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High-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes for Li-ion batteries obtained by sol–gel combustion method: effects of fuel-type and silver doping

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High-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode materials are highly desirable for the fabrication of next-generation lithium-ion batteries (LIBs). In this study, citric acid, glycine, and sucrose fuels were used to optimize the structural and electrochemical properties of LNMO materials obtained by sol–gel combustion synthesis (SCS). The experimental results showed that the type of fuel used in the SCS process influenced the enthalpy of combustion, crystallite size, morphology, cationic disorder and electrochemical properties of the LNMO materials. XRD results indicated that all the LNMO materials have a phase-pure spinel structure with the $Fd\bar{3}m$ space group. The glycine fuel composition produced LNMO material (LNMO-G) with the least crystallite size, less cationic disorder and the highest crystallinity compared with those having the citric acid fuel (LNMO-C) and sucrose fuel (LNMO-S) compositions. As a result, the LNMO-G cell delivered the highest first discharge capacity of $115.83 \text{ mA h g}^{-1}$ and retained 80.06% of its initial capacity after 200 cycles at a current density of 1C. Moreover, the LNMO-G cell had the best rate capability compared with the LNMO-C and LNMO-S cells, with a discharge capacity of 60 mA h g^{-1} at a rate of 2C between 3.50 and 5.30 V. Furthermore, Ag doping (LNMAO) improved the rate capability and Li-ion kinetics of the LNMO-G cathode material. The LNMAO cathode achieved a reversible discharge capacity of 100 mA h g^{-1} at a rate of 2C between 3.50 and 5.30 V. These findings show that LNMO cathode materials can be optimized for ultra-high-voltage ($>5.0 \text{ V}$) performance in LIBs for advanced applications.

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1. Introduction

The use of lithium-ion batteries (LIBs) has increased significantly across various sectors, including portable electronic devices, electric vehicles (EVs), and energy storage systems (ESSs). This surge in demand is driven by their extensive cycle life, superior energy density, affordability, and portability.^{1–7} Interestingly, cathode materials are the most critical components of LIBs as they determine the battery's energy density and power density and account for over 30% of the total cost.⁸ Thus, it is crucial to fabricate cathode materials that offer high capacity, long cycle life, and cost-effectiveness to ensure that they remain affordable for widespread commercialization.⁸

The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel is highly regarded for its high voltage (4.7 V) and energy density (650 Wh kg^{-1}), which are

20–30% greater than those of the commercialized LiCoO_2 and LiFePO_4 cathodes.^{9,10} LNMO can be grouped into disordered ($Fd\bar{3}m$ space group) and ordered ($P4_332$ space group) crystal structures based on calcination temperatures. The disordered structure is formed at calcination temperatures above 700°C , while the ordered structure is formed below 700°C . In the disordered structure, nickel (Ni) and manganese (Mn) occupy the 16d site, while lithium (Li) and oxygen (O) ion occupy the 8a and 32e sites, respectively. In contrast, in the ordered structure, Mn, Ni, and Li occupy the 4b, 12d, and 4c sites, respectively, while O ions are located at the 8c and 24e sites. The major difference between these two structures is that the disordered form contains Mn^{4+} along with a small amount of Mn^{3+} , while the ordered structure contains only Mn^{4+} . Thus, the presence of Mn^{3+} ions in the disordered structure enhances electronic conductivity, improves Li^+ ion diffusion pathways and offers better electrochemical performance than that of the ordered structure.^{11,12}

The spinel structure offers a 3D diffusion channel for lithium ions; thus, it aids the rapid extraction–insertion of lithium ions during LIB operation. The higher the mobility of the ions, the higher the electrical conductivity, the better the electrochemical properties of the electrode material. Moreover, the cobalt-free

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composition of these materials significantly lowers the cost of LIBs, as cobalt is both expensive and limited in supply.^{8,13} Conversely, the LNMO material experiences transition metal (TM) dissolution, Jahn–Teller distortion, rock-salt phase transitions, and electrolyte decomposition due to side reactions during cycling.¹⁴ These limitations hinder the widespread use of LNMO materials in practical applications.¹²

Researchers have studied the relationship between synthesis methods, conditions, and the physical and electrochemical properties of the LNMO spinel materials to enhance their electrochemical performance.¹⁵ These studies show that the synthesis method directly affects the particle size, crystallite size, phase structure, and morphology of LNMO materials, which in turn significantly influences their electrochemical performance.¹⁵ Thus, different synthesis methods have been explored for LNMO materials, including the solid-state method,¹⁶ coprecipitation method,¹⁷ sol–gel preparation,¹⁸ the molten salt method,¹⁹ hydrothermal synthesis²⁰ and others.²¹ Each of these methods presents distinct advantages and limitations. The solid-state method is straightforward and easily scalable, but it typically produces large particles. Coprecipitation offers improved particle homogeneity but requires precise pH control. The hydrothermal method facilitates the formation of highly crystalline materials with well-defined morphologies, although it demands costly equipment. The molten salt method enhances the purity and diffusion properties of the synthesized materials; however, it involves complex post-synthesis washing steps to remove residual salts.

Synthesizing LNMO materials with excellent electrochemical properties for practical application remains difficult due to factors, such as impurities, the high cost of starting materials, and the complexity of the synthesis process.²¹ Thus, the sol–gel combustion synthesis (SCS) method offers an eco-friendly, facile, and highly scalable alternative for producing LNMO materials. It is characterized by high crystallinity and enhanced microstructures, which make it a promising approach for improving material properties.^{1,21,22} SCS combines the sol–gel and combustion methods, involving an exothermic, self-sustaining reaction between a solution of metal salts and a fuel, such as urea, glycine, sucrose, or citric acid, which also acts as a chelating agent. The properties of the resulting product, including specific surface area, particle size and morphology, are influenced by the fuel-to-oxidizer ratio and, more specifically, the type of fuel used.^{1,21,22}

Furthermore, doping strategies, particularly with 3D TMs such as Fe, Co, and Cu, have been widely used to enhance the electrochemical performance of LNMO materials by suppressing impurities, stabilizing the crystal structure, and enhancing conductivity.^{23,24} However, fewer studies report doping LNMO materials with 4D TMs, such as Ru and Ag. Due to the larger radius of the 4D orbitals than the 3D orbitals, they overlap more effectively with oxygen 2p orbitals, which enhances the crystal structure and improves cycling performance.^{23,24} Notably, fuels such as citric acid, glycine, and sucrose have been previously used in the combustion synthesis of LNMO materials.^{21,25,26} However, in this study, we present the first direct comparison of the effects of these fuels on the structural and electrochemical

performance of LNMO cathode materials. The different fuels yielded LNMO cathodes with different microstructural and morphological properties, leading to differences in their electrochemical performance. In addition, the obtained LNMO cathode materials were electrochemically tested at ultra-high voltage windows of 3.50–4.98 V and 3.50–5.30 V, which is lacking in most reports in the literature. Finally, we studied the effect of silver (Ag) doping as a strategy to optimize the structural and electrochemical performance of the LNMO cathode materials. These results show that glycine fuel produced LNMO materials with optimal structural properties, resulting in its superior electrochemical performance.

