



Exploring layered lithium-rich spinel composite cathodes for lithium-ion battery obtained by the solution combustion-mechanochemical synthesis

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ABSTRACT

In this study, layered lithium-rich oxides (LLO) cathode materials were modified with different amounts of the spinel phase to form integrated layered-layered-spinel (LLS) hetero-composites $[0.5\text{Li}_2\text{MnO}_3 \cdot (0.5 - x)\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2 \cdot x\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4 \text{ (} 0.05 \leq x \leq 0.25 \text{)}]$ using a facile solution combustion mechanochemical synthesis method for the first time. The XRD results indicate that all the LLS materials have distinct layered and spinel phases with R3m, C2/m and Fd3m space groups. Notably, the initial coulombic efficiency of the LLS materials increased with increase in the spinel content but showed a reduction both in their charge and discharge capacities. The LLS doped with 5 % spinel content (651LLS), exhibited the best electrochemical performance compared to the ones doped with 15 % spinel (642LLS) and 25 % spinel (633LLS). The 651LLS cathode which had the lowest spinel content, gave the smallest particle size and the largest unit cell volume. Consequently, the 651LLS cell delivered the highest initial discharge capacity of 279.58 mAh g⁻¹ and a capacity retention of 84.71 % after 50 cycles at a current density of 10 mA g⁻¹ within a voltage window of 2.0 – 4.8 V. Additionally, the 651LLS cell demonstrated superior rate capability with the average capacities 275, 225, 200, 155, and 90 mAh g⁻¹ at 10, 20, 50, 100, and 200 mA g⁻¹. This enhanced performance is attributed to the optimised spinel amount and the smaller particle size which facilitated faster Li-ion transport during cycling. Also, the optimal electrochemical behaviour of the 651LLS cathode is linked to its optimum spinel content (~5 %) which contributed to its improved structural stability. The results show that the amount of spinel in these LLS materials must be carefully tuned in relation to the operating cycling parameters to produce optimum electrochemical performance.

1. Introduction

Lithium-ion battery (LIB) has been the most widely used energy storage device for portable electronics because it has many advantages, including long cyclic life, high energy density, and environmental friendliness, compared to other secondary batteries [1–3]. The layered lithium-rich oxides (LLO) are considered to be one of the most promising next generation cathode materials for LIB due mainly to its attractive specific capacity > 250 mAh g⁻¹ and extremely high working voltage

> 4.6 V [4–7]. In spite of the excellent capacities and high energy densities, the LLOs still face challenges in their practical applications which include continuous capacity fading and decrease of average voltage upon repeated cycling, high initial irreversible capacity loss, and relatively poor rate capability.

Various studies have focused on enhancing the rate performance of layered LLO cathode materials with spinel structure [2,8–19]. These pioneer concepts were first introduced by Thackeray and co-workers, who proposed that incorporating a spinel phase content of

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approximately 6–12 % yields optimal electrochemical capacity in composite cathode materials [19,20]. The addition of the Mn-based spinel component to this integrated composite cathode material has been shown to be a viable option to increasing the reversible capacity, Coulombic efficiency, cyclability and rate performance of LLO cathodes due to: (i) excess Li can be accommodated during discharge into octahedral 16c sites of the spinel lattice accompanied by the reduction of Mn (as occurs in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ to form $\text{Li}_2\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$); (ii) the spinel component has three-dimensional paths for Li^+ diffusion which improve rate capability for the composite structure; (iii) the spinel phase can stabilize the layered component at high potentials and vice versa, improving the cathode cycling stability.

Recently, Sakran and co-workers enhanced the electrochemical performance of LIBs by engineering a layered-spinel heterostructure cathode. Electrochemical performance showed that the optimized composition, containing trace amount of spinel phase, delivered a high specific capacity of $299.38 \text{ mAh g}^{-1}$ at 0.1 C. At a 1 C rate, this composition retained 175.3 mAh g^{-1} after 100 cycles, corresponding to a capacity retention of 76.89 %. The improved performance was attributed to the synergistic effect of the ultrathin spinel material, which enhanced Li-ion diffusion kinetics and provided structural protection against electrolyte-induced degradation [21]. Xu et al. also reported the design of a layered-spinel intergrown cathode structure via an ion-exchange process, offering high structural tunability. This approach facilitates the ordered arrangement of manganese oxide layers while integrating the high capacity of the layered phase with the structural stability imparted by the spinel component. The resulting heterostructure exhibited an initial discharge capacity of 254.3 mAh g^{-1} at 0.1 C. The study demonstrated that the intergrown architecture enables synergistic Li-ion transport properties, thereby contributing to enhanced electrochemical performance in lithium-ion batteries [22].

Remarkably, the LLO cathode materials modified with a spinel structure have been synthesized, in the ‘composite’ form, as an intergrowth of the LiMO_2 R-3m, Li_2MnO_3 C2/m and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Fd-3m phases forming an integrated layered-layered-spinel (LLS) heterostructure [2,8,11,14–17]. Also, the surface modification engineering of the LLO with a spinel skin to improve their structural and electrochemical performance has been reported [11,12,18]. In addition, a study has shown that the formation of a spinel phase in these materials can be simply controlled by the calcination temperature [23]. It was reported that a calcination temperature of 750–800 °C is required for the formation of a spinel phase in these LLO materials while a calcination temperature of ~700 °C and ~900 °C gave a material with only a Fd-3m spinel and only a C2/m layered phase, respectively. The type of spinel compound integrated into these materials can also influence the structural and electrochemical properties of the LLS materials. Out of them, the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ spinel materials have been intensively investigated due to their high-voltage electrochemical activity, excellent rate capability as well as cycling stability. Also, it is well known that the composition of the LLO determine their structural and electrochemical properties. Many LLOs have already been reported in literature as high energy density and power cathode materials which includes $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (or $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) [2,8,18–23], $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.28}\text{Co}_{0.12}\text{O}_2$ (or $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.35}\text{Co}_{0.15}\text{O}_2$) [5], and $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ (or $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$) [20].

Typically, these integrated LLS materials have been synthesized by the co-precipitation and solvothermal methods [8,10,15,16,24]. These methods that have been used to synthesise these integrated LLS materials are tedious, toxic and economically unfeasible for the commercial applications of these materials. Also, many of these methods that have been used to synthesise these integrated LLS materials are unable to control the amount of spinel phase in the materials. Controlling the spinel fraction in these materials is critical to obtaining an optimized electrochemical performance [14,19]. Precise Kim et al. employed ball-milling method to prepare these materials from the three different

components which were commercially obtained [17]. Even though it was an efficient and a robust method to prepare integrated layered-spinel LLS materials, the spinel fractions were > 25 % leading to unattractive electrochemical performance. The solution combustion-mechanochemical synthesis (SC-MS) is an energy efficient and cost-effective method to prepare composite cathode materials. Unlike the co-precipitation and solvothermal methods, the SC-MS is scalable and could be used for the large-scale production of these composite electrode materials for LIBs. Unlike the co-precipitation method, the solution combustion route allows for the quantification and control of each LLO component even with the structural similarities of the layered components. Therefore, the SC-MS method allows for the precise control of all the components to achieve the desired LLS compositions. Previously, we have reported the electrochemical performance of composite and core-shell $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ ($0 \leq x \leq 0.7$) cathodes prepared by the SC-MS [25]. The results showed that the $\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.20}\text{Co}_{0.08}\text{O}_2$ (or $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$) composition gave the best electrochemical performance.

