



Influence of graphene wrapped-cerium oxide coating on spherical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles as cathode in high-voltage lithium-ion batteries



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ABSTRACT

Cobalt-free $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Lithium Nickel Manganese Oxide; LNMO) has garnered considerable interest as a cathode material due to its high working voltage, lower cost, and environmental friendliness. However, LNMO cathodes currently exhibit low cyclability and capacity deterioration, severely restricting their use on a broader scale. To this end, microwave-assisted chemical co-precipitation was used to produce spherical aggregated nanoparticles of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) coated with CeO_2 (LNMO-Ce) and wrapped in graphene (LNMO-Ce-GO). Structural analysis demonstrates that the ceria coating along with the graphene wrapping prevents unwanted phases from forming and altering the morphology of the LNMO microspheres. LNMO-Ce-GO exhibits a discharge capacity of 132.4 mAhg^{-1} at the C/10 rate with a capacity retention of 95.3 % after 100 cycles, compared to LNMO-Ce and bare LNMO samples that provide a capacity retention of 91.6 % and 84.7 % respectively. DSC analysis elucidate that the ceria coating helps to suppress the adverse reactions at the electrode/electrolyte interface and reduce the Mn^{3+} dissolution due to the Jahn Teller effect, increasing cell cyclability. The graphene wrapping reduces material aggregation and provides conductive pathways that significantly improve the electrochemical performance of the LNMO cathode. This innovative material design strategy can be efficiently expanded to other classes of lithium-ion battery cathode materials to enhance their electrochemical performance.

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1. Introduction

After 40 years of intensive research on lithium-ion batteries (LIBs), a sizable portion of the market for LIB cathodes is, even now, dominated by the first-generation active material LiCoO_2 [1]. Since major carmakers have announced plans for converting a substantial portion of their traditional fuel powered fleets into electric vehicles, there has been a resultant rise in awareness of the need for more sustainable and ecologically friendly cell production [2]. Indeed, given the vast number of cells necessary to accomplish this goal, enhancing LIBs sustainability is just as critical as increasing their energy density, cycle life, and safety [3]. One key objective in this direction is the decrease or, preferably, total substitution of toxic, expensive, and scarce cobalt. The gradual removal of cobalt from

$\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) and $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA); with $x + y + z = 1$, is progressing towards the cobalt deficient LiNiO_2 . Despite its extremely favorable electrochemical characteristics, LiNiO_2 is currently limited by thermal and mechanical instability, a difficult synthesis process, and the requirement for handling in an inert or dry atmosphere [4]. Less problematic, but also cobalt-free, the high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), which has a de-lithiation potential of around 4.7 V; corresponding to the redox potentials of $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$, provides a 20 % increase in energy density (700 Whkg^{-1}) compared to LiCoO_2 [5]. Structurally, spinel LNMO can be synthesized in two different cubic variations according to the metal-ions (Ni, Mn) ordering at the octahedral sites within the structure. The ordered P-type (P4₃32) LNMO contains Ni at the 4b sites and Mn at the 12d sites, while the disordered F-type (Fd3m) cubic structure contains Ni and Mn randomly distributed at the 16d sites [6]. During cycling, the disordered structure undergoes a single-phase transition whereas the ordered crystal structure requires a two-step phase transition. The lithium-ion availability and the vacancy between the two phases dictate the rate of the two-step transition in an ordered

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crystal structure. At lower current rates the lithium-ions have enough time to de-intercalate from the ordered structure providing good cyclability, however, at higher rates this two-step phase transition cannot be accomplished in time, this results in poor rate capability of the ordered structure compared to the disordered structure [7].

Moreover, during synthesis at a lower annealing temperature of less than 700 °C; the Ni/Mn ordering occurs at two distinct octahedral sites within the ordered structure, resulting in the favorable formation of Mn^{4+} ions through oxidation of the Mn^{3+} ions [8]. The disordered spinel, on the other hand, provides approximately twice the electronic conductivity compared to the ordered spinel due to the existence of Ni/Mn disordering and presence of Mn^{3+} ions [9]. However, the Mn^{3+} ions easily transform into Mn^{2+} ions via a disproportionation reaction – Jahn-Teller distortion, curtailing electrochemical performance [10]. Additionally, these Mn^{2+} ions diffuse into the electrolyte and collect on the anode surface. As a result of this buildup, the cell's impedance increases, causing the capacity to deteriorate. This phenomenon is exacerbated at elevated temperatures and high potentials. Hence, the presence of Mn^{3+} ions can reduce a cell's cycling and storage life, even when the disordered spinel's electrical conductivity is sufficiently more compared to the ordered spinel. Typically, disordering of Ni/Mn may be generated by regulating the amount of Mn^{3+} ions produced by oxygen loss at temperatures over 700 °C or by extended quenching. However, the oxygen loss causes oxygen vacancies in the crystal and results in formation of rock-salt phase. The rock-salt phase has low lithium-ion intercalation/de-intercalation rate and contributes to further capacity loss [11,12]. Another issue with LNMO is the cathode's incompatibility with the electrolyte. Carbonate compounds in the electrolyte breakdown at the LNMO working voltage (4.7 V), producing fumes and decomposition products [13]. These electrically insulating compounds reform on the surface of the cathode, forming a solid-electrolyte interface (SEI) that prevents lithium-ion transfer from the crystal. Furthermore, due to trace amounts of moisture, hydrogen fluoride (HF) may be generated, further etching the cathode surface, and exacerbating Mn dissolution [14]. The constant breakdown and rebuilding of the SEI layer promote polarization, which has a negative impact on the electrochemical performance of the cell. Furthermore, gas production may induce electrode degradation, exposing greater surface area for SEI development. A combination of these methods can result in increased polarization, significant capacity decline, and cell failure [15].

Numerous strategies for overcoming the limitations associated with the LNMO spinel have been documented throughout the years. At higher voltages, the electrode's integrity can be significantly increased by the use of improved electrolytes [16,17], ionic doping of the LNMO crystal [18–21], developing nanostructured LNMO [22,23], utilizing electrolytic additives or different solvents [17,24–27] and coating the bare LNMO particles with protective coatings [15,28,29]. A surface coating applied to cathode materials can operate as a barrier, preventing direct contact between the cathode and the electrolyte. Coatings can suppress phase transitions and, as a result, decreasing Ni/Mn disorder inside the lattice. Additionally, coatings can inhibit metal ion dissolution and improve HF scavenging from electrolytic solution. Numerous research groups have utilized a variety of coating materials, including metal oxides [29], conductive coatings [13], polymers [30], and carbon coatings [31] that can enhance the performance of LNMO. Rare-earth metal oxides have superior electrochemical properties and are more electrically stable than the host ionic species, facilitating the migration of electrical and ionic species. It is stated that CeO_2 is an electrochemically active and feasible coating material for LNMO, providing rapid transformation between Ce^{3+} to Ce^{4+} [32–34]. Previous reports state the improvement in cyclic performance due to the use of ceria coating

over $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $LiCoO_2$, $LiFePO_4$, $Li_4Ti_5O_{12}$ and other Lithium rich cathodes [32,35–39]. However, the coating methods employed for accomplishing the ceria coating provide difficulty in controlling the homogeneity of the coating layer [40,41]. Moreover, metal oxide coatings lend extra resistance to the mobility of ions and electrons and lower the rate capability of LNMO [42]. Hence, due to graphene's exceptional electrical characteristics, stable chemical properties, and large surface area, it has been keenly investigated for energy storage applications [43]. Graphene and Graphene oxide have been stated to enhance the cyclability and rate performance of spinel LNMO, $LiCo_{0.1}Ni_{0.8}Mn_{0.1}O_2$, $LiFePO_4$ and $LiMn_2O_4$ by enhancing the conductivity and decreasing the charge transfer resistance [44–50]. Graphene is usually dispersed or wrapped around the cathode particles instead of being coated on the surface, due to its hydrophobic nature. Hence, Graphene oxide is often utilized as a coating precursor as it attaches easily to the cathode surface owing to the oxygen-containing groups that it possesses [51]. However, the electronic conductivity of graphene oxide is lower compared to graphene, so a calcination process is often utilized that reduces the graphene oxide into graphene sheets and enables efficient coverage of the cathode material [42,52].