2. Materials and methods

2.1. Materials

LiNO₃ (Suprapur, purity ≥99%), C₄H₆MnO₄·4H₂O (Sigma-Aldrich, purity ≥99%), C₆H₁₀O₈ (EMSURE ACS), Ni(NO₃)₂·6H₂O (Alfar Aesar-Puratronic, purity ≥99%), C₂H₅NO₂ (Sigma-Aldrich ≥99%), C₁₂H₂₂O₁₁ (Sigma-Aldrich, purity ≥98%), PVDF binder (Solvay Solef 6020), carbon black (TIMCAL Super C65), and 1-methyl-2-pyrrolidone (Merck EMPLURA) were used in the experiments.

2.2. LNMO synthesis

The LNMO powders were synthesized by the sol–gel combustion method using citric acid, glycine or sucrose as a fuel in stoichiometric ratio with the metal nitrates. Stoichiometric amounts of LiNO₃, Ni(NO₃)₂·6H₂O, Mn(C₂H₃O₂)₂·4H₂O, and C₆H₁₀O₈ were dissolved in 20 mL of distilled water and stirred magnetically at 80 °C to form a viscous gel. This gel was placed on a hot plate preheated to 300 °C to produce auto-combusted powders. The powders were annealed at 800 °C for 10 hours in a muffle furnace using a heating rate of 2 °C min^{−1} and then cooled to room temperature. The resulting powder, which was well mixed, was labelled LNMO-C and used for further characterization. It is important to note that 5% stoichiometric excess of the LiNO₃ salt was used to make-up for lithium loss during annealing. The same procedures were used in the synthesis of LNMO-G and LNMO-S powders by employing glycine and sucrose as fuels, respectively, in place of citric acid fuel. In addition, the same procedures were followed for glycine-assisted sol–gel combustion synthesis of Ag-doped LNMO (LNMAO), in which 0.102 g of AgNO₃ was added to stoichiometric amounts of LiNO₃, Ni(NO₃)₂·6H₂O, Mn(C₂H₃O₂)₂·4H₂O, and C₆H₁₀O₈.

2.3. Characterization

Thermogravimetric analysis (TGA) was conducted on the precursor gels for LNMO-C, LNMO-G, and LNMO-S materials using a Netzsch Jupiter instrument at 449 °C. The measurements were made in nitrogen over a temperature range of 30–1000 °C, with a heating rate of 3 °C min^{−1}. The elemental compositions of the LNMO-C, LNMO-G, and LNMO-S powders were determined using ICP-OES (iCAP 7600DUO). The phase composition and crystal structures of the synthesised LNMO-C,

LNMO-G, and LNMO-S materials were determined by powder X-ray diffraction (STOE STADI MP, Cu-K α radiation). Moreover, the local structures of the LNMO-C, LNMO-G, and LNMO-S powders were analyzed by Raman spectroscopy using a Horiba LabRAM Evolution HR microscope equipped with a 632.81 nm HeNe solid-state excitation laser (17 mW), a 100 $\times$ objective, and 600 grooves per millimetre grating. Furthermore, the morphology of the LNMO-C, LNMO-G, and LNMO-S powders was determined by scanning electron microscopy (Zeiss Merlin GEMINI 2).

2.4. Electrochemical tests

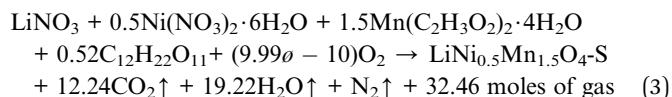
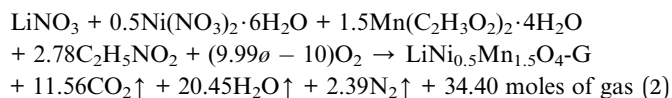
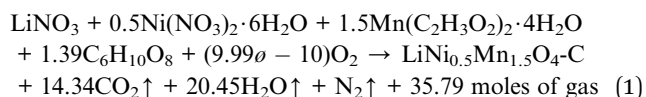
The slurries of the LNMO samples were formed by mixing the active materials (80%), carbon black (10%), and polyvinylidene fluoride binder (10%) in 1-methyl-2-pyrrolidone solvent. Subsequently, the slurries formed were coated on a cleaned aluminium foil (with a wet thickness of 200 μm), dried and cut into 12 mm circular diameter discs to be used as working electrodes, which gave an electrode loading of 2.3–2.6 mg cm^{-2} . The CR2032 coin cells were assembled in an MBraun Ar-filled glovebox using the working electrode discs as the cathodes, lithium metal foil as anodes, separated by 16 mm Celgard 2325, and 1 M lithium hexafluorophosphate in 1:1 v/v ethylene carbonate/dimethyl carbonate (LP30 selectylite, BASF) as the electrolyte. The galvanostatic cycling tests were performed in the 3.5–4.98 V and 3.5–5.30 V ranges on a Biologic VMP3 potentiostat at 25 $^{\circ}\text{C}$. The EIS tests were performed at frequencies between 1 MHz and 1 Hz with a 10 mV-amplitude AC signal.

3. Results and discussion

3.1. Thermodynamic analysis of the sol-gel combustion synthesis of LNMO materials

In combustion synthesis, the type of fuel influences the combustion reaction mechanism, volume of gases produced, and the size distribution, crystallinity, porosity and texture of the synthesized materials.^{1,22} In this study, citric acid, glycine and sucrose fuels, which also acted as chelating agents, were used in the SCS of LNMO materials. Our previous studies^{1,18} have shown that the use of stoichiometric fuel composition in SCS results in violent reactions, leading to the loss of some powder. Therefore, a fuel-rich environment was created for the SCS of LNMO powders by replacing manganese nitrate salt with manganese acetate to achieve excess reducing valency based on propellant chemistry calculations. Moreover, the fuel-rich condition helped in the reduction of the exothermicity of the combustion reactions.

Under equilibrium conditions, the complete SCS of LNMO materials assisted by the different fuels (in fuel-rich compositions) can be represented by eqn (1)–(3).



