O2 and Li/LiNi0.1Mg0.1Co0.8O2 + Fullerene–MWCNT Cells

Electrochemical impedance spectroscopy analysis further confirms the beneficial effect of the integrated fullerene–MWCNT hybrid in enhancing the electrochemical efficiency of the Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell relative to that of the pristine Li/LiNi0.1Mg0.1Co0.8O2 cell.

Figure 10a shows the Nyquist plot of the Li/LiNi0.1Mg0.1Co0.8O2 and Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell recorded between 200 kHz and 100 mHz. The semicircle observed at the high-frequency area correlates with the mobility of lithium ions across the surface film [33]. The leaning line was a clear indicator of the Warburg behaviour and was observed at the low-frequency side owing to the process of Li+ ions diffusion through the synthesized cathode materials. The Li/LiNi0.1Mg0.1Co0.8O2 + fullerene–MWCNT cell recorded a lower Rct value of 40.4Ω when compared with LiNi0.1Mg0.1Co0.8O2 (Rct = 55.03Ω), suggesting that the presence of fullerene–MWCNT hybrid facilitates the Li-ion diffusion process in LiNi0.1Mg0.1Co0.8O2. The Warburg factor σ was calculated from the impedance spectra using Eq. (1).
in which $\omega$, $R_s$, and $R_{ct}$ represent the angular frequency, solution resistance, and charge transfer resistance respectively [34]. The Lithium diffusion coefficient $D$ was calculated using Eq. (2) in which the parameters $R$, $A$, $T$, $F$, $C$, $\sigma$ and $n$ represent the universal gas constant, the surface area of the as-prepared cathode, absolute temperature, Faraday constant, lithium-ion concentration, Warburg factor, and the number of electrons/molecule in oxidation process respectively [35]. The Warburg factor was calculated from the graphical plot between $Z'$ and $\omega^{-1/2}$ as shown in Fig. 10b. Using the calculated value of the Warburg factor $\sigma$, lithium diffusion coefficients were determined and tabulated in Table 1. Using Eq. (3) exchange current density $I_0$ was calculated [34]

$$I_0 = \frac{RT}{nF}$$

The lithium diffusion coefficient increased from $5.13 \times 10^{-13}$ to $8.31 \times 10^{-13}$ cm$^2$ s$^{-1}$ due to the surface modification of pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ by fullerene–MWCNT hybrid. Also, the exchange current density increased from 42.74 mA g$^{-1}$ for pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ to 58.22 mA g$^{-1}$, due to the improved kinetics of the Li insertion/extraction process for the LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT composite.

The EIS results suggest that incorporation of fullerene–MWCNT hybrid in LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cathode material decreases the charge transfer resistance more effectively than pristine LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$. The unique nanostructured fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ composite material was found to greatly improve the storage capacity of lithium ions and the cycle stability of the battery. The electrochemical properties of fullerene–MWCNT hybrid draped LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ composite are closely related to their structures. The edges and defects present in graphene layers provide enough space for storing lithium ions. The excellent conductivity of graphene provides its composites with excellent lithium storage capacities and enhanced electrochemical performances.

Enhanced charge transfer is attributed to the fullerene–MWCNT hybrid network, decorating the surface of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cathode material. The inclusion of fullerene–MWCNT hybrid in the layered LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ cathodic material demonstrates a good reversibility cycle, enhanced charge transfer kinetics, improved lithium-ion diffusion at lithiation and delithiation, and good structural stability of the layered cathode material for lithium-ion batteries.

![Nyquist plots of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT cell and plot between $Z'$ and $\omega^{-1/2}$ for LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT cell](image)

**Table 1** Calculated values of Warburg factor, lithium diffusion coefficient, and exchange current density of LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ and LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT

| System | $\sigma$ (Ωs$^{1/2}$) | $D$ (cm$^2$ s$^{-1}$) | $I_0$ (mA g$^{-1}$) |
|--------|----------------------|----------------------|---------------------|
| LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$ | 43.35 | $5.13 \times 10^{-13}$ | 42.74 |
| LiNi$_{0.1}$Mg$_{0.1}$Co$_{0.8}$O$_2$/fullerene–MWCNT | 34.09 | $8.31 \times 10^{-13}$ | 58.22 |

$Z' = R_s + R_{ct} + \sigma \omega^{-1/2}$

(1)

in which $\omega$, $R_s$, and $R_{ct}$ represent the angular frequency, solution resistance, and charge transfer resistance respectively [34].
4 Conclusion

We have synthesized successfully a novel nanocomposite material by interweaving the layered LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} within the fullerene–MWCNT hybrid matrix using a simple chemical route. Promising results were obtained by modifying the cathode with a fullerene–MWCNT hybrid. Layerstructured LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}/fullerene–MWCNT composite cathode material with good hexagonal ordering was evident from XRD and Raman studies. The FESEM images of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}/fullerene–MWCNT composite shows the cubical shaped LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} particles embedded with the transparent MWCNT which enhanced the electrochemical properties of the cathode. The existence of strong bonding between MWCNTs and LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} composite was evident from HRTEM which revealed the well-dispersed nature of LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} particles, bound onto the spherical fullerene molecules, and enwrapped by the transparent MWCNT. Facilitated by the interconnecting and conductive fullerene–MWCNT hybrid network, this newly designed nanocomposite material offers a significantly larger initial discharge capacity of 208 mAh g⁻¹ with good cycling stability and stable electrochemical reversibility. As fullerene–MWCNT hybrid improves the particle–particle connectivity, it constructs an efficient Li-ion and electron channel, which significantly enhances the Li-ion diffusion rate and reduces the charge transfer resistance. The Rct value of the Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}+fullerene–MWCNT cell (40.4Ω) is much lower than that of the pristine Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} cell (55.03Ω). Also, an increased lithium diffusion coefficient from 9.98 × 10⁻¹⁴ cm² s⁻¹ to 8.31 × 10⁻¹³ cm² s⁻¹ was evident for the Li/LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2}+fullerene–MWCNT cell. The promising results of our study with an emphasis on doping and surface modification highlighted that the synergistic effect that occurs between LiNi_{0.1}Mg_{0.1}Co_{0.8}O_{2} and fullerene–MWCNT hybrid, pave way for the substantial improvement in the electrode performance in high capacity lithium batteries.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this research paper.

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