Careful control of reaction parameters is required to obtain LNMO spinel with increased metal-ion disorder and resultantly enhanced electrochemical performance. LNMO particles of various structure and sizes have been prepared by common processes like sol-gel, hydrothermal, solid-state, Atomic Layer deposition, microwave-assisted process etc. [33,53–55]. For manufacturing LIB active materials, coprecipitation has been documented extensively in the literature for its simplicity, flexibility, uniform mixing, and control over particle shape. Co-precipitation is commonly used to synthesize nanoparticles due to its straightforward morphological control and low-cost raw materials [56]. However, nanoparticles decrease the tap density of the cathode because they provide a large surface area. Therefore, it is required to develop an approach that can be utilized to synthesize LNMO secondary microspheres that contain primary nanoparticles, without the formation of secondary phases. Such an approach would enable the realization of enhanced electrochemical performance along with a high volumetric specific energy. Furthermore, microwave heating is an efficient method for preparing $LiNi_{0.5}Mn_{1.5}O_4$ that can save time and energy. Other cathode materials ($LiMn_2O_4$, Li_2FeSiO_4 , and $LiFePO_4$) have been developed utilizing microwave-assisted methods [57–60]. Microwave irradiation is critical for grain development in microwave-assisted processes. During the heat treatment process, microwave sintering has been reported to enhance the crystal structure and thus boosts the capacity of the spinel LNMO [61,62].

Using existing metal oxide coatings, graphene coatings, and microwave sintering techniques, this work proposes a unique way for synthesizing Ceria (CeO_2) coated LNMO microspheres that are wrapped with graphene. The required cathode material, $LiNi_{0.5}Mn_{1.5}O_4$, is generated using a combination of microwave irradiation and chemical precipitation. The ceria coating over the secondary microspheres of LNMO is also realized by utilizing coprecipitation technique, succeeded by a simple hydrothermal method for achieving the graphene wrapping. While several spinel structures have been synthesized using microwave assisted processes, to the authors' knowledge, CeO_2 -coated $LiNi_{0.5}Mn_{1.5}O_4$ microspheres covered in graphene have not been previously disclosed. The significant increase in cyclic stability suggests that the proposed synthesis approach and subsequent design are an effective method of improving the electrochemical performance of LNMO as a cathode material. The material architecture is meant to minimize parasitic interactions between the cathode and the electrolyte, hence increasing cyclability. The approach of material development described herein may be successfully applied to different families of cathode materials.

2. Materials and methods

2.1. Material synthesis

2.1.1. Synthesis of spherical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

For the pristine LNMO synthesis a co-precipitation technique is utilized as exhibited in Fig. 1(a). Stoichiometric amounts of precursors $\text{NiSO}_4 \cdot (\text{H}_2\text{O})_6$ (Nickel Sulfate Hexahydrate; purity > 98 %, Carl Roth GmbH + Co. KG, Germany) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Manganese (II) sulfate monohydrate; AnalaR NORMAPUR ACS/Reagent, VWR Chemicals, USA) are prepared in an aqueous solution (500 mL of de-ionized water) in a continuous stirred tank reactor. Na_2CO_3 (Sodium carbonate; purity > 99.5 %, ACS reagent, Sigma-Aldrich, USA) solution is added dropwise as a reagent to initiate the precipitation reaction; a pH of 8 is maintained to ensure an alkaline environment. The Na_2CO_3 solution to the metal ion ratio will be kept as 2:1; the temperature of the reaction is kept constant at 80 °C for 2 h while holding the pH steady by utilizing ammonia solution (35 % (W/W) pure assay, Honeywell Riedel-de Haen, Germany); which also behaves like a chelating agent. Afterwards, the solution is vacuum filtered, and the resulting precipitate (Spherical $(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{CO}_3$) is stored in a vacuum oven at 120 °C. The resulting $(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{CO}_3$ is ground using a mortar and pestle; calcinated in a microwave furnace (VBCC HYTHERM, VBCC/MF/14/15) at 550 °C for 15 min at the rate of

10 °C/min, to convert the carbonate into oxide. Subsequently, a 5 % excess stoichiometric amount of lithium carbonate (Li_2CO_3 ; purity > 99 %, Honeywell Fluka, USA) is added, for lithiation, to the sample by grinding them together using a mortar and pestle. The resulting sample is then be sintered at 850 °C at 10 °C.min⁻¹ for 30 min in a microwave furnace, followed by annealing to 700 °C at the rate of 10 °C.min⁻¹ for 15 min to obtain phase pure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, this sample is labelled as LNMO.

2.1.2. Formulation of ceria (CeO_2) coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Microwave assisted co-precipitation technique was also utilized for preparing LNMO coated with a 1 wt. % cerium oxide layer (CeO_2). 0.05 g of cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; purity > 99 % trace metals basis, Sigma-Aldrich, USA) was added to 100 mL of de-ionized water and made into a solution. Next, 2 g of solid pristine LNMO was added into the solution and heated at 60 °C in a continuous stirred tank reactor; with the pH maintained at 6. Subsequently, 0.0369 g of Na_2CO_3 solution is prepared in 50 mL de-ionized water and added dropwise as a reagent to initiate the precipitation reaction. The resulting precipitate is vacuum filtered and sintered at 500 °C for 15 min in a microwave furnace to obtain cerium-oxide coated LNMO labelled as LNMO-Ce, as illustrated in Fig. 1(b).