In this study, different amounts of the spinel component were embedded in $\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.20}\text{Co}_{0.08}\text{O}_2$ material to obtain integrated layered-spinel LLS materials with chemical formula $[0.5\text{Li}_2\text{MnO}_3 \cdot (0.5-x)\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2 \cdot x\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4]$ ($0.05 \leq x \leq 0.25$) compositions. It is important to clarify the contributions of the spinel component to the electrochemical performance of these LLO materials as previous studies have shown disparate synergistic effects. The integrated LLS materials were successfully synthesized using the SC-MS method. The results showed that the amount of spinel content influenced the morphology, cationic disorder and electrochemical performance of the synthesized LLS cathode materials. The 651LLS cell with ~5 % spinel content ($x = 0.05$) displays the best electrochemical performances, while the samples with 633LLS (25 % spinel content) give the poorest performance.

2. Experimental methods

2.1. Materials

Reagents used in the synthesis include analytical grade LiNO_3 (Suprapur $\geq 99\%$), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfar Aesar-Puratronic, purity $\geq 99\%$), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich $\geq 99\%$), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich $\geq 98\%$), $\text{C}_6\text{H}_{10}\text{O}_8$ (Emsure ACS), PVDF binder (Solvay Solef 6020), carbon black (TIMCAL Super C65), and 1-methyl-2-pyrrolidone (Merck EMPLURA). Deionised water was used to prepare all aqueous solutions. The following integrated layered-layered-spinel (LLS) represented with the chemical formula $[0.5\text{Li}_2\text{MnO}_3 \cdot (0.5-x)\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2 \cdot x\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4]$ ($0.05 \leq x \leq 0.25$) were synthesized. First, each component of the integrated layered (Li_2MnO_3), layered ($\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$), and spinel ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) material was prepared separately using the citric acid fuel rich assisted solution combustion method as shown in our previous study [25]. Second, appropriate amounts of each component of the LLS material, synthesized in the first stage, were mechanically alloyed in a ball mill (Pulverisette 7, Fritsch) in the presence of acetone at 300 rpm for 3 h. The resulting powder mixtures were annealed at 750 °C for 10 h in air at a heating rate of 2°C min^{-1} and were then allowed to cool to room temperature slowly. Hereafter, the composition with $x = 0.25$, $x = 0.15$, and $x = 0.05$ were labelled 633LLS, 642LLS, and 651LLS, respectively. The prepared samples were used for further structural characterization and electrochemical testing in this study.

2.2. Characterization methods

The phase composition and crystal structures of the synthesized 633LLS, 642LLS, and 651LLS materials were determined by powders X-ray diffraction (STOE STADI MP, Cu-K α radiation) with a step width of 0.015° in the 2θ range of $3^\circ - 80^\circ$. Also, the local structure of the 633LLS,

642LLS, and 651LLS powders were analyzed by Raman spectroscopy (Horiba LabRam Evolution HR microscope equipped with a 632.81 nm HeNe solid-state excitation laser (17 mW), a 100 × objective, and 600 grooves per millimetre grating). Furthermore, the morphologies of the 633LLS, 642LLS, and 651LLS powders were determined by scanning electron microscope (Zeiss Merlin GEMINI 2) with a primary electron energy of 10 keV and an in-lens detector.

2.3. Electrochemical tests

The slurries of the LLS samples were formed by mixing the active materials (80 %), carbon black (10 %), and polyvinylidene fluoride binder (10 %) in 1-methyl-2-pyrrolidone solvent. Subsequently, the slurries formed were coated on a cleaned aluminium foil (with a wet thickness of 200 µm), dried and cut into 12 mm circular diameter discs to be used as the working electrodes. The CR2032 coin cells were assembled in an MBraun Ar-filled glovebox using the working electrode discs as the cathodes, lithium metal foil as the anodes, separated by 16 mm Celgard 2325, and LP30 selectylite (BASF) serving as the electrolyte. The galvanostatic cycling tests were performed between 2.0 – 4.8 V and 2.0 – 4.9 V on a Biologic VMP3 potentiostat at 25 °C.

3. Result and discussion

3.1. Structural and morphological characterization

The XRD pattern of the synthesized LLS materials is presented in Fig. 1. The XRD patterns were analysed based on the mixture of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_2$ (R3m), layered Li_2MnO_3 (C2/m) and spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Fd3m) phases for all the samples. The peaks of the two layered phases in all the samples are similar except for the superlattice peaks around 20 – 23 °C [2,10,14]. The decrease of the peaks with increasing amounts of spinel correlates with the crystallinity of the materials. Except for the 651LLS sample where there is an integration of all the three phases; the other samples show the non-integration of the layered and spinel phases as shown in the double peaks in the 003 and 104 peaks (Fig. 1). In these materials, the layered and spinel peaks overlap due to their structural compatibility. However, an optimum amount of the spinel that should be added to the LLO material must be established to ensure structural stability of the LLS material which has implications for its electrochemistry [19]. The $I_{(003)}/I_{(104)}$ ratio for 633LLS, 642LLS and 651LLS are 1.84, 1.50 and 1.37, respectively. This

suggests that the higher the spinel content, the lesser the cationic disorder. As presented in Table 1, the calculated lattice parameters a , c , and unit cell volume (V) for the LLS samples are as follows: 2.8506 Å, 14.2694 Å, and 100.42 Å³ for 633LLS; 2.8502 Å, 14.2902 Å, and 100.54 Å³ for 642LLS; and 2.8516 Å, 14.2902 Å, and 100.63 Å³ for 651LLS, respectively. Even though the materials are made up of composite layered R3m, layered C2/m and spinel Fd3m crystal phases, the layered R3m phase was used to calculate the unit cell volume (V). These composite materials are typically the Li-rich oxide material usually indexed to the layered R3m crystal phase. The results indicate no significant impact on the lattice parameters, as the values obtained for the three samples are closely comparable. However, 651LLS sample with only about 5 % spinel content showed the highest cell volume compared to the 633LLS and 642LLS samples with 15 % and 25 % spinel contents, respectively.