Since fuel-rich compositions were used for all the reactions, $\theta > 1$ is applicable to eqn (1)–(3). The fuel-rich condition refers the ratio at which the quantity of oxygen in the combustible mixture is lower than that required for complete combustion of the fuel, and so, a portion of atmospheric oxygen would be needed for completion of the reaction.²⁷

The different fuel-assisted reactions will present different mechanisms for the combustion reactions, as shown in eqn (1)–(3). The enthalpy of the combustion reactions can be calculated theoretically based on thermodynamic principles using eqn (4):

$$\Delta H_{\text{combustion}} = \left(\sum n\Delta H_f \right)_{\text{products}} - \left(\sum n\Delta H_f \right)_{\text{reactants}} \quad (4)$$

where $\Delta H_{\text{combustion}}$ is the enthalpy of the combustion reaction, n is the number of moles, and ΔH_f is the heat of formation. The thermodynamic data of the reactants and gaseous by-products in the combustion reactions are presented in Table S1. The enthalpy of the formation of LNMO is constant throughout the combustion process due to the lack of thermodynamic data. Therefore, the enthalpy of combustion for the synthesis of LNMO can be calculated using the data presented in Table S1 and eqn (1)–(4).

The influence of fuel type on the enthalpy of the combustion reaction ($\Delta H_{\text{combustion}}$) and the quantity of gases produced during the combustion reaction are shown in Table S2. Significant differences were observed in the $\Delta H_{\text{combustion}}$ values of the combustion reactions producing the LNMO-C, LNMO-G, and LNMO-S samples. The citric acid fuel gave the highest $\Delta H_{\text{combustion}}$ value ($-6463.33 \text{ kJ mol}^{-1}$), while the glycine fuel gave the lowest $\Delta H_{\text{combustion}}$ value ($-6046.13 \text{ kJ mol}^{-1}$). Usually, the combustion reaction with glycine is highly exothermic and violent. However, the fuel-rich condition reduced the exothermicity of the reaction, which is particularly recommended for glycine-assisted combustion. Moreover, the NH_2 group present in glycine lowered the $\Delta H_{\text{combustion}}$ compared with the carbohydrate-based fuels (citric acid and sucrose). Citric acid combustion produced 35.79 moles of gases, while sucrose-assisted combustion produced 32.46 moles of gases, which was the least. The result showed that citric acid-assisted combustion gave the highest $\Delta H_{\text{combustion}}$ and the highest amount of evolved gas. These could increase the crystallinity and porosity of the LNMO product compared with the ones obtained using the other fuels.

3.2. Thermogravimetric analysis of the LNMO precursor gels

TGA analyses of the LNMO precursor gels were carried out to study the effect of the different fuel types on the combustion process, and the results are presented in Fig. 1. The first TGA

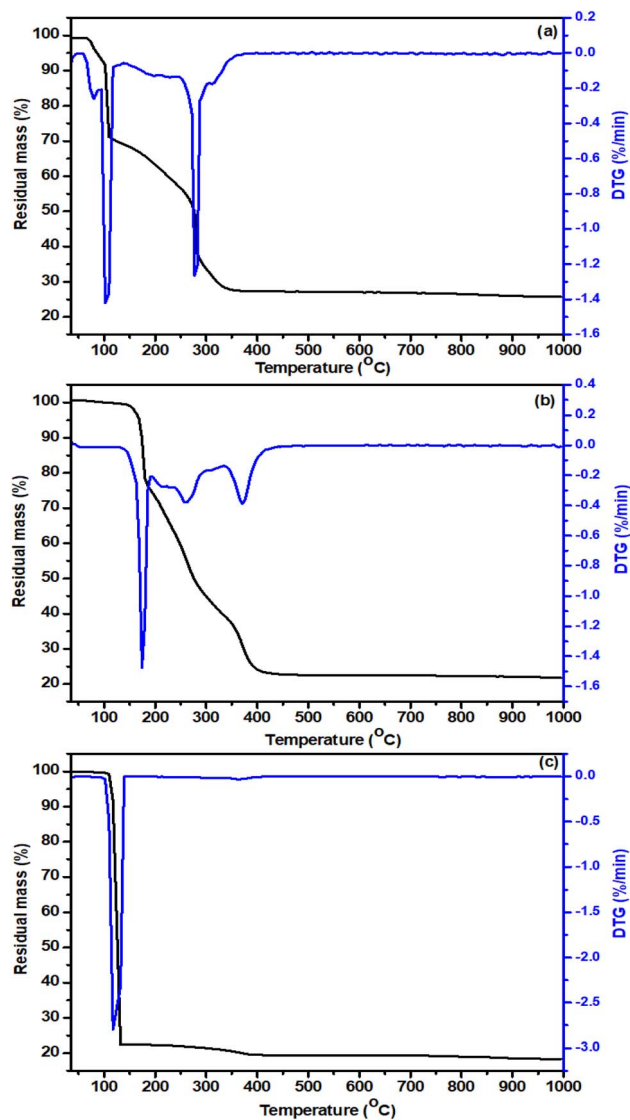


Fig. 1 TGA curves of the (a) LNMO-C precursor gel, (b) LNMO-G precursor gel and (c) LNMO-S precursor gel.

mass losses for LNMO-C, LNMO-G, and LNMO-S were 28%, 25%, and 73%, corresponding to their sharp DTG exothermic peaks at 103 °C, 173 °C and 120 °C, respectively. These losses are attributed to the evaporation of water and organic content from the gels.²² Notably, a single mass loss was observed for the LNMO-S precursor gel, which might be attributed to the poor chelating property and high carbon content of sucrose compared with citric acid and glycine fuels. However, a second mass loss of 44% and 35% was observed for LNMO-C and LNMO-G, related to the DTG exothermic peaks at about 280 °C and 260 °C, respectively. These sharp weight losses indicate the decomposition of the metal nitrate-fuel gels during the combustion reaction. A third mass loss of 17% was observed for the glycine fuel composition. Overall, the total mass losses were 72%, 77% and 73% for LNMO-C, LNMO-G, and LNMO-S, respectively. Furthermore, no mass loss was observed for the samples above 400 °C, suggesting total thermal decomposition

Table 1 Elemental analysis of the synthesized LNMO powders

Sample	Transition metal (TM)				Li + TM	Li/TM
	Li	Mn	Ni	TM		
Target composition	1.00	1.50	0.50	2.00	3.00	0.50
LNMO-C	0.96	1.53	0.48	2.01	2.97	0.48
LNMO-G	1.04	1.51	0.49	2.00	3.04	0.52
LNMO-S	1.03	1.51	0.49	2.00	3.03	0.52

of the gels.^{28,29} Like the thermodynamic considerations of the combustion processes, the fuel type greatly influenced the thermal decomposition of the metal nitrates-fuel precursor gels resulting in the LNMO materials.²²

3.3. Elemental analysis

The elemental compositions of the synthesized LNMO materials were evaluated by inductively coupled plasma optical emission spectroscopy, and the results are presented in Table 1. The Li, Mn, Ni, Li + TM, and Li/TM content in LNMO-G, and LNMO-S was close to the nominal composition of LNMO. Notably, the amounts of Li and Li/TM content in the LNMO-C material has less than the stoichiometric amount of Li and Li/TM which could affect the electrochemistry of the material. The LNMO-G and LNMO-S samples displayed Li and Li/TM amounts slightly higher than the stoichiometric amounts, which could be due to the additional 5% LiNO₃ salt used. These results show that the citric acid fuel used in the synthesis of the LNMO-C sample facilitated the removal of Li from the material, affecting its surface characteristics and electrochemistry.