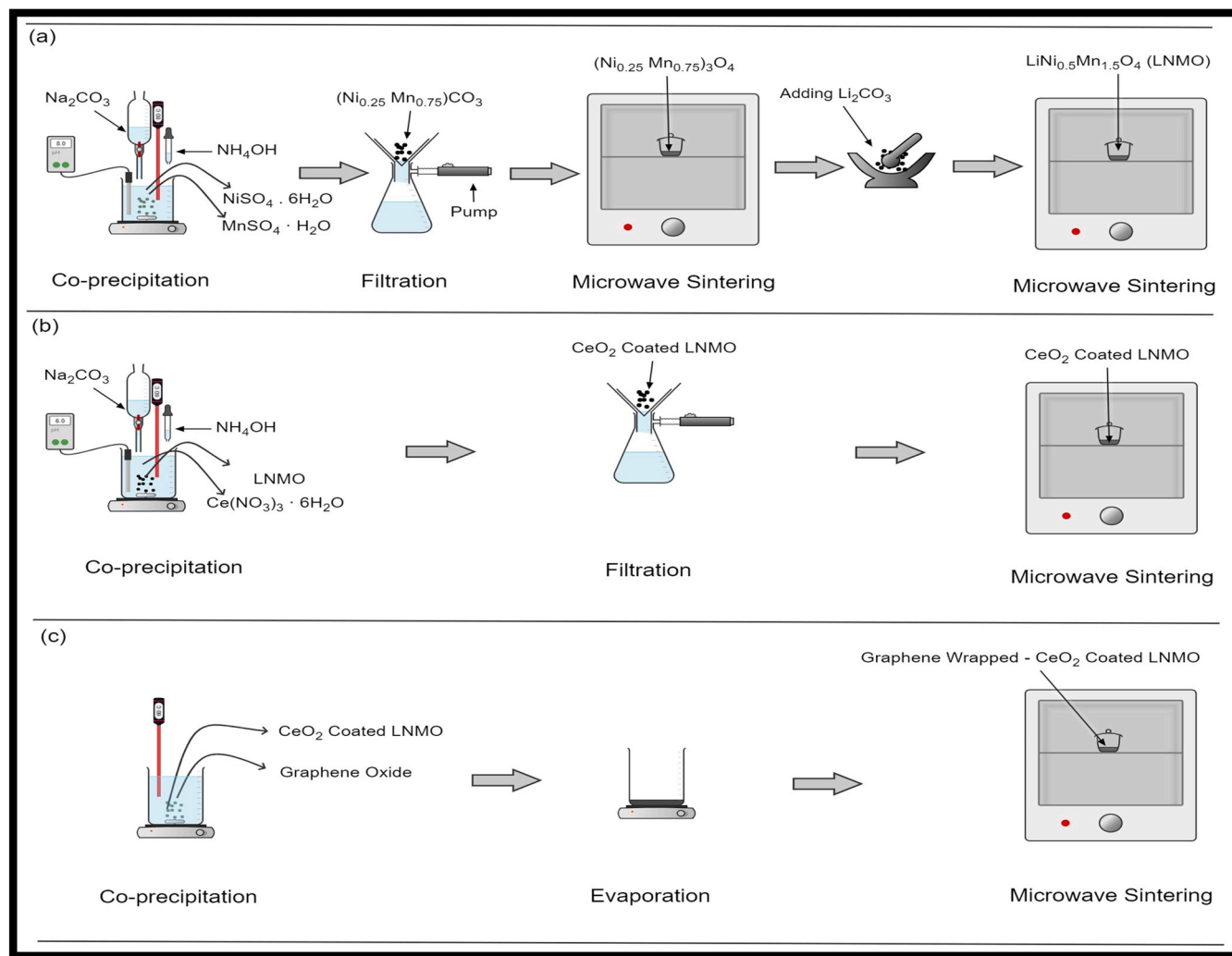


Fig. 1. Schematics for the synthesis of; (a) pure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), (b) CeO_2 coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce), and (c) Graphene wrapped CeO_2 coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce-GO).

2.1.3. Synthesis of graphene wrapped CeO₂ coated LiNi_{0.5}Mn_{1.5}O₄.

2 g of LNMO-Ce powder was added to 300 mL de-ionized water with 0.02 g (1 wt. %) graphene oxide (graphene oxide water dispersion 0.4 wt. %, Graphenea, USA) the solution was stirred gently to form graphene wrapped CeO₂ coated LNMO, indicated in the text as LNMO-Ce-GO. After 30 min of sonication, the mixture was homogenized. Finally, the suspension was filtered, and dried at 60 °C. The filtrate was then sintered in a microwave at 600 °C for 15 min, to cure the coatings. Due to the size difference between the LNMO-Ce microspheres and the graphene sheets, graphene may not completely coat the LNMO particles but will possibly wrap around them. This procedure, Figure 1(c), resulted in graphene-wrapped CeO₂-coated LiNi_{0.5}Mn_{1.5}O₄ spinel particles that retained their original spherical shape.

2.2. Material characterization

2.2.1. Physical characterization. The crystal structure arrangement and phase purity of synthesized materials was studied using an X-ray diffractometer (XRD, PANalytical diffractometer, Almelo, Netherlands) at a scan rate of 2 degrees per minute and a step size of 0.02°, using Cu-K α radiation between 20° and 70°. The data was analyzed using PANalytical X'Pert Highscore software.

The morphologies, microstructures and elemental composition of the materials were investigated using a field emission scanning electron microscope (FE-SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Nova NanoSEM 450 with Bruker EDX Detector, FEI). The FE-SEM utilized a Schottky FEG hot tip with acceleration voltage from 50 V to 30 kV and a magnification scale from 35x to 1 000 000x. Moreover, to study the topographical, crystallinity and morphological aspects of the synthesized samples a 200 kV high-resolution transmission electron microscope (HR-TEM, TECNAI G2 TEM TF20, FEI) was utilized.

Vibrational spectroscopic analysis for the samples were carried out using Thermo fisher scientific DXR Raman Microscope with a wavelength of 532 nm, 40 times scan, and the laser power was 10 using 10X microscope objectives. Also, Fourier Transform Infrared Spectroscopy (FTIR; PerkinElmer, USA) instrument was used to analyze the presence of functional groups within the synthesized samples. All the spectra were recorded from 4000 to 500 cm⁻¹ at a spectra resolution of 4.0 cm⁻¹.

Thermal gravimetric analysis was used to determine the thermal stability of the created materials using a TGA analyzer (Pyris 4000, PerkinElmer-USA); TGA profiles were obtained at temperatures ranging from 25° to 700°C at a rate of 10 °C/min in the presence of nitrogen. The thermal stability of the lithiated and the de-lithiated samples were conducted to analyze the interfacial interaction between the samples and the electrolyte; investigated using differential scanning calorimetry (DSC 8500, PerkinElmer-USA). Initially, to prepare the de-lithiated samples the coin cells were first charged at the rate of 0.1 C and equilibrated at 4.9 V. Subsequently, the cells were moved into an argon-filled glovebox and the cells were disassembled to obtain the electrode. Approximately 5 mg of the cathode material was scraped from the aluminum current collector and collected within a 30 μ L stainless steel pan that was sealed shut by use of a gold-plated copper seal. The DSC was conducted from room temperature up to 300 °C at a rate of 10°.min⁻¹ in a nitrogen environment.

2.2.2. Electrode fabrication. To determine the electrochemical performance of the graphene wrapped- ceria coated LNMO, ceria coated LNMO and pristine LNMO cathodes, the samples will first be made into coin cells (CR-2032) in a glovebox with an argon environment. To prepare the cathode material for coin cell fabrication, the cathode samples will be made into a slurry coated on a battery grade aluminum foil, utilizing the doctor blade method. The slurry will be made in the ratio of 80: 10:10 of cathode material,

Acetylene Black, and Polyvinyl difluoride (PVDF), respectively. The chemicals are combined and stirred using the N-Methyl-2-pyrrolidone solvent (NMP) for 6 h. After the slurry is coated on the aluminum foil, the foil is kept in a vacuum oven at 120 °C for 2 h, to evaporate the solvent completely. The coated foil is cut into 14 mm diameter electrodes using a punching machine and then placed again in the vacuum oven for 24 h, before being moved to an argon filled glovebox. Within the glove box, the coin cells will be fabricated using Lithium metal as the anode (half-cell), and the electrolyte solution used will be 1 M Lithium Hexafluorophosphate (LiPF₆) in ethyl carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v), the separator used would be a glass fiber separator (Whatman GF/D).

2.2.3. Electrochemical measurements. A battery cyler equipment (Won A Tech; WBCS3000L, Seoul, South Korea) will be used for performing galvanostatic charge/discharge tests in a voltage range of 3.5–4.9 V (vs. Li/Li+). The electrochemical tests will be carried out to determine the charge and discharge profiles of the cell, analyze the behavior of the redox couples, and determine the cathode material's storage capacity. Cyclability tests (CCCV, CC-CV) will be carried out to determine the battery's capacity change over a range of cycles and at various charge rates. Moreover, Galvanostatic Intermittent Titration Technique (GITT) will be used to provide insight; respective to electronic and structural changes during intercalation/deintercalation cycles, the kinetics of intercalation and electrochemical stability. GITT was measured at a rate of C/10 with a 10 min galvanostatic stage and a 1 h relaxation interval. Cyclic Voltammetry (CV) was conducted at 0.1 mV/s.