The Raman spectra of the synthesized LLS materials is shown in Fig. 2. It shows two prominent peaks observed at 645 cm⁻¹ and 500 cm⁻¹, attributed to A_{1g} and E_g vibration mode of layered materials [2,26]. Additionally, weak peaks observed around 300–400 cm⁻¹ could be attributed to the Li_2MnO_3 phase [8,26]. Compared with 633LLS and 642LLS samples, the peak observed at 645 cm⁻¹ becomes broader and the peak around 500 cm⁻¹ shift to the left for 651LLS, indicating the spinel phase is integrated into the layered structure as already confirmed by XRD spectra [2].

The SEM micrograph illustrates the morphological characteristics of 633LLS, 642LLS, and 651LLS (Fig. 3). All the images show particles of irregular shapes whose sizes reduced with decreasing amounts of spinel content. Fig. 4 shows the SEM micrograph and EDS mapping of 633LLS, 642LLS and 651LLS revealing the homogeneous distribution of the

Table 1

Crystallographic parameters obtained from XRD patterns.

Sample	633LLS	642LLS	651LLS
a (Å)	2.8506	2.8502	2.8516
c (Å)	14.2694	14.2902	14.2902
V (Å ³)	100.42	100.54	100.63
$I_{(003)}/I_{(104)}$	1.84	1.50	1.37

Note: The cell volume for a layered R3m phase is calculated using $V = \frac{\sqrt{3}}{2} a^2 c \sin(\alpha)$

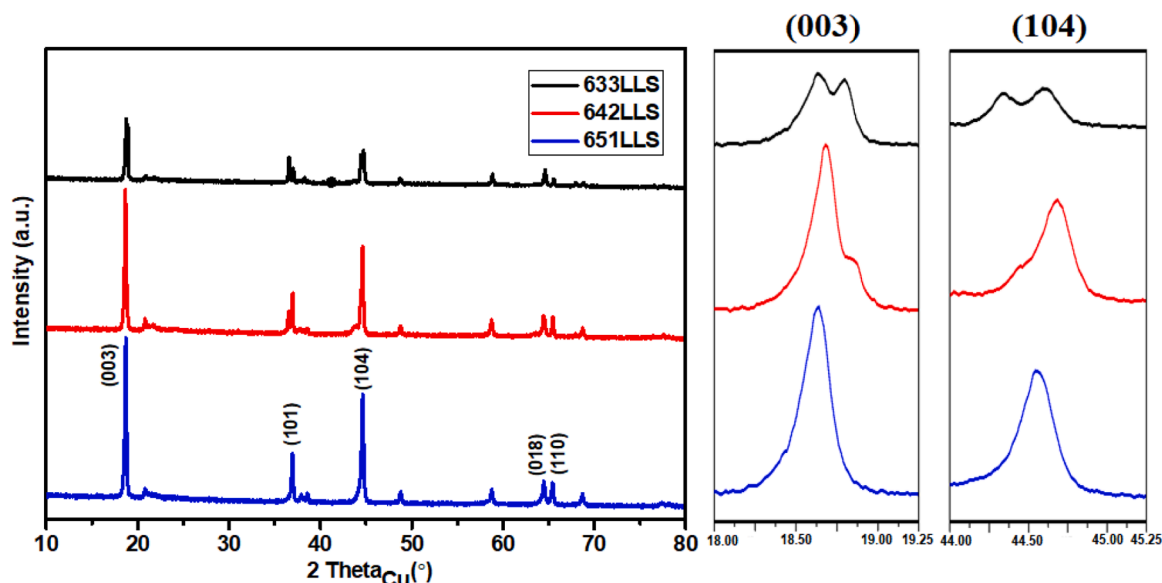


Fig. 1. X-ray diffraction patterns of the samples, and the Miller indices of the R3m symmetry.

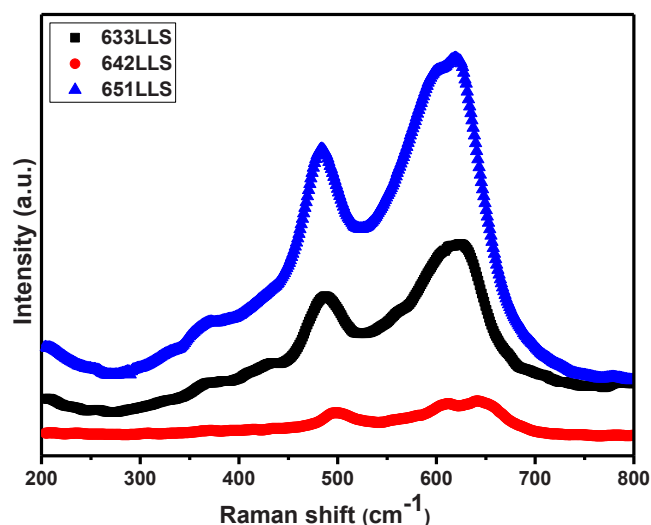


Fig. 2. Raman spectra of the LLS samples.

elemental composition (manganese, nickel and cobalt) in the synthesized LLS materials.

3.2. Electrochemical performances of the LLS cells

The influence of varying spinel compositions in the synthesized LLS on its electrochemical performance was systematically investigated. The first charge/discharge profiles, corresponding dQ/dV plots, and cycling performance of the LLS cells cycled at 10 mA g^{-1} using $2.0 - 4.8 \text{ V}$ and $2.0 - 4.9 \text{ V}$ voltage windows are shown in Fig. 5. The cycling capacities of the LLS cells cycled at different voltage windows after 50 cycles are presented in Table 2.

Fig. 5(a) and (d) gives the initial charge-discharge curves of LLS cells at $2.0 - 4.8 \text{ V}$ and $2.0 - 4.9 \text{ V}$, respectively. The initial charge curves show the contributions of the three distinct LLS phases to the capacities, most clearly seen in the 633LLS cell [17,27]. Li^+ ions are firstly extracted mainly from the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_2$ at the beginning of charging. Since 633LLS has the least amounts of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_2$, it recorded the lowest capacity in this region, compared to others. This is then followed by a plateau near 4.5 V (vs Li/Li^+) which is due to the activation of Li_2MnO_3 . All the LLS material had the same amount of

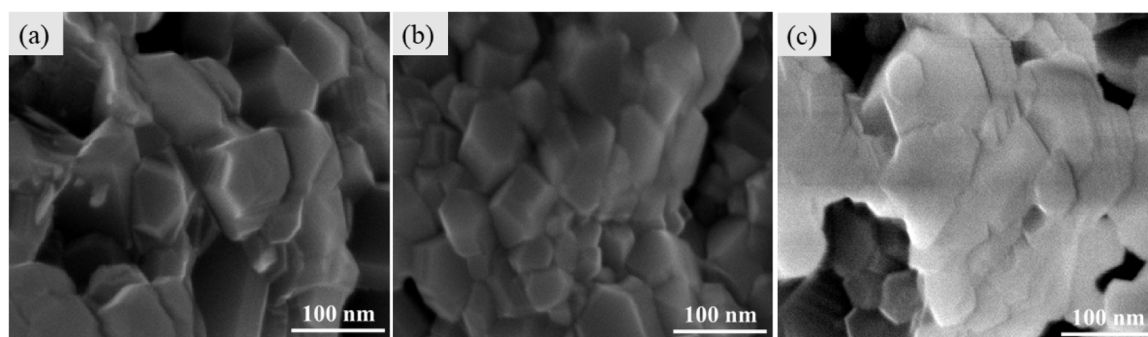


Fig. 3. SEM images of (a) 633LLS (b) 642LLS (c) 651LLS.