3.4. Structural analysis

The X-ray diffraction (XRD) patterns of the sol-gel combustion-prepared LMNO materials are presented in Fig. 2. The peaks of

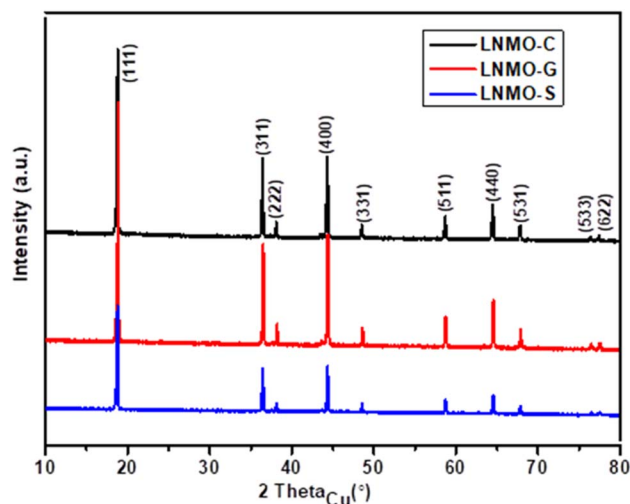


Fig. 2 XRD patterns of the calcined LNMO products after heat treatment at 800 °C for 10 h.

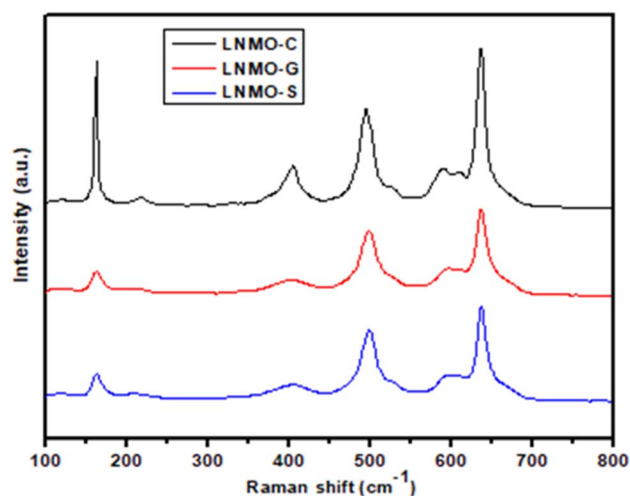
Table 2 Crystallographic parameters obtained from the XRD patterns

Sample	LNMO-C	LNMO-G	LNMO-S
Space group	<i>Fd3m</i>	<i>Fd3m</i>	<i>Fd3m</i>
<i>a</i> (Å)	8.167	8.165	8.164
<i>V</i> (Å ³)	544.68	544.38	544.14
Crystallite size, <i>D</i> (nm)	49.17	47.44	52.20
<i>I</i> ₍₃₁₁₎ / <i>I</i> ₍₄₀₀₎	0.99	1.03	0.97

all the samples were indexed to a cubic spinel-type structure with the *Fd3m* space group (JCPDS card no.: 80-2162). The XRD peaks of all the three samples were sharp with no detectable impurities, indicating the crystalline nature of all the synthesized LNMO materials.¹² However, the LNMO-G sample gave the highest crystalline peaks, while the LNMO-S sample gave the least. The *I*₍₃₁₁₎/*I*₍₄₀₀₎ ratio of LNMO-C, LNMO-G and LNMO-S were 0.99, 1.03 and 0.96, respectively, suggesting the better stability of the synthesized samples.^{30,31} These results show that the LNMO-G sample had the least cationic disorder. The

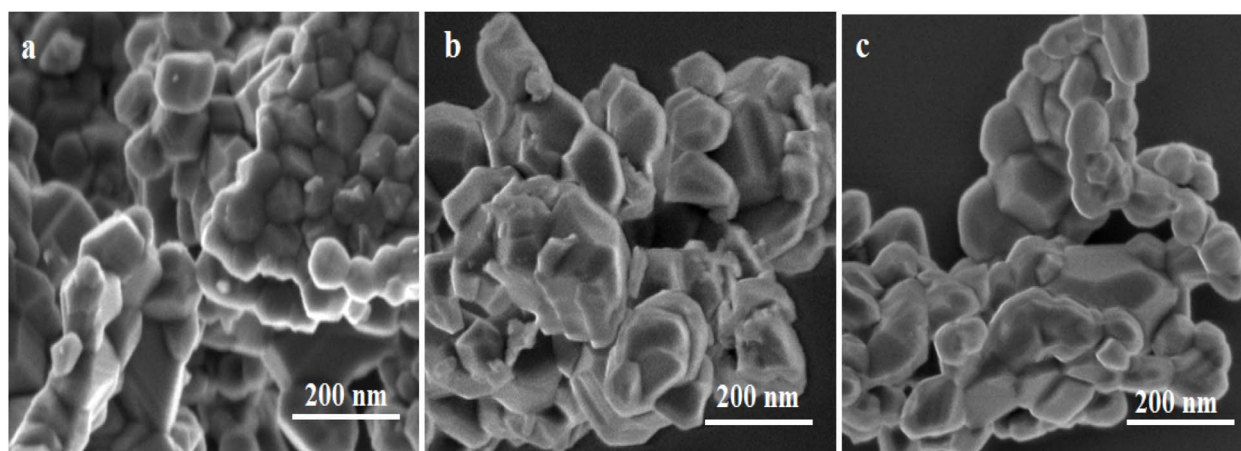
calculated lattice parameters (*a*), cell volume (*V*) and average crystalline size (*D*) were 8.167 Å, 544.68 Å³ and 49.17 nm, respectively for LNMO-C; 8.165 Å, 544.38 Å³ and 47.44 nm for LNMO-G; and 8.165 Å, 544.14 Å³ and 52.20 nm for LNMO-S, respectively, as presented in Table 2. These results show that fuel type had no substantial effect on the lattice parameters or cell volume since the values obtained for the three samples are comparable. However, the type of fuel used affected the crystallite size of the synthesized LNMO materials, with sucrose aiding the formation of the largest LiNi_{0.5}Mn_{1.5}O₄ crystallite size, while glycine resulting in the smallest crystallite size.

The Raman spectra of the sol-gel combustion-prepared LNMO materials are shown in Fig. 3. It shows two prominent peaks at 645 cm⁻¹ and 500 cm⁻¹, attributed to Mn–O vibrations within the MnO₆ octahedron and Ni–O bond stretching vibrations, respectively. These peaks are unique characteristics of the *Fd-3m* space group, suggesting that the synthesized sample exhibited disorder structures.^{32,33} Additionally, weak signals were observed at 161 cm⁻¹ and 402 cm⁻¹, corresponding to the characteristic peaks of the *P4₃32* structure.^{32,33} This suggests that the samples possessed small proportions of ordered structures. Notably, the LNMO-C sample, which has the most intense peaks, has the least disordered structure compared with the LNMO-G and LNMO-S samples with comparable peak intensity.