3. Results and discussion

The X-ray diffractograms of LiNi_{0.5}Mn_{1.5}O₄ (LNMO), Ceria coated LiNi_{0.5}Mn_{1.5}O₄ (LNMO-Ce) and Graphene wrapped ceria coated LiNi_{0.5}Mn_{1.5}O₄ (LNMO-Ce-GO) are exhibited in Fig. 2. All spectra exhibit the LNMO structure's signature peak. The sharp and strong peaks demonstrate that the materials are extremely pure and crystalline, with (111) peak position being the most intense. All of the Bragg peaks may be assigned to the disordered spinel $Fd\bar{3}m$ space group, where Lithium ions occupy tetrahedral (8a) sites while Manganese and Nickel ions statistically remain in the octahedral (16d) sites; with a = b = c = 8.15 (ICSD #98-018-7804). Due to the high temperature synthesis process, minor amounts of rock-salt secondary phases such as Li_xNi_{1-x}O or NiO are observed in the pristine LNMO sample. These minor impurities correspond to the weak peaks at 37.5° and 63.2°, these peaks are characteristic to the disordered space group and are denoted by asterisks in Fig. 2. However, these other phases are not present in the cerium oxide coated or the graphene wrapped ceria coated sample; illustrating the feasibility of using microwave sintering to synthesize pure disordered coated LNMO. The lack of the CeO₂ and graphene peaks in the LNMO-Ce and LNMO-Ce-GO spectra is due to their extremely low concentrations, approximately 1 wt. %. The lack of the (220) peaks indicates that the tetrahedral (8a) locations within the crystal structure are not occupied by larger transition metal ions [33]. The prepared materials' lattice parameters are listed in Table 1. The diffusion of Ce⁴⁺ into the surface lattice causes contraction of the LNMO particles resulting in cell volume reduction due to the higher bonding energy of the Ce-O bond compared to the Mn-O and Ni-O bonds, lowering the lattice constant of the LNMO-Ce sample compared to bare LNMO [63,64]. Moreover, the coating layer can generate slight ordering of the lattice structure towards ordered P4₃32 phase, reducing the lattice constant. However, this phenomenon might happen at a very small scale as the XRD spectra is typical of the disordered spinel $Fd\bar{3}m$ spinel space group. This reduction of lattice constant is in agreements with other studies published in the literature pertaining to coated LMO or LNMO spinel oxides [62,64–66]. Additionally, the graphene wrapping and ceria coating of

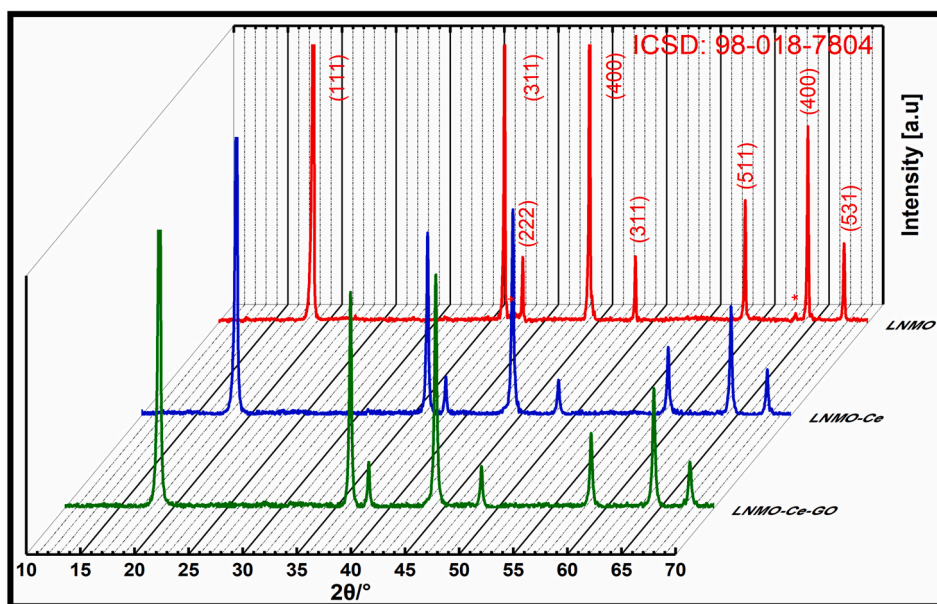


Fig. 2. XRD patterns of synthesized samples.

LNMO did not enter the spinel system but remained attached to the particle surface, as seen by a modest increase in cell volume. Additionally, it implies that the specified microwave sintering did not alter the parent LNMO spinel structure. According to XRD patterns, there are no noticeable differences in the crystalline structure of the samples. The ratio of the I_{311}/I_{400} peaks, on the other hand, is significantly different between LNMO and LNMO-Ce samples, which may indicate the structural stability of the $[\text{Mn}_2]\text{O}_4$ spinel framework. According to previous research, spinel LiMn_2O_4 with I_{311}/I_{400} ratios between 0.96 and 1.1 typically exhibits superior electrochemical properties than those with ratios outside this range [23,67]. According to Table 1, the I_{311}/I_{400} ratio value of both LNMO-Ce and LNMO-Ce-GO can be comparable with that of spinel LiMn_2O_4 with the I_{311}/I_{400} ratios within the optimal range. As a result, it is plausible to conclude that LNMO-Ce and LNMO-Ce-GO samples exhibit superior electrochemical performance.

Since manganese and nickel have comparable X-ray light scattering patterns, Raman and FTIR spectroscopy were used to highlight the distinctive vibrational bands of the ordered ($P4_32$) and disordered ($Fd\bar{3}m$) structures of the synthesized LNMO samples [68]. Fig. 3(a) illustrates two main peaks at 490 and 630 cm^{-1} , exhibiting the Ni-O and Mn-O stretching modes on the Raman spectrum, respectively. The absence of intense peaks at 220 and 240 cm^{-1} along with the distinctive split peaks for the Mn-O bands at around 630 cm^{-1} are characteristics of the disordered spinel [46,50]. Additionally, Fig. 3(b) illustrates the characteristic Mn-O and Ni-O bonds on the FTIR spectrum at 750 and 500 cm^{-1} , respectively. These bonds were utilized to assess the order of cations in the spinel lattice's 16d sites. The synthesized sample was verified to be the disordered spinel at the 16d octahedral sites due to the extremely low intensity of the distinctive bands at 650 and 556 cm^{-1} . The vibrational band at 628 cm^{-1} , accredited to the Mn-O stretching mode,

was more intense than the band at 590 cm^{-1} , symptomatic of the disordered structure. Moreover, the Ni-O stretching mode in the structure was attributed to the two vibrations at 584 and 507 cm^{-1} , and the results were in good accord with prior studies [62].

Thermal gravimetric analysis was utilized to assess the thermal stability of the produced materials and estimate the graphene wrapping of the LNMO particles. The temperature-induced shift in sample weight was monitored, resulting in a variation in graphene concentration. From Fig. 4, no substantial measurable weight loss occurs over the full heating range. Because of the inclusion of a cerium oxide coating that may enhance thermal stability, the LNMO-Ce sample has the smallest extent of weight reduction. However, as the samples are heated from ambient temperature to $700\text{ }^\circ\text{C}$, the LNMO-Ce-GO sample loses more weight than LNMO. The weight-loss region in the TGA plot for the LNMO-Ce-GO sample extends beyond $700\text{ }^\circ\text{C}$, indicating carbon degradation. The overall computed carbon loss value for the LNMO-Ce-GO sample is roughly around 1.2%. Furthermore, it can be noted that all three created materials have good thermal stability up to $700\text{ }^\circ\text{C}$, since no substantial weight loss is seen.

Fig. 5 exhibits FE-SEM micrographs of LNMO, LNMO-Ce, and LNMO-Ce-GO, samples. Even following high-temperature microwave sintering, the LNMO retains its characteristic spherical form. The LNMO sample is composed up of spheres with diameters ranging from 1 to $3\text{ }\mu\text{m}$. However, many tiny holes on the surface of the LNMO particles may be detected, which may have been caused by carbon dioxide escape during sintering. In comparison, because of the thin nano size coating, the FE-SEM images of LNMO (Fig. 5a and b) and LNMO-Ce (Fig. 5c and d) do not differ significantly. The surface of the ceria coated sample is partially wrapped by graphene in the LNMO-Ce-GO sample (Fig. 5e-h); its crinkled cover has the shape of sheets (Fig. 5h). Fig. 5i and (j) depicts an EDX examination of the LNMO-Ce and LNMO-Ce-GO samples, which validates the presence of the elements that the produced material is composed of. The EDX studies shows that the LNMO particles were effectively coated with CeO_2 and enveloped by the graphene nanosheets. The homogenous CeO_2 nano-coating is intended to minimize unwanted contact between the electrolyte and the electrode surface, thereby improving cycling performance. The nanoscale layer would not restrict the internal channels that might prevent lithium-ion diffusion. The LNMO-

Table 1
Lattice parameters for the synthesized samples.