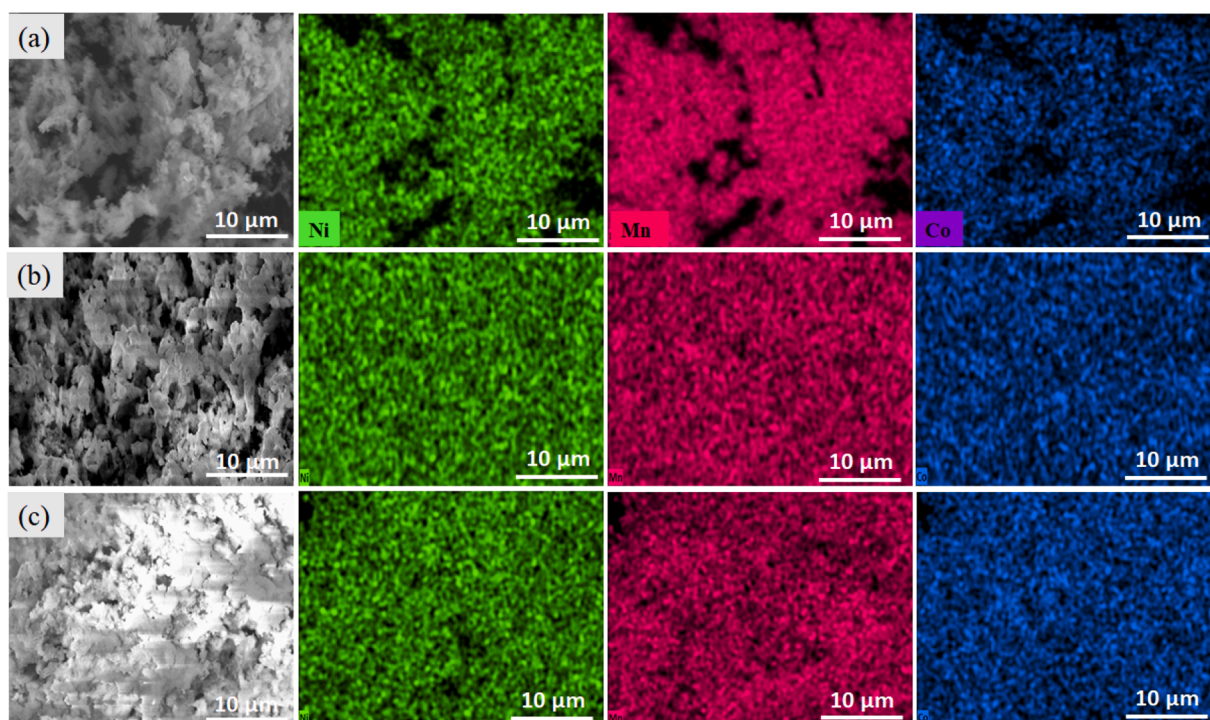


Fig. 4. SEM images, and the corresponding EDS mapping showing the distribution of Ni, Mn, and Co elements in the materials of (a) 633LLS (b) 642LLS (c) 651LLS.

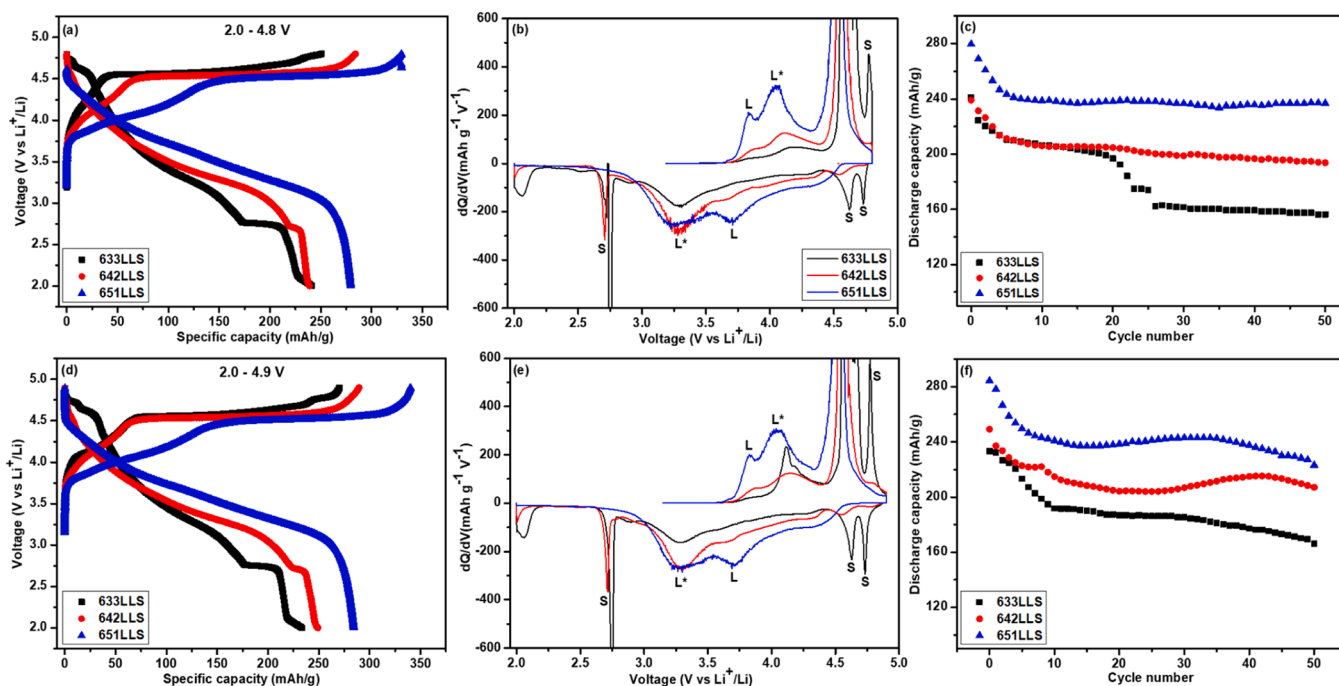


Fig. 5. The initial charge-discharge profiles (a, d), corresponding dQ/dV plots (b, e), and cycling performance (c, f). The LLS cells were cycled at 10 mA g⁻¹ over a voltage range of 2.0 – 4.8 V and 2.0 – 4.9 V at 25 °C. Note: L* is Li₂MnO₃ (C2/m), L is the LiNi_{0.5}Mn_{0.5}Co_{0.5}O₂ (R3m), and S is the spinel LiNi_{0.5}Mn_{1.5}O₄ (Fd3m) phases.