**Fig. 3** Raman spectra of the calcined LNMO products.

3.5. Morphological characterization

The effect of the type of fuel used for the SCS of LNMO particles was investigated using SEM, and their micrographs are presented in Fig. 4. The LNMO-C sample presented a smooth, homogeneous, uniform, and faceted surface, while the LNMO-G and LNMO-S had rough surfaces, irregular particle shapes and slightly larger agglomerated particles. This result shows that the type of fuel used in SCS has a substantial impact on the morphologies of the LNMO powders. Fig. 5 shows the SEM micrographs and EDX mappings of LNMO-C and LNMO-G, revealing the homogeneous distribution of constituent elements in the synthesized LNMO materials.

**Fig. 4** SEM images (a) LNMO-C, (b) LNMO-G and (c) LNMO-S.

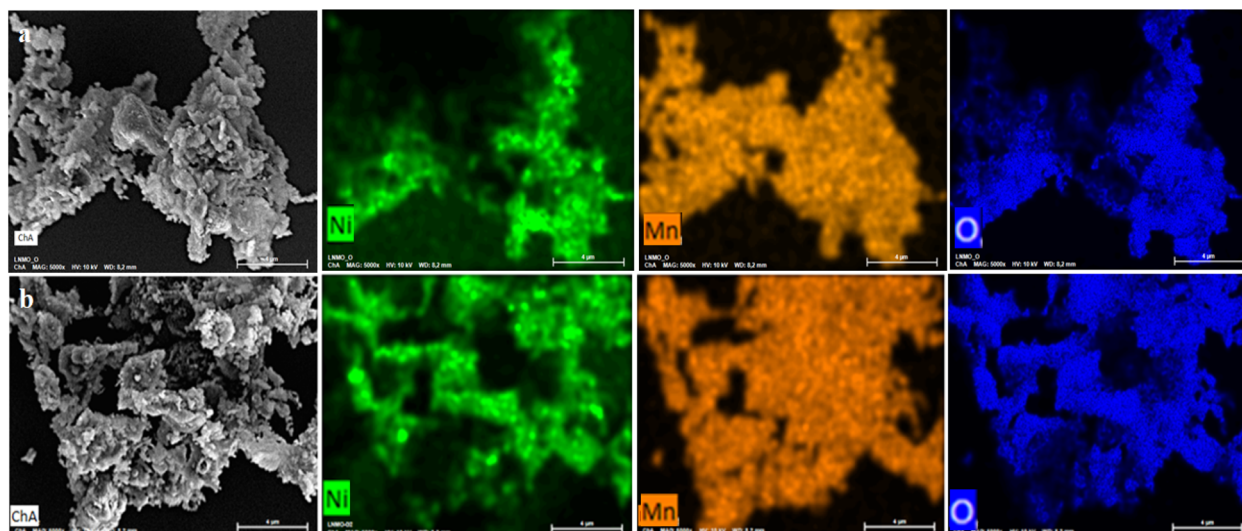


Fig. 5 SEM/EDX images of (a) LNMO-C and (b) LNMO-G.

3.6. Electrochemical performances of the LNMO cells

The effect of different fuels used for the SCS of LNMO on their electrochemical performance was investigated. The initial charge–discharge profiles, corresponding dQ/dV plots, and cycling performance of the LNMO cells cycled at 147 mA g^{-1} (1C) using 3.50–4.98 V and 3.50–5.30 V voltage windows are shown in Fig. 6. The cycling performance capacities of the

LNMO cells cycled at different current densities and voltage windows are given in Table 3. The initial charge–discharge plots display typical plateaus of the disordered LNMO ($Fd\bar{3}m$) space group.¹² Fig. 6a shows that the initial discharge capacity of the LNMO-C, LNMO-G, and LNMO-S cells between 3.5 and 4.98 V were 107.96, 72.43, and $10.38 \text{ mA h g}^{-1}$, with initial coulombic efficiency (ICE) values of 121.75%, 89.16% and 67.76%, respectively (Table 3). Moreover, their initial discharge

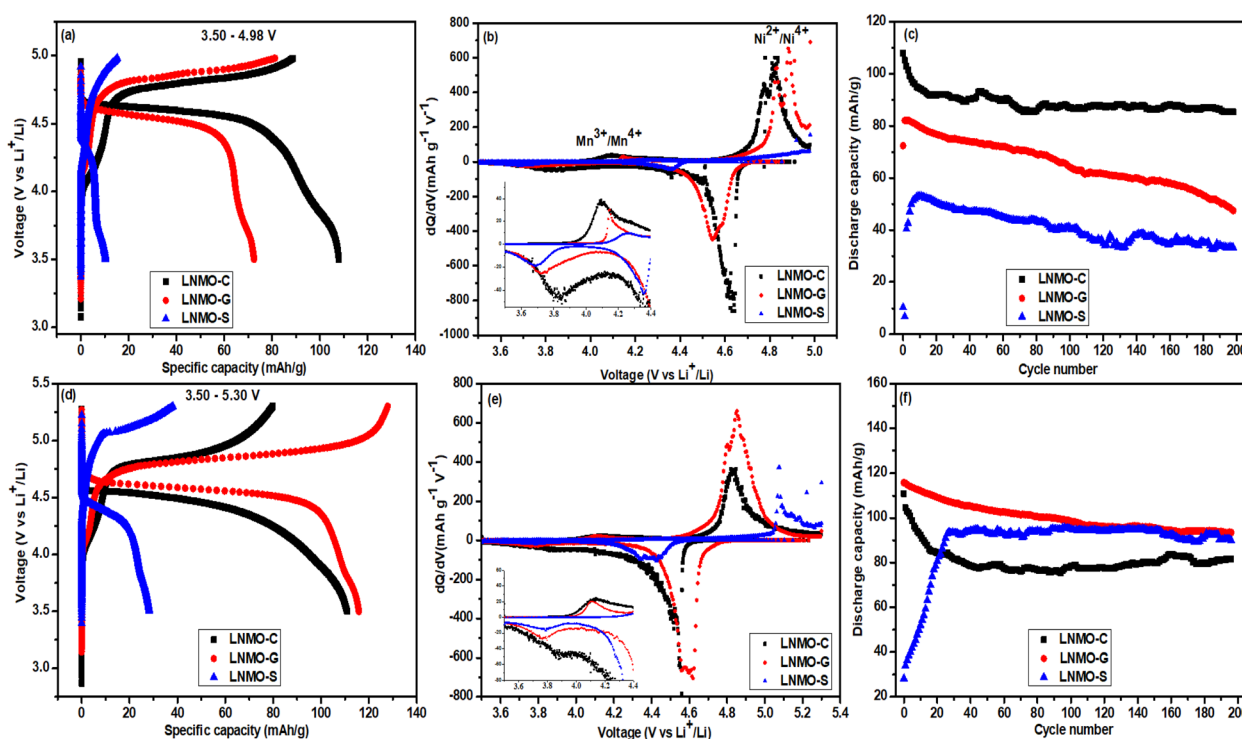


Fig. 6 Initial charge–discharge profiles (a and d), corresponding dQ/dV plots (b and e), and cycling performance (c and f). The insets in the dQ/dV plots in (b and e) show enlarged peak in the 3.6–4.4 V potential window, which is due to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. The LNMO cells were cycled at 1C (146 mA g^{-1}) over voltage ranges of 3.50–4.98 V and 3.50–5.30 V at 25°C .