Sample	Lattice Constant (\AA)	Volume (\AA^3)	I_{311}/I_{400}
LNMO-Ce-GO	8.174	546.1	0.9863
LNMO-Ce	8.128	536.9	0.9670
LNMO	8.151	541.6	0.9952

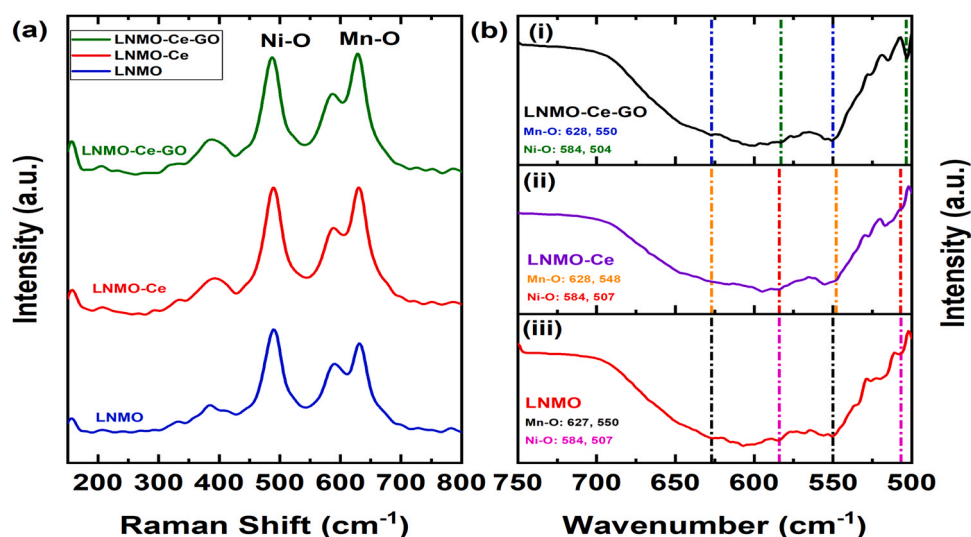


Fig. 3. (a) Raman spectra and (b) FTIR spectra of (i) Graphene wrapped ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce-GO) (ii) Ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce) and (iii) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), samples.

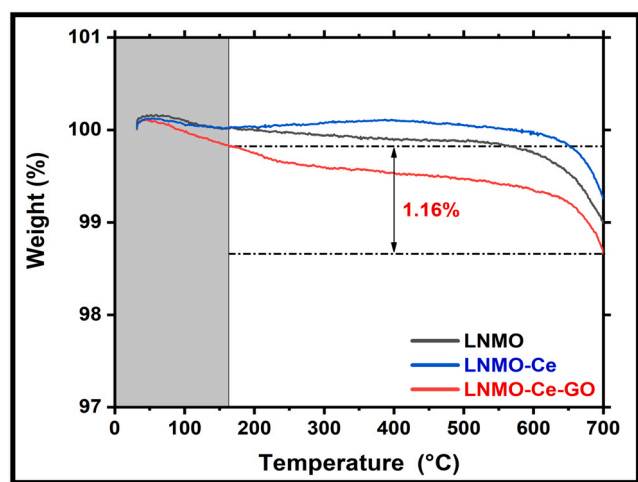


Fig. 4. Thermal gravimetric analysis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), Ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce) and Graphene wrapped ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce-GO), in nitrogen environment.

Ce-GO microspheres include internal radial channels that enable regulated electrolyte-protected wettability, enhanced electronic conductivity, and ionic leaching protection.

To further corroborate the presence of ceria coating and graphene wrapping over $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, High-resolution transmission electron microscopy (HR-TEM) was utilized. The HR-TEM figures for LNMO, LNMO-Ce and LNMO-Ce-GO are presented in Fig. 6. The sample particles were ground by a mortar before mounted on a carbon-coated copper TEM grid. The smooth particles observed in Fig. 6(a) and (b) are attributed to pristine LNMO. Fig. 6(c)–(f), on the other hand, exhibit grainy appearance, mainly due to the existence of ceria film and graphene sheets [62]. The nanometric coating of CeO_2 can be clearly observed in Fig. 6(d), the film has an approximate thickness of 1–3 nm. The electrochemically active ceramic ceria coating ensures protection of the LNMO cathode from direct exposure to the electrolyte, minimizing undesirable reactions between the active material and the electrolyte. Furthermore, due to the ceramic nature of the coating, the LNMO cathode is also protected from HF attack and the integrity of the cathode is preserved due to suppression of Mn dissolution. In general, when the thickness of the cerium oxide coating increases, the contact resistance and load

transfer resistance rise significantly, particularly as coating thickness exceeds 10 nm [28]. However, in this work, the ceria coating thickness is 1–3 nm (Fig. 6d and f), guaranteeing that polarization and power depletion are successfully circumvented. Furthermore, the presence of graphene enhances the cathode's electrical conductivity, hence improving its electrochemical performance. Fig. 6(h) exhibits the selected area diffraction (SAED) pattern of an independent graphene wrapped ceria coated LNMO particle, the pattern demonstrates that the increased crystallinity results in a lower energy barrier for lithium-ion insertion, resulting in rapid ionic diffusion. Additionally, as shown in Fig. 6(g), the distance between lattice fringes is 0.472 nm, corresponding to the interplanar division of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (111) plane in accordance with the XRD data. On the basis of the energy dispersive X-ray analysis and selected area diffraction, it can be determined that microwave-assisted chemical coprecipitation is a feasible method to manufacture phase pure spinel cathodes.

After coin-cell fabrication the charge and discharge behaviour for the three samples were conducted in the voltage window of 3.5–4.9 V, characteristic of the redox couples for Mn and Ni within LNMO. The cells were tested at a constant current rate of 0.1 C. Fig. 7 illustrates the cyclability and the charge/discharge profiles for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), Ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce) and Graphene wrapped ceria coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO-Ce-GO) cells. The lithium intercalation may be traced back to the two-stage extraction process as the cycles advance; the charging plateau climbs upwards to greater potential owing to cathode polarization, while the discharging plateau lowers down to lower potential. The voltage plateaus at around 4 V and at 4.7 V are distinctive to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couples, respectively. From Fig. 7(b), the coin-cell with the pristine LNMO sample provides a high initial discharge capacity of approximately 133 mAhg^{-1} but dropping down to 112.6 mAhg^{-1} after 100 cycles. According to reports, the first charge/discharge cycle is commonly disregarded since there is persistent capacity degradation due to the formation of a solid electrolyte interface (SEI) layer [69]. From Fig. 7(c) and (d), the LNMO-Ce and LNMO-Ce-GO cells provide an initial discharge capacity of 137.3 mAhg^{-1} and 139 mAhg^{-1} respectively. And a reversible capacity of 125.8 mAhg^{-1} and 132.4 mAhg^{-1} respectively after cycling 100 times. This translates into a capacity retention of 95.3 % for LNMO-Ce-GO sample, compared to 91.6 % and 84.7 % for LNMO-Ce and LNMO, respectively. Moreover, on comparison of Fig. 7(b), (c) and (d), it can be observed that the capacity fading observed on cycling diminishes