Table 2

Cycling performance results of the LLS cells cycled at 10 mA g⁻¹ and 25 °C.

Cell	633LLS		642LLS		651LLS	
Voltage window	2.0–4.8 V	2.0–4.9 V	2.0–4.8 V	2.0–4.9 V	2.0–4.8 V	2.0–4.9 V
1st cycle Discharge capacity (mAh g ⁻¹)	241.08	233.19	240.17	249.09	279.58	284.48
1st cycle Coulombic Efficiency (%)	96.12	86.26	84.10	86.01	84.88	83.63
50th cycle Discharge capacity (mAh g ⁻¹)	156.30	169.26	193.76	208.38	236.83	227.06
Capacity Retention (%)	64.83	72.58	80.68	83.66	84.71	79.82

Li₂MnO₃ and showed the same length of plateau. Only the 633LLS cell gave capacity which is due to the activation of the spinel LiNi_{0.5}Mn_{1.5}O₄ at about 4.7 V (this result is further explained by the dQ/dV plot below). The initial discharge curves show that the discharge capacity of the 633LLS, 642LLS, and 651LLS cells at 2.0 – 4.8 V (Fig. 5a) are 241.08, 240.17, and 279.58 mAh g⁻¹, with initial coulombic efficiency of 96.12 %, 84.10 % and 84.88 %, respectively (Table 2). Also, their initial discharge capacities at 2.0 – 4.9 V (Fig. 5d) are 233.19, 249.09, and 284.48 mAh g⁻¹, with initial coulombic efficiency of 86.26 %, 86.01 % and 83.63 %, respectively. The discharge curves also show the characteristic plateau at about 2.7 V which wasn't seen in the 651LLS. Notably, an increase in the spinel content reduced both the charge and discharge capacities in the LLS material. Furthermore, the initial coulombic efficiency of the LLS materials increased with increase in the spinel content. 633LLS with the highest spinel content gave the highest initial coulombic efficiency which is due to the spinel material which enhances Li⁺ penetrability/exchange in the LLS material and with the electrolyte.

The corresponding differential capacity (dQ/dV) for the initial charge-discharge plot at 2.0 – 4.8 V and 2.0 – 4.9 V are presented in Fig. 5(b) and (e), respectively. The plots revealed two main oxidation peaks around 3.8 V and 4.2 V, corresponding mainly to nickel oxidation (in LiNi_{0.5}Mn_{0.5}Co_{0.5}O₂) and manganese oxidation (in Li₂MnO₃). The 3rd peak around 4.5 V is due to the activation of Li₂MnO₃ while the peak around 4.7 V is due to Ni²⁺/Ni⁴⁺ redox in the spinel material. This peak is only present in the 633LLS material which has the highest amount of the spinel content. In addition, both the 633LLS and the 642LLS show

reduction peak at about 2.7 V confirming the plateau seen at same discharge voltage in Fig. 5(a) and (d). This result aligns with the highest discharge capacity observed for 651LLS cell.

The cycling performance of the LLS cells at 2.0 – 4.8 V and 2.0 – 4.9 V voltage windows is given in Fig. 5(c) and (f), respectively. Table 2 shows that the discharge capacities of 633LLS, 642LLS, and 651LLS cells after 50 cycles at 2.0 – 4.8 V are 156.30, 193.76, and 236.83 mAh g⁻¹, with corresponding capacity retention of 64.83 %, 80.68 %, and 84.71 %, respectively. The discharge capacities of 633LLS, 642LLS, and 651LLS cells after 50 cycles at 2.0 – 4.9 V are 169.26, 208.38, and 227.06 mAh g⁻¹, with corresponding capacity retention of 72.58 %, 83.66 %, and 79.82 %, respectively. In both voltage windows, the 651LLS cell delivers superior discharge capacities after 50 cycles while the 633LLS cell delivers the lowest discharge capacities. Additionally, the 633LLS cell gave the least capacity retentions while the 651LLS cell delivered the highest capacity retentions. Even though the 633LLS cell with the highest spinel content gave the lowest cationic disorder and highest initial Coulombic efficiency, the discharge capacity after 50 cycles were much reduced. This could be attributed to the diminishing structural stability of the material with cycling as a result of the excess spinel content. Excessive spinel doping can dilute the redox-active layered component and lead to a mismatch between the spinel and layered phases thereby reducing the capacity of the LLS cathode. It has been shown that spinel cathode delivers a capacity of less than 150 mAh g⁻¹ at above 3 V cycling [28,29].

Also, the cycling performance of the LLS cells show a decrease in

capacity with cycling which has also been observed in previous study of similar LLS cathode material [17]. However, in other studies of these LLS cathode materials (with a spinel content of $\sim 6\text{--}12\%$), mainly from Thackeray and co-workers [19,20,30], it has been reported that there is a gradual increase in capacity upon cycling. This capacity increase is due to Li^+ ions entering the empty 16c octahedral sites of the spinel phase since they cannot reinsert back to the layered-layered cathode, as explained by Thackeray and co-workers. Therefore, the decreasing capacity with cycling in these LLS cathode materials (mostly in the 633LLS and 642LLS) could be due to more than optimum amounts of spinel. Notwithstanding, it can be seen that the discharge capacities and capacity retentions of the 633LLS and 642LLS cells increased in a higher voltage window (2.0 – 4.9 V), whereas a reduction was observed in the discharge capacity and capacity retention of the 651LLS.

Fig. 6 presents the charge-discharge plots for the 5th, 10th, and 25th cycles of the LLS cells, along with their corresponding dQ/dV plots

within the voltage range of 2.0 – 4.8 V. The 651LLS cell (Fig. 6e) shows superior overlap after the 25th cycle, as compared to the 642LLS (Fig. 6c) and 633LLS cells (Fig. 6a), indicating enhanced cycling stability [30]. The discharge capacities of 633LLS cells after 5th, 10th and 25th cycles are 215, 213, and 175 mAh g^{-1} , respectively; while the 642LLS cell exhibited discharge capacities of 213, 213, and 200 mAh g^{-1} for the same cycles. The 651LLS cell gave the highest discharge capacities of 250, 245, and 245 mAh g^{-1} after 5th, 10th and 25th cycles, respectively.