Table 3 Cycling performance of the LNMO cells cycled at different current densities and voltage windows at 25 °C

Cathode	LNMO-C			LNMO-G			LNMO-S		
	3.50–4.98 V		3.50–5.30 V	3.50–4.98 V		3.50–5.30 V	3.50–4.98 V		3.50–5.30 V
Current density	1C	1C	0.2C	1C	1C	0.2C	1C	1C	0.2C
1st cycle discharge capacity (mA h g ⁻¹)	107.96	110.87	94.70	72.43	115.83	111.25	10.38	28.28	76.41
1st cycle coulombic efficiency (%)	121.75	138.96	89.16	89.16	90.60	88.41	67.76	74.08	79.00
200th cycle discharge capacity (mA h g ⁻¹)	85.36	81.68	—	47.39	92.73	—	34.06	92.02	—
Capacity retention (%)	79.07	73.67	—	65.43	80.06	—	328.13	325.39	—

capacities between 3.5 and 5.30 V (Fig. 6d) were 110.87, 115.83, and 28.28 mA h g⁻¹, with initial coulombic efficiency values of 138.96%, 90.60% and 74.08%, respectively. The anomalously high ICE (>100%) observed for the LNMO-C sample can be attributed to the side reactions occurring during the first charge cycle, including surface oxygen loss and activation of the Mn³⁺/Mn⁴⁺ redox couple along with the Ni²⁺/Ni⁴⁺ redox couple.³⁴ Chemicals such as oleic and boric acids have been used to treat Li-rich, Mn-based cathode materials as this facilitates H⁺/Li⁺ exchange.^{35,36} This exchange forms oxygen vacancies on their surfaces and increases the amounts of Mn³⁺, thereby activating the Mn³⁺/Mn⁴⁺ redox, which provides extra capacity and increases the ICE.^{34,35} The elemental analysis of the LNMO samples (Table 1) shows that only the LNMO-C sample had lesser than the stoichiometric amount of Li, even with the additional 5% LiNO₃ salt used during synthesis, indicating the presence of oxygen vacancies in the material. Further, the LNMO-C sample had slightly higher amounts of Mn than the other samples. Therefore, it is clear that citric acid, which was used in the synthesis of LNMO-C, activated higher Mn³⁺/Mn⁴⁺ redox activity and disproportionation in the material, thereby increasing its initial discharge capacity and ICE to >100% compared with LNMO-G and LNMO-S cathodes.

It is worth noting that increasing the voltage range increased the initial discharge capacity and ICE of all the synthesized LNMO materials. The corresponding differential capacity (dQ/dV) of the initial charge–discharge plot obtained at 3.50–4.98 V and 3.50–5.30 V voltage windows are presented in Fig. 6b and e, respectively. The capacity of the synthesized LNMO materials is predominantly influenced by the Ni redox reaction, as evidenced by the stronger peak intensities observed at around 4.7 V compared to the peak at around 4.1 V.³⁵ In principle, all of the Mn in LNMO are supposed to be in the +4 oxidation state. However, trace Mn³⁺ can still be present in pristine LNMO due to the formation of oxygen vacancies and impurity phases during synthesis.³⁶ The dQ/dV plots revealed notable redox peaks at around 4.7 V, typical of LNMO cathodes due to the Ni²⁺/Ni⁴⁺ redox couple.³⁴ In addition, LNMO-C displayed peaks at around 4.1 V, which can be attributed to Mn³⁺/Mn⁴⁺ redox activity, providing extra capacity and increasing its ICE (see the inset in Fig. 6b and e). This peak was marginal in the dQ/dV plots of the LNMO-S and LNMO-G cathodes. In the higher voltage window (3.50–5.30 V), the initial discharge capacity of the LNMO-C cathode (110.87 mA h g⁻¹) was slightly lesser than

that of the LNMO-G cathode (115.83 mA h g⁻¹). This reduction in the discharge capacity of LNMO-C could be due to the higher number of Mn³⁺, which is prone to the Jahn–Teller effect at higher voltage (>4.9 V), facilitating the distortion of the crystal structure and degrading battery performance.³⁷ Furthermore, the LNMO-S cell showed very poor redox activity, mostly at 3.50–4.98 V, accounting for its poor capacity.

The cycling performance of the LNMO cells at 3.50–4.98 V and 3.50–5.30 V voltage windows is given in Fig. 6c and f, respectively. At 3.50–4.98 V, the discharge capacities of the LNMO-C, LNMO-G, and LNMO-S cells after 200 cycles were 85.36, 47.39, and 34.06 mA h g⁻¹, respectively, as given in Table 3. The LNMO-C cell delivered a superior discharge capacity after 200 cycles, while the LNMO-S cell delivered the lowest discharge capacity. This superior discharge capacity of the LNMO-C cathode is due to the additional Mn³⁺/Mn⁴⁺ redox in the material. The LNMO-G cell gave the least capacity retention of 65.43%, while the LNMO-S cell delivered an increased capacity retention of 328.13%. At a higher voltage window (3.50–5.30 V), the discharge capacities of the LNMO-C, LNMO-G, and LNMO-S cells after 200 cycles were 81.68, 92.73, and 92.02 mA h g⁻¹, with capacity retention of 73.67%, 80.06%, and 325.39%, respectively. These results show that the capacities and capacity retention of the LNMO-G and LNMO-S cells increased with increasing voltage window, while they decreased in the LNMO-C cell. As explained previously, this reduction in the LNMO-C discharge capacity could be due to the Jahn–Teller effect, which facilitates the distortion of the crystal structure and degrades battery performance.³⁷ The increase in capacities of the LNMO-G and LNMO-S cells at a higher voltage window could be due to the higher redox of the Ni mixed oxidation states (Ni²⁺ → Ni³⁺/Ni⁴⁺) and oxygen redox, which contributes extra capacity.³⁸ As shown by the elemental analysis (Table 1), the LNMO-G and LNMO-S samples with higher than stoichiometric amounts of Li can undergo oxygen redox at high voltages, contributing to extra capacity.³⁹ In addition, at higher voltages, there is usually improved Li⁺ diffusion, which allows for more utilization of the theoretical capacity of LNMO and the formation of a more stable cathode-electrolyte interface (CEI), which reduces side reactions and improves capacity retention.⁴⁰

Furthermore, the capacity retention observed for the LNMO-S sample indicates gradual activation of this material.^{8,41} This activation can likely be attributed to the use of sucrose as a chelating agent during the synthesis of the LNMO material.