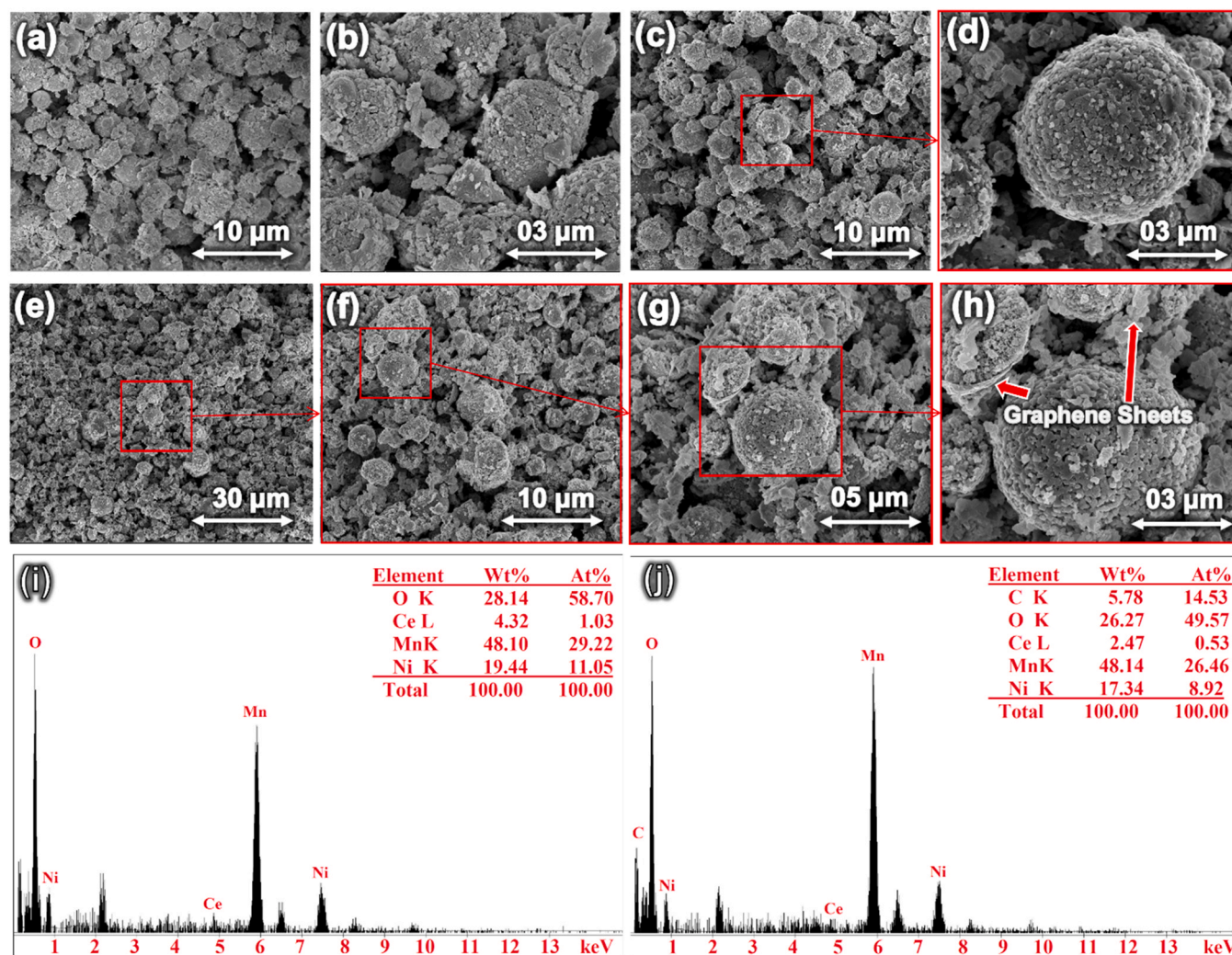


Fig. 5. FE-SEM micrographs of; (a-b) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles (c-d) Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles (e-h) Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles wrapped with 1 wt. % graphene; EDX analysis of (i) Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles and (j) Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles wrapped with 1 wt. % graphene.

for the LNMO-Ce-GO sample. A similar observation can be made about the coulombic efficiency, the cell with the graphene wrapping (LNMO-Ce-GO) exhibits high performance compared to both LNMO-Ce and LNMO. Previous reports illustrate the efficacy of electrochemically active ceria coated LNMO. According to Yi et al., 3 wt. % CeO_2 coated LNMO provided a high capacity retention of 98.3% at 1C rate, over a 100 cycles [33]. However, the spinel LNMO synthesized by Yi's group was ordered spinel LNMO, with a lower initial discharge capacity, that already is much more stable while cycling compared to the disordered spinel synthesized in the current study. Similarly, Tang et al. studied the effect of 4.7 wt. % graphene wrapping over ordered LNMO nanorods, declaring that the LNMO-graphene wrapped rods provided a 94% capacity retention and a reversible capacity of 115 mAhg^{-1} after 200 cycles at 0.1C rate [51]. As elucidated earlier, the disordered spinel has a high discharge capacity with low cyclability, while the ordered spinel exhibits good cyclability at the compromise of discharge capacity. The aim of this work was to improve the cyclability of disordered LNMO spinel by using a combination of ceria coating and graphene wrapping, resulting in a high-voltage cathode material that is energy dense and exhibits good cyclability. Hence, it can be concluded that the novel method of utilising ceramic coating and graphene wrapping combination can improve the electrochemical performance of the disordered spinel LNMO.

The cyclic voltammograms shown in Fig. 8 for the cells are used to determine the lithium intercalation kinetics for LNMO, LNMO-Ce, and LNMO-Ce-GO, by analysing the energy levels of the redox couples present within LNMO. The prominent peaks at 4.7 V are caused by the oxidation of Ni^{2+} to Ni^{4+} , whereas additional peaks at 4.0 V are caused by the lower current required to oxidize Mn^{3+} to Mn^{4+} . The maximal intensity of the manganese redox pair in the pure LNMO cell is larger than that of ceria coated LNMO (LNMO-Ce) cell and the graphene wrapped ceria coated LNMO (LNMO-Ce-GO) at 4.0 V. This signifies that the ceramic ceria coating somehow suppresses manganese oxidation, providing credulity to the cycling data as can be observed from the weak voltage plateau at 4.0 V in Fig. 7(c). In contrast, the nickel redox couple is more prevalent in LNMO-Ce and LNMO-Ce-GO, compared to that of the pure LNMO cell. Peak-to-peak differentiation is greater in the LNMO-Ce and LNMO-Ce-GO cells, suggesting superior lithium intercalation reversibility and faster kinetics.

Between 3.5 V and 4.9 V, the fabricated cells were charged and discharged at 0.1 C, 0.5 C, and 1 C to test their effectiveness at higher current rates. Diverse capacities are attained, which can be related to the different current rates used and the regulating electrochemical processes that contribute to the cells' degradation in efficiency. From Fig. 9(a), the LNMO cell's discharge capacity is significantly reduced from 136 mAhg^{-1} at 0.1 C to 124 mAhg^{-1} at 1 C rate. At 0.1C, the