The dQ/dV plots for the 5th, 10th and 25th cycles of all the LLS cells are presented in Fig. 6b, d and f. The results show that the electrochemical activity of the spinel phases (in 633LLS and 642LLS) decreases and shifts to lower voltages with cycling indicating the polarisation of the material observed earlier in the cycling performances (Fig. 5c and f). It can be seen that the dQ/dV reduction peaks of 651LLS cell (Fig. 6f) show good overlaps of the 5th – 25th cycles which accounts for the stable cycling performance. These results are consistent with the

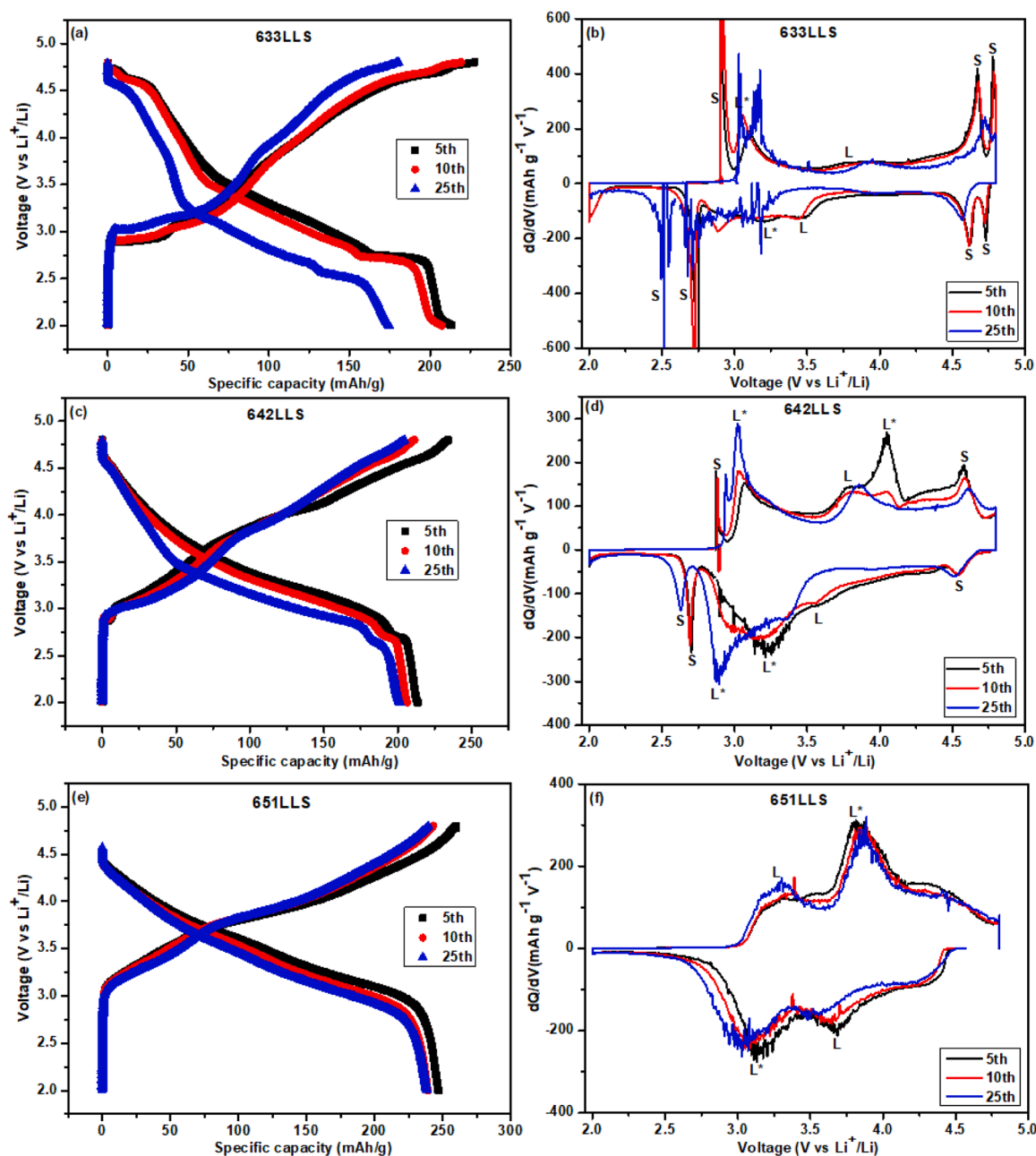


Fig. 6. Charge-discharge profiles of the LLS cells and their corresponding dQ/dV plots (a, b) 633 (c, d) 642 (e, f) 651. The cells were cycled at 10 mA g^{-1} over a voltage range of 2.0 – 4.8 V at 25°C. Note: L* is Li_2MnO_3 (C2/m), L is the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_2$ (R3m), and S is the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Fd3m) phases.

superior capacity observed for the 651LLS cell compare to the 642LLS and 633LLS cells.

Fig. 7 presents the charge-discharge plots for the 5th, 10th, and 25th cycles of the LLS cells, along with their corresponding dQ/dV plots in the voltage range of 2.0 – 4.9 V. The 651LLS cell (Fig. 7e) shows superior overlap after the 25th cycle, as compared to the 642LLS (Fig. 7c) and 633LLS cells (Fig. 7a), suggesting enhanced cycling stability [30]. The discharge capacities of 633LLS cell after 5th, 10th and 25th cycles are 225, 200, and 185 mAh g⁻¹, respectively, while the discharge capacities of 642LLS cells after 5th, 10th and 25th cycles are 225, 224, and 200 mAh g⁻¹, respectively. The 651LLS cell gave the highest discharge capacities after 5th, 10th and 25th cycles of 252, 245, and 245 mAh g⁻¹, respectively. The corresponding dQ/dV plots at the 5th, 10th, and 25th cycles for all LLS cells (Fig. 7b, d, and f) exhibit similar characteristics to those observed in the dQ/dV plots within the 2.0 – 4.8 V range (Fig. 6b, d and f).

Fig. 8a shows the influence of varying spinel content in the cathode on the rate capability of LLS cells. The charge-discharge cycles were conducted at current densities of 10, 20, 50, 100, and 200 mA g⁻¹ at 2.0

– 4.8 V, with five cycles performed at each specific current density. The average capacities of the 633LLS are 225, 190, 130, 90 and 30 mAhg⁻¹ at 10, 20, 50, 100, and 200 mA g⁻¹, respectively. The corresponding average capacities of the 642LLS are 225, 200, 175, 150 and 100 mAhg⁻¹ at 10, 20, 50, 100, and 200 mA g⁻¹, respectively; while the 651LLS cell delivered the highest capacities of 275, 225, 200, 155, and 90 mAh g⁻¹ at the same current densities. The results indicate that as the current rate increases, discharge capacity decrease due to the influence of current density on the cathode material structure, which modulates Li-ion mobility [25,28–32]. The 651LLS cells delivered the best rate capability compared to 642LLS and 633LLS at 10 – 100 mA g⁻¹ current densities. However, at the highest current density (200 mA g⁻¹), 642LLS cell delivered slightly higher capacity than the 651LLS cells. The superior rate capability of the 651LLS cell compared to the 642LLS and 633LLS cells can be attributed to its minimal spinel amount which enhances 3D Li⁺ insertion/extraction in the material. Also, the 651LLS material presented the smallest particle size and highest unit cell volume (Table 2), which can facilitate shorter diffusion pathways, enhanced electrolyte contact, and faster Li-ion transport during cycling [28]. The