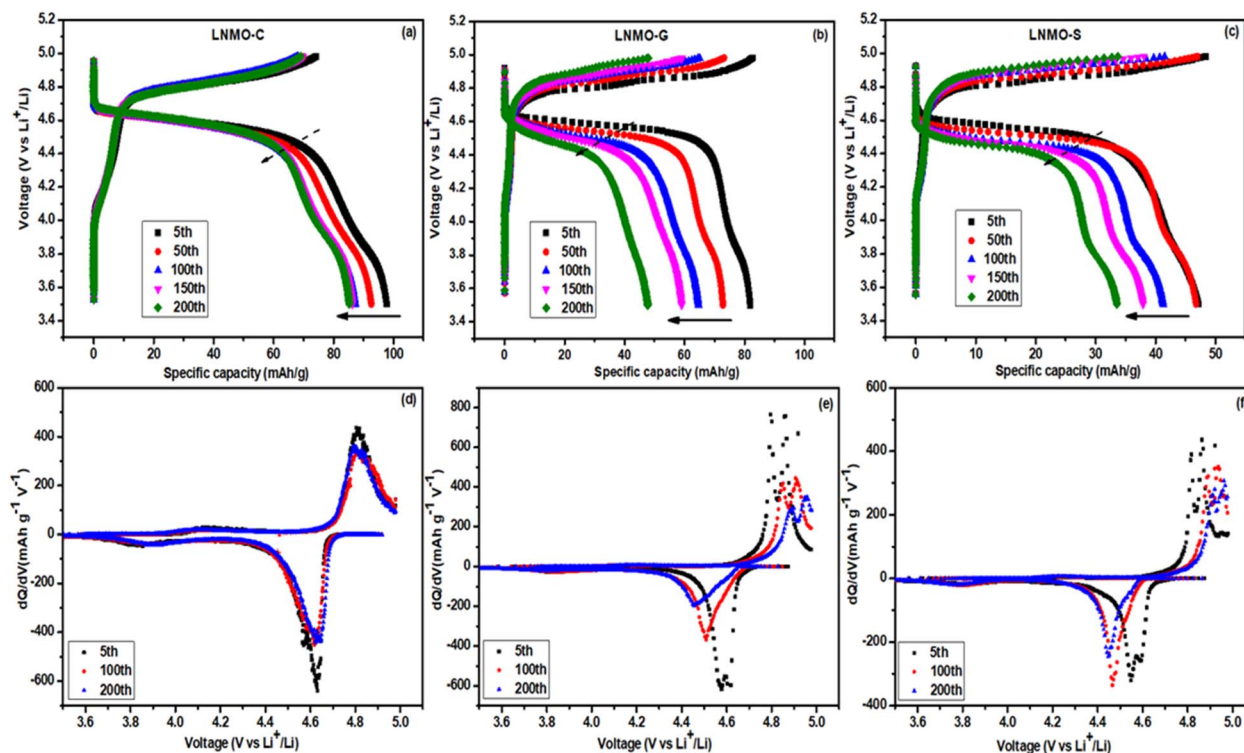


Fig. 7 Charge–discharge profiles of the LNMO cells and their corresponding dQ/dV plots: (a and d) LNMO-C (b and e) LNMO-G (c and f) LNMO-S. The cells were cycled at 1C in a voltage range of 3.50–4.98 V at 25 °C.

This chelating agent introduces higher cationic disorder and particle agglomeration, which initially leads to poor electronic conductivity and limited lithium-ion diffusion during the initial charge–discharge process, as observed in Fig. 6a. However, with continuous cycling, the lithium-ion diffusion pathways improve, and more redox-active sites become electrochemically active.⁴² This leads to a gradual increase in discharge capacity and anomalous capacity retention after 200 cycles. In addition, the large agglomerated particles of the LNMO-S sample (Fig. 4) enhance slower and uniform CEI formation, ensuring better long-term stability. However, it may suffer from slower Li^+ diffusion kinetics, thereby affecting the rate performance. These results show that the fuel type and voltage window influence the electrochemical performance of the LNMO cathodes.

Fig. 7 presents the charge–discharge plots for the 5th, 50th, 100th, 150th, and 200th cycles of the LNMO cells, along with their corresponding dQ/dV plots, in the voltage range of 3.50–4.98 V. The LNMO-C cell (Fig. 7a) shows superior overlap after long-term cycling, as shown by the arrows, compared to the LNMO-G (Fig. 7b) and LNMO-S cells (Fig. 7c). It can be seen that the coulombic efficiency (CE) of the LNMO-C cell still exceeds 100% in subsequent cycles, suggesting unconventional electrochemical behaviour of the LNMO-C cathode material that deviates from typical intercalation chemistry. Usually, $\text{CE} > 100\%$ is only expected in the first cycle due to irreversible side reactions.⁴³

The continued observation of $\text{CE} > 100\%$ in subsequent cycles implies ongoing contributions from mechanisms, such

as $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox activity. Another mechanism that can cause $\text{CE} > 100\%$ in LIBs is residual lithium from electrolyte oxidation or redox shuttle effects caused by the decomposition of the LiPF_6 -based electrolytes at high voltages, thereby generating oxidizable species, which contribute to charge capacity.⁴⁴ This mechanism might not be implicated separately for the LNMO-C cathode since $\text{CE} > 100\%$ was not observed for the LNMO-G and LNMO-S cathodes even though the same type of binders, additives, electrolyte, and cycling conditions were used for all the LIBs. Similar redox activity was observed in the dQ/dV plots of all the LNMO cells. The dQ/dV plots (Fig. 7d–f) revealed strong peaks at around 4.7 V, indicating that the Ni redox mainly accounts for capacity after the initial cycles. Like the dQ/dV plots of the initial cycle (Fig. 6b and e), a significant peak at around 4.1 V due to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple was present in the LNMO-C cathode (Fig. 7d), explaining the extra capacity recorded. This peak (at about 4.1 V) was very marginal in the LNMO-G (Fig. 7e) and LNMO-S (Fig. 7f) cathodes, which demonstrated much-reduced discharge capacity values. Furthermore, the dQ/dV plots of the LNMO-C cell (Fig. 7d) presented better reversibility, suggesting suppressed voltage decay and polarization,¹ compared to the LNMO-G (Fig. 7e) and LNMO-S (Fig. 7f) cells. The shift in reduction peaks observed for the LNMO-G and LNMO-S cells indicates less active Ni redox during cycling. This is responsible for their polarization, which reduces Li-ion kinetics during cycling.¹