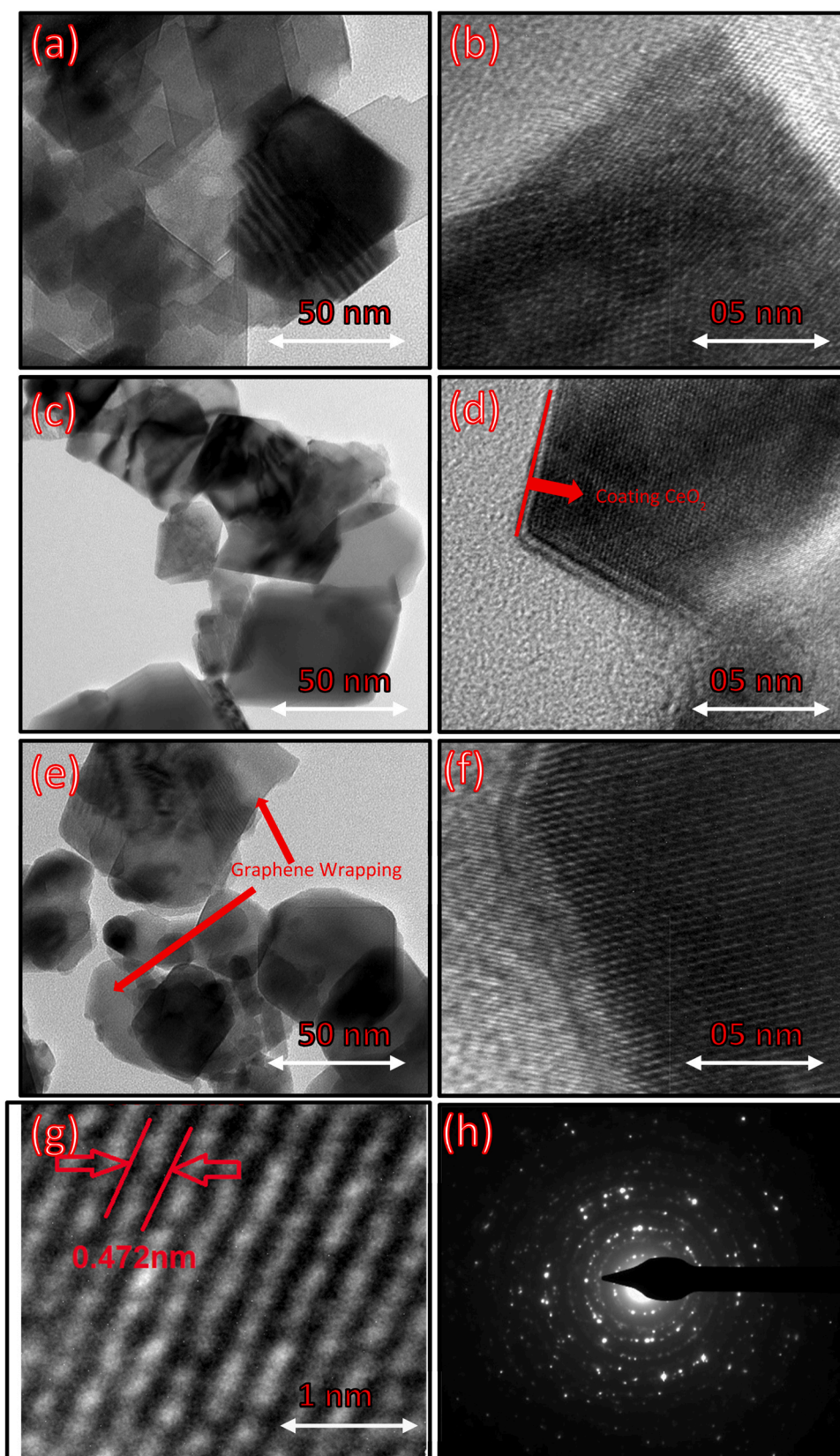


Fig. 6. HR-TEM micrographs: (a, b) pristine LNMO particles (c, d) CeO₂ (5–8 nm) coated LNMO particles (e, f) 1 wt. % graphene wrapped CeO₂ coated LNMO particles (g) Lattice fringes of LNMO-Ce-GO and (h) SAED pattern of LNMO-Ce-GO.

discharge capacities of the LNMO-Ce and LNMO-Ce-GO cells are 132 mAhg⁻¹ and 138 mAhg⁻¹, respectively. More crucially, at 1C, LNMO-Ce and LNMO-Ce-GO cells demonstrate a considerable increase in

discharge behaviour, with discharge capacities of 127 mAhg⁻¹ and 135 mAhg⁻¹, respectively. The outcomes from the rate capability analysis indicate that increasing the rate of charge transfer at the

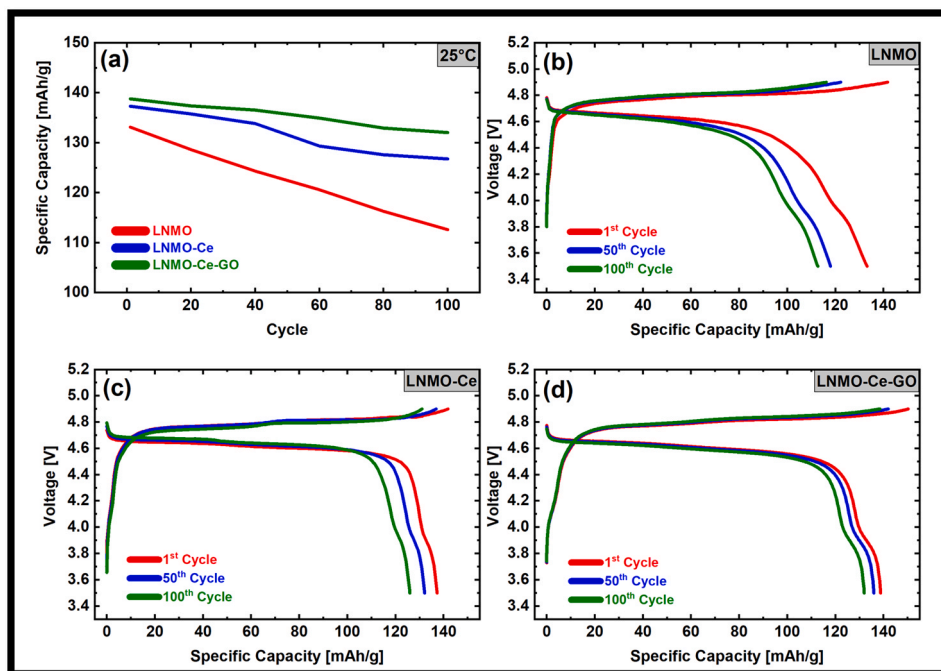


Fig. 7. (a), Cycling performance of the synthesized samples at 25 °C, Galvanostatic charge/discharge profiles of, (b) Pristine $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO), (c) 1 wt. % Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO-Ce), and (d) 1 wt. % Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles wrapped with 1 wt. % graphene (LNMO-Ce-GO).

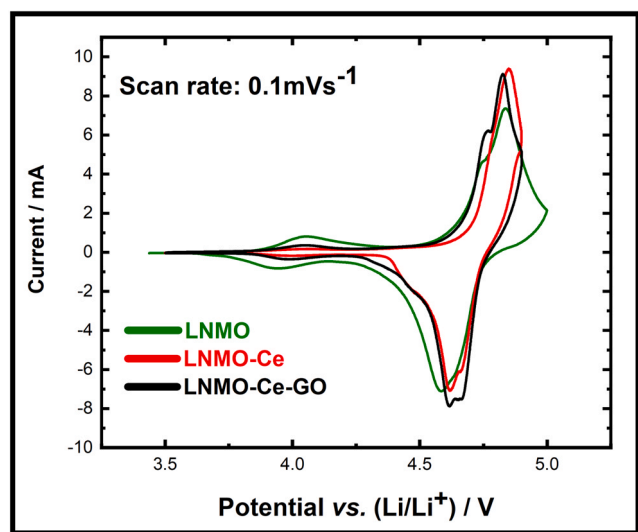


Fig. 8. Cyclic Voltammograms of the synthesized samples, at a scan rate of 0.1 mV/s.

cathode-electrolyte boundary or lithium-ion transport can limit the electrochemical performance of the fabricated cells. The results suggest that the resultant higher discharge capacity of LNMO-Ce and LNMO-Ce-GO might be a result of the ceramic coating in tandem with the graphene packaging. But mainly due to graphene's influence on enhancing electrical conductivity and shortening lithium diffusion paths [70]. In comparison to the uncoated LNMO cell, the LNMO-Ce and LNMO-Ce-GO cells exhibit outstanding discharge behaviour and no discernible fading on rapid discharging.