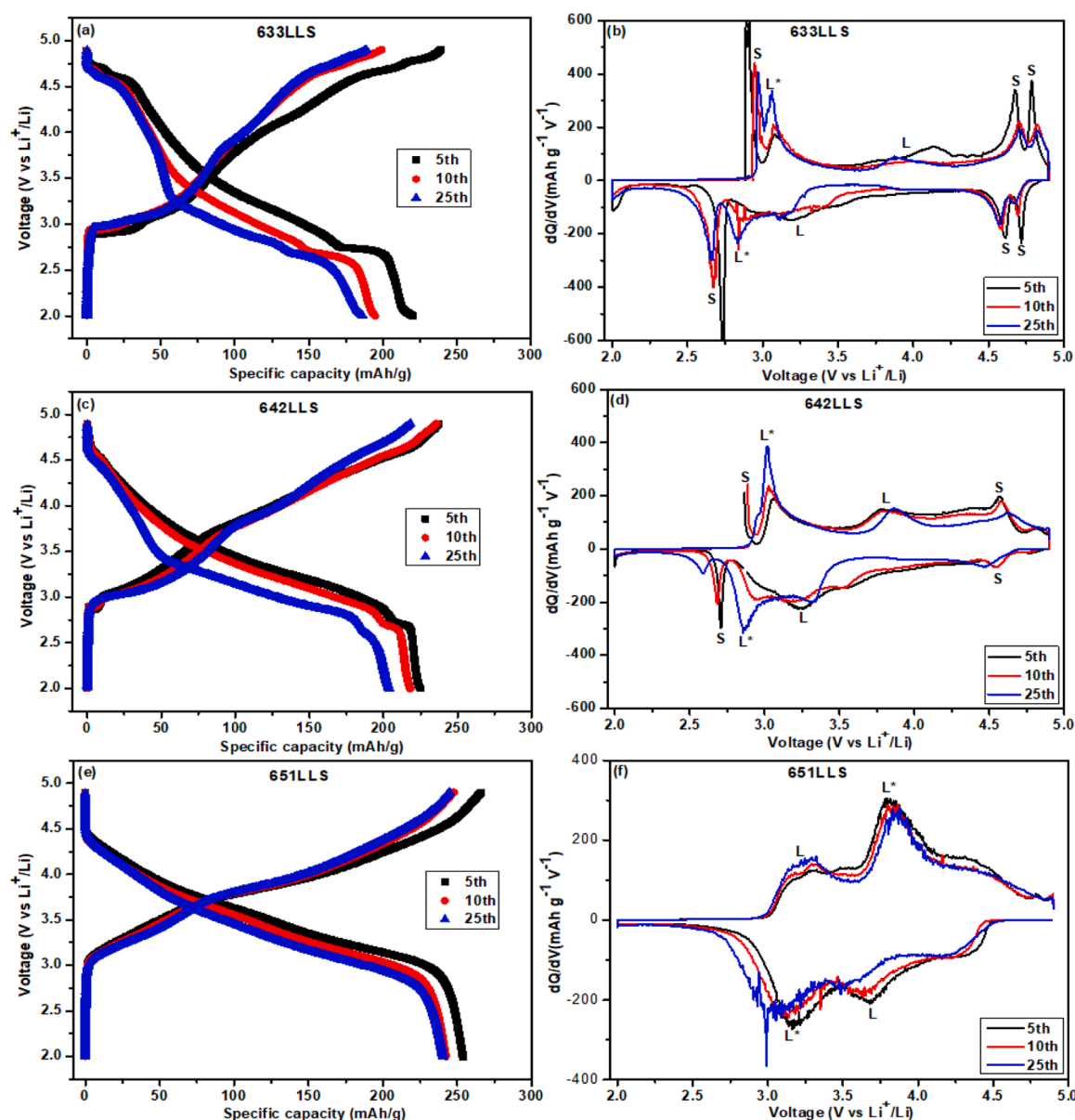


Fig. 7. Charge-discharge profiles of the LLS cells and their corresponding dQ/dV plots (a, b) 633 (c, d) 642 (e, f) 651. The cells were cycled at 10 mA g⁻¹ over a voltage range of 2.0 – 4.9 V at 25°C. Note: L* is Li₂MnO₃ (C2/m), L is the LiNi_{0.5}Mn_{0.5}Co_{0.5}O₂ (R3m), and S is the spinel LiNi_{0.5}Mn_{1.5}O₄ (Fd3m) phases.

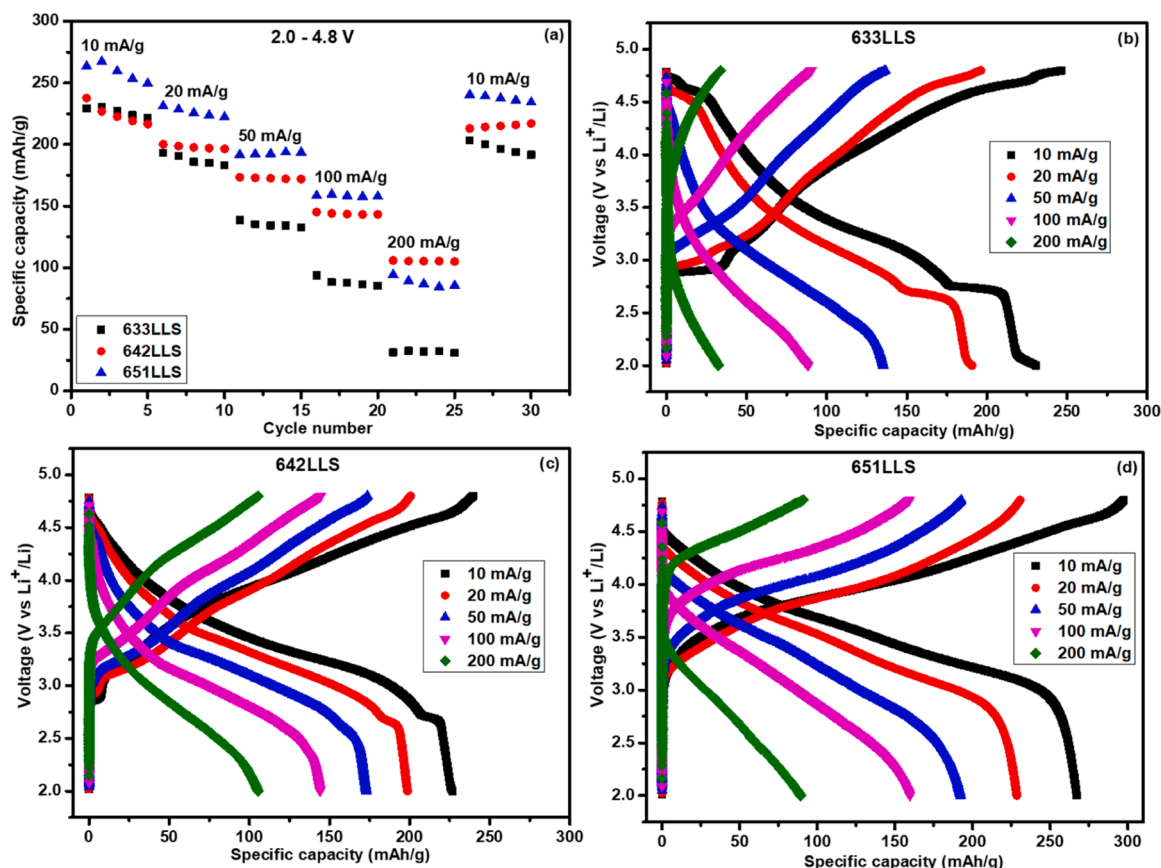


Fig. 8. (a) Rate performance of the LLS cells, (b–d) and their representative charge-discharge curves (2nd cycles) at different current densities. The cells were cycled using a voltage range of 2.0 – 4.8 V at 25°C.

651LLS cell showed superior reversibility of capacity when the current density returned to 10 mA g⁻¹ after cycling at higher current densities. However, it displays a gradual capacity decrease while the 642LLS show a gradual increase on reverting to 10 mA g⁻¹ current density. Also, the 642LLS cathode displayed the highest capacity at 200 mA g⁻¹ and an increased capacity retention when it was cycled at higher voltage window (Table 2) exhibiting potentials of a high-power cathode material. Be that as it may, the 651LLS cathode material containing 5 % spinel content, exhibited the best overall electrochemical performance, whereas the 633LLS cell with 25 % spinel content demonstrated the poorest performance. Fig. 8b–d give the charge-discharge curves of the LLS cathodes at different current densities. It can be seen that there is a disappearance of the spinel plateau (around 2.7 V) noticeable in the discharge curves of 633LLS and 642LLS cells (Fig. 8b and c) when cycled at higher than 50 mA g⁻¹. This suggests increased voltage decay and polarization at higher current density cycling. The results show that the amount of spinel in these LLS materials must be carefully tuned in relation to the operating cycling parameters to produce optimum electrochemical performance.

In our previous study on LLO material (0.5Li₂MnO₃·0.5LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂), similar to the 651LLS without the spinel content [25], an initial discharge capacity of 208 mAh g⁻¹ and a coulombic efficiency of 68.9 % were obtained when it was cycled at 10 mA g⁻¹ and 2.0 – 4.8 V. After 50 cycles, the LLO material exhibited a discharge capacity of 210.08 mAh g⁻¹ with 101 % capacity retention. Compared with the 651LLS material (in this study), these results highlight that the incorporation of a 5 % spinel component in LLO material enhances the reversible capacity and initial Coulombic efficiency. However, in the rate performance test, the LLO material displayed higher capacity at a higher current density (200 mA g⁻¹) compared to the 651LLS material. Similar behaviour was observed in the rate performance test in this

study where the 651LLS cathode displayed lesser capacity (at 200 mA g⁻¹) than the 642LLS cathode and a reduced capacity retention when it was cycled at higher voltage window (Table 2). Generally, many studies have reported the best cycling stability and capacity retention when about ~10–30 % spinel is added to LLO cathodes. However, there is trade-off with a slight initial capacity reduction (~5–10 %) which is due to the dilution of the high capacity layered phase. In this study, the 651LLS cathode had low spinel (~5 %) and delivered the best electrochemical performance at 2.0 – 4.8 V. The 642LLS cathode with moderate spinel (~15 %) showed the best cycling stability and capacity retention at 2.0 – 4.9 V even though it had reduced discharge capacities compared to the 651LLS cathode [19,20,33]. The high spinel 633LLS cathode (~25 %) displayed the least electrochemical performances of all the LLS cathodes at both voltage windows. In the low spinel 651LLS, oxygen redox dominates the transition metal redox resulting in high capacity but unstable mostly at high current density and voltage window. In the moderate spinel 642LLS, there is a balance in the oxygen and transition metal redox leading to stable and decent capacity mostly at 2.0 – 4.9 V. Lastly, in the high spinel 633LLS, transition metal redox dominates resulting in low capacity which can be unstable [19,33,34]. The initial discharge capacity and cycling stability of 633LLS cathode are comparable with the results of Kim et. al [17] which used same composite cathode composition. However, the electrochemical performance of the 651LLS and 642LLS in this work were much better than the ones reported in their report. This study shows that an appropriate spinel content in the LLO material enhances 3D Li⁺ kinetics and buffer volume changes but too much of it could disrupts the Li⁺ pathway of the layered structure and even possibly cause microcracks [19,35,36].

4. Conclusion

Layered-layered spinel and cathode materials with nominal compositions of $[0.5\text{Li}_2\text{MnO}_3 \cdot (0.5 - x)\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2 \cdot x\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4]$ ($0.05 \leq x \leq 0.25$) compositions have been synthesized using a solution combustion-mechanochemical synthesis. The structural and morphological analyses show that the 651LLS material gave the highest unit cell volume and least particle size compared with the 642LLS and 633LLS samples. The 651LLS cell with 5 % spinel content ($x = 0.05$) displays the best electrochemical performances, while the samples with 633LLS (25 % spinel content) give the poorest performance. The electrochemical results show that an optimum spinel amount is required for the desirable electrochemical performance of these LLS cathode materials. A comparative study of the performance of 651LLS in this study to our previous reports on LLO cathode (without the spinel content) shows that 651LLS improved the reversible capacity and initial Coulombic efficiency over 50 cycles. However, the 651LLS cathode displayed lower capacity at a higher current density (200 mA g^{-1}) compared to the LLO cathode. In addition, the 642LLS cathodes (15 % spinel content) gave higher capacity retention and discharge capacity when cycled at higher voltage windows and higher current density (200 mA g^{-1}) compared to the 651LLS cathode. Therefore, the electrochemical performance of the LLS material with high spinel content such as the 642LLS cathodes could be further investigated at higher voltage and current densities for high energy and long-life applications. Also, future research could focus on gradient doping of the spinel in these LLO cathodes to maximise electrochemical performance of the LLS cathodes.

CRediT authorship contribution statement

Mohammed A. Assiri: Writing – review & editing, Methodology, Funding acquisition. **Mahmoud M. Hessian:** Writing – review & editing, Validation, Resources. **Chioma V. Abiazim:** Writing – review & editing, Methodology. **Sam E. Sunday:** Writing – review & editing, Resources, Methodology. **Mkhulu K. Mathe:** Writing – review & editing, Project administration. **Ehi-Eromosele Cyril Osereme:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Conceptualization. **Samuel O. Ajayi:** Writing – review & editing, Writing – original draft, Methodology, Data curation. **Shaaban Ibrahim A:** Writing – review & editing, Investigation, Funding acquisition.

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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