To get insight into the electrochemical performance of developed cathode materials, galvanostatic intermittent titration (GITT) tests were conducted. To allow adequate time for possible equilibrium, the cells were cycled in phases separated by rest intervals [62]. At C/10, measurements were taken to determine the quasi-equilibrium

profile for the reaction kinetics, which are depicted in Fig. 9(b-d). Comparing the GITT curves of the three cells in the nickel redox window, reveals a smooth lithium insertion and extraction profile due to minor polarization. Lithium ions reside at 8a sites and travel along over to the vacant octahedral 16c sites within the LNMO spinel lattice. Increased applied voltage results in a decrease in lithium diffusion due to the high polarization of the LNMO sample, which may be attributed to $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox couples. However, this phenomenon is not observed for the LNMO-Ce and LNMO-Ce-GO cells, as they display smoother profiles. In comparison to the LNMO sample, the short relaxation spikes seen for LNMO-Ce and LNMO-Ce-GO indicate faster kinetics with low polarization. The LNMO-Ce-GO sample displays the smoothest profile, exhibiting superior electrochemical performance and complete lithium extraction. The relaxation spikes are smaller during charging, indicating that the oxidation phase is outperforming the reduction phase. The oxidation peak regions are significantly larger than the reduction peak areas, which is consistent with the asymmetry of oxidation and reduction as illustrated by the cyclic voltammograms (Fig. 8).

Lastly, the thermal stability of the lithiated and the de-lithiated samples were conducted utilizing DSC. Fig. 10(a) illustrates the DSC thermograms for the bare $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO), CeO_2 coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO-Ce), and CeO_2 coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ wrapped in graphene (LNMO-Ce-GO) samples after charging the cells to 4.9 V at 0.1C. The pristine LNMO sample exhibits an exothermic peak around 256 °C, which is consistent with earlier literature reports [71]. The interaction between the electrolyte and the charged spinel cathode is mainly the cause for such a peak. The oxygen emitted from the de-lithiated LNMO structure oxidizes the electrolyte solvent at this high operating voltage, resulting in heat being evolved [72]. The protective ceria ceramic coating protects the cathode surface from these exothermic side reactions with the electrolyte, and it can be observed from Fig. 10(a), that the LNMO-Ce and LNMO-Ce-GO cathode samples do not show any considerable exothermic activity around the same temperature range. Concluding that the microwave-assisted co-precipitation induced surface modification increases the thermal stability of the LNMO-Ce and LNMO-Ce-GO

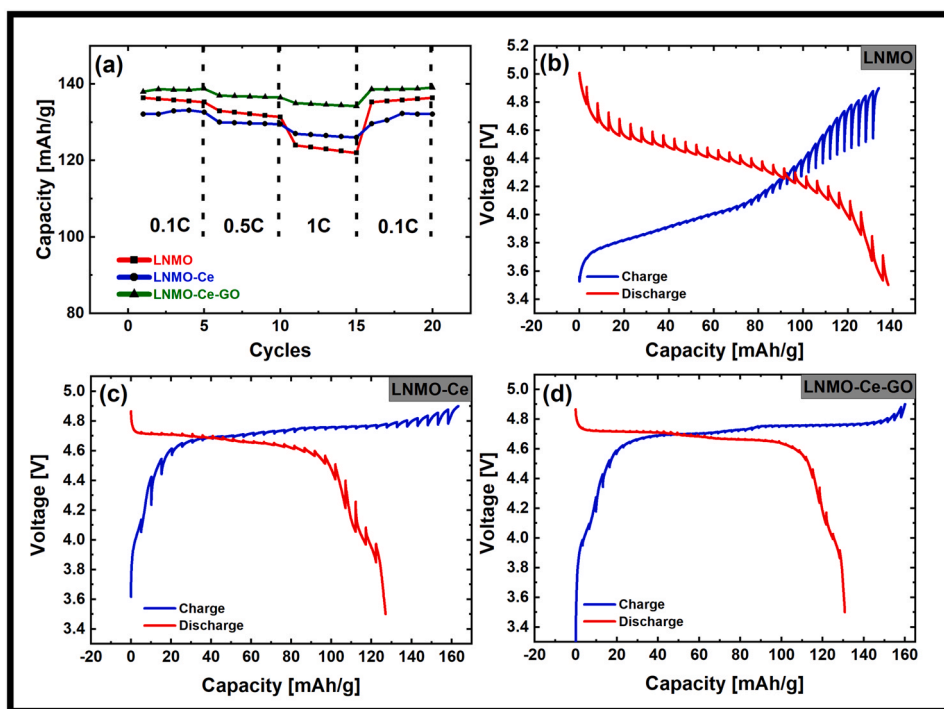


Fig. 9. (a) Rate capability of the cells at ambient temperature, and GITT analysis at C/10 rate of (b) LNMO, (c) Ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO-Ce), and (d) Graphene wrapped-ceria coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO-Ce-GO) cells.

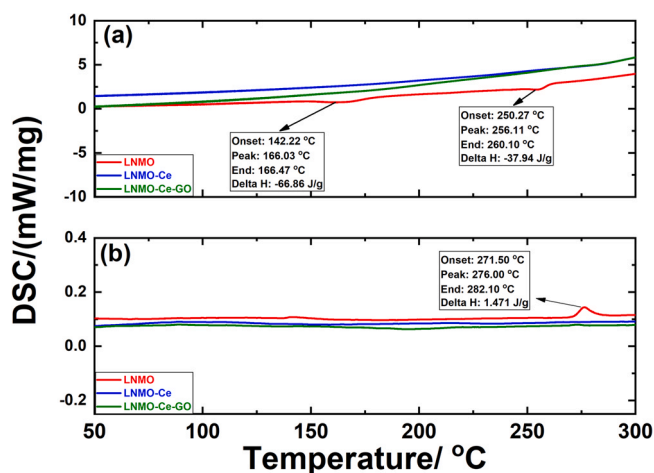


Fig. 10. DSC thermograms until 300 °C for (a) Charged samples equilibrated at 4.9 V at 0.1 C and (b) discharged samples: of LNMO, LNMO-Ce and LNMO-Ce-GO.

samples compared to the bare LNMO sample. Moreover, for comparison the lithiated or uncharged DSC curves for the samples are also illustrated in Fig. 10(b). Hence, this work elucidates the physical, structural, and electrochemical basis of performance enhancement of the high-voltage spinel LNMO cathode material surface modified with CeO_2 and wrapped with graphene. This work can also be utilized as a roadmap to improve the other next generation cathode materials for LIBs.

4. Conclusion

Spherical microspheres of phase pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO), CeO_2 coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO-Ce), and CeO_2 coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ wrapped in graphene (LNMO-Ce-GO) were produced using a microwave-assisted chemical co-precipitation process. The inclusion of the ceramic ceria coating and graphene nanosheet

wrapping has significantly improved the cyclability and capacity retention of the LNMO spinel; countering major limitations associated with $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. The enhanced performance can be accredited to the suppression of the side-reactions occurring between the cathode and the electrolyte due to the ceramic coating and graphene addition. Moreover, the novel approach protects the cathode from HF attack and subsequent manganese dissolution due to the Jahn-Teller distortion, obstructs the development of undesirable SEI layer and increases the lithium-ion transport kinetics.

CRediT authorship contribution statement

Zawar Alam Qureshi: Investigation, Data curation, Methodology, Conceptualization, Formal analysis, Software, Writing – original draft, Writing – review & editing. Hanan Abdurehman Tariq: Conceptualization, Methodology, Software, Formal analysis, Resources, Writing – review & editing. Hiba Mohammad Hafiz: Investigation, Data curation, Software, Visualization, Writing - original draft. Rana Abdul Shakoor: Conceptualization, Validation, Resources, Formal analysis, Writing – review & editing, Supervision, Project administration, Funding acquisition. Ramazan Kahraman: Supervision, Validation, Project administration, Funding acquisition, Resources. Siham AlQaradawi: Supervision, Validation, Project administration, Funding acquisition, Resources.

Declaration of Competing Interest

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

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