The charge–discharge profiles for the 5th, 50th, 100th, 150th, and 200th cycles of the LNMO cells, along with their corresponding dQ/dV plots, obtained in the 3.50–5.30 V voltage range

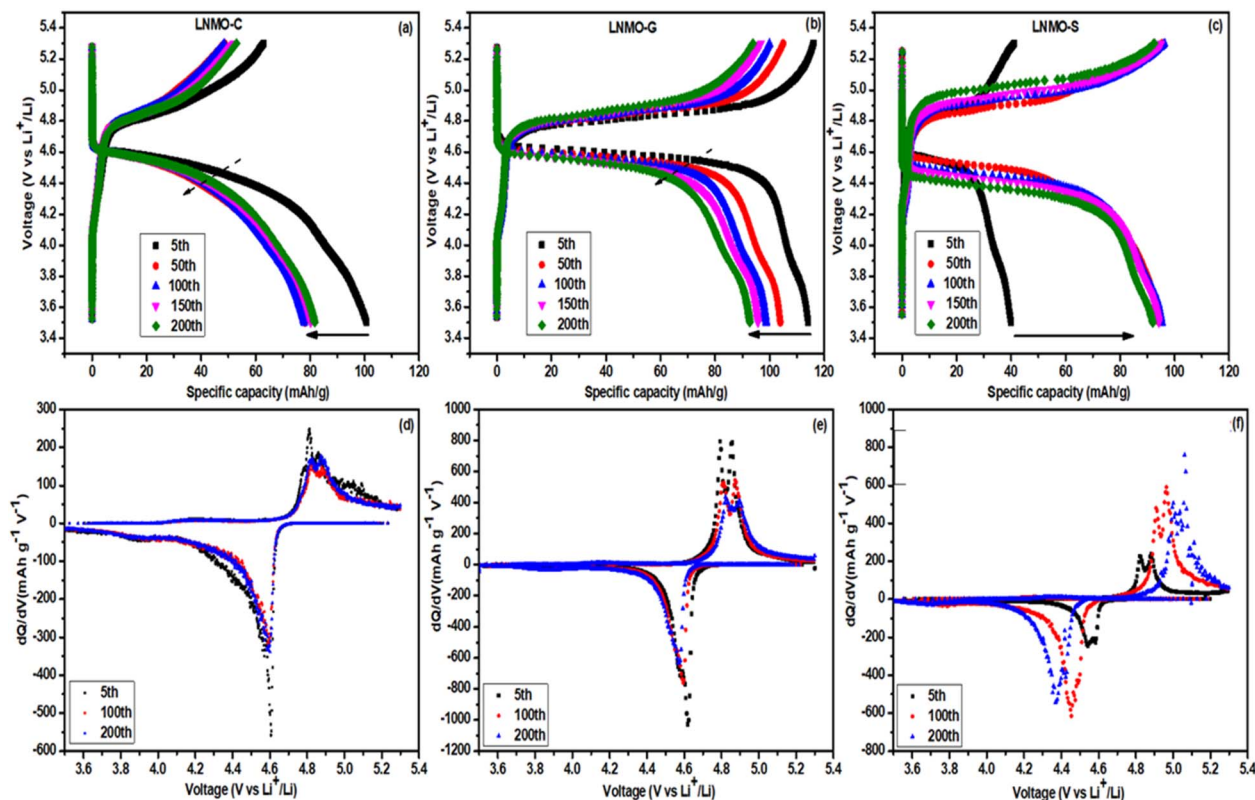


Fig. 8 Charge–discharge profiles of the LNMO cells and their corresponding dQ/dV plots: (a and d) LNMO-C (b and e) LNMO-G (c and f) LNMO-S. The cells were cycled at 1C in a voltage range of 3.50–5.30 V at 25 °C.

are presented in Fig. 8. The charge and discharge patterns of all the LNMO cells are similar and agree with the electrochemistry of LNMO, showing two distinct discharge plateaus at ~ 4.7 V and ~ 4.1 V.^{6–17} However, LNMO-G displayed the most stable plateau at ~ 4.7 V, while LNMO-C had a sloped plateau with the least discharge voltages. These differences observed in the discharge patterns of LNMO-C, LNMO-G, and LNMO-S (Fig. 8) can be explained by the distinct morphological and structural characteristics of these materials, which influence their electrochemical performance. In this higher voltage window, similar $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox activity also accounts for $\text{CE} > 100\%$. As explained previously, the reduction in the LNMO-C discharge capacity at a higher voltage window could be due to the Jahn–Teller effect, which facilitates the distortion of the crystal structure and degrades battery performance.³⁷ The dQ/dV plots of the LNMO cells showed a main redox peak at ~ 4.7 V corresponding to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ chemredox couple, while the LNMO-C cathode displayed another distinct redox peak at ~ 4.1 V due to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. At this higher voltage window, the LNMO-G cell (Fig. 8b) showed the best overlap after long-term cycling, as indicated by the arrows and the Ni reduction peaks in the dQ/dV plot (Fig. 8e), compared to the LNMO-S cell (Fig. 8c and f). The shift of the reduction peaks of the LNMO-S cell to lower voltages (Fig. 8f) indicates increased polarization of the cell with cycling, stemming from its interfacial structural instability. The dQ/dV plot of the LNMO-G cell (Fig. 8e) presented better reversibility, indicating lesser polarization

compared to the LNMO-S cell (Fig. 8f). However, the LNMO-G cell displayed higher stable discharge plateaus and voltage compared to the other cells. Generally, at a higher voltage window, the discharge capacities and capacity retention of all the LNMO cathodes increased, which might be related to the full activation of the material, electrolyte wetting of the electrode pores and increased kinetics of the Li^+ (de)intercalation process.

Fig. 9 shows the effect of the different fuels used during synthesis on the rate capability of the LNMO cells. The charge–discharge cycles were performed at current densities of 0.2C, 0.5C, 1C, and 2C within 3.0–5.3 V, with ten cycles performed at each specific current density. The average capacities of LNMO-G were 112, 103, 85, and 60 mA h g^{-1} at 0.2C, 0.5C, 1C, and 2C, respectively. The LNMO-C and LNMO-G cells delivered comparable capacities at 0.2–1C. However, at a higher current density (2C), the LNMO-G cell delivered a higher capacity and better reversibility than the LNMO-C cell. This reduction in the capacity of the LNMO-C cathode at higher current density (2C) can be attributed to Jahn–Teller effect, which facilitates the distortion of the crystal structure and degrades battery performance.³⁷ Even though the LNMO-S cell gave the least discharge capacities at all the current densities, it displayed excellent reversibility. These results indicate that as the current rate increases, the discharge capacity decreases because of the current rate on the spinel structure, which modulates Li-ion mobility.^{45,46} The superior rate capability of LNMO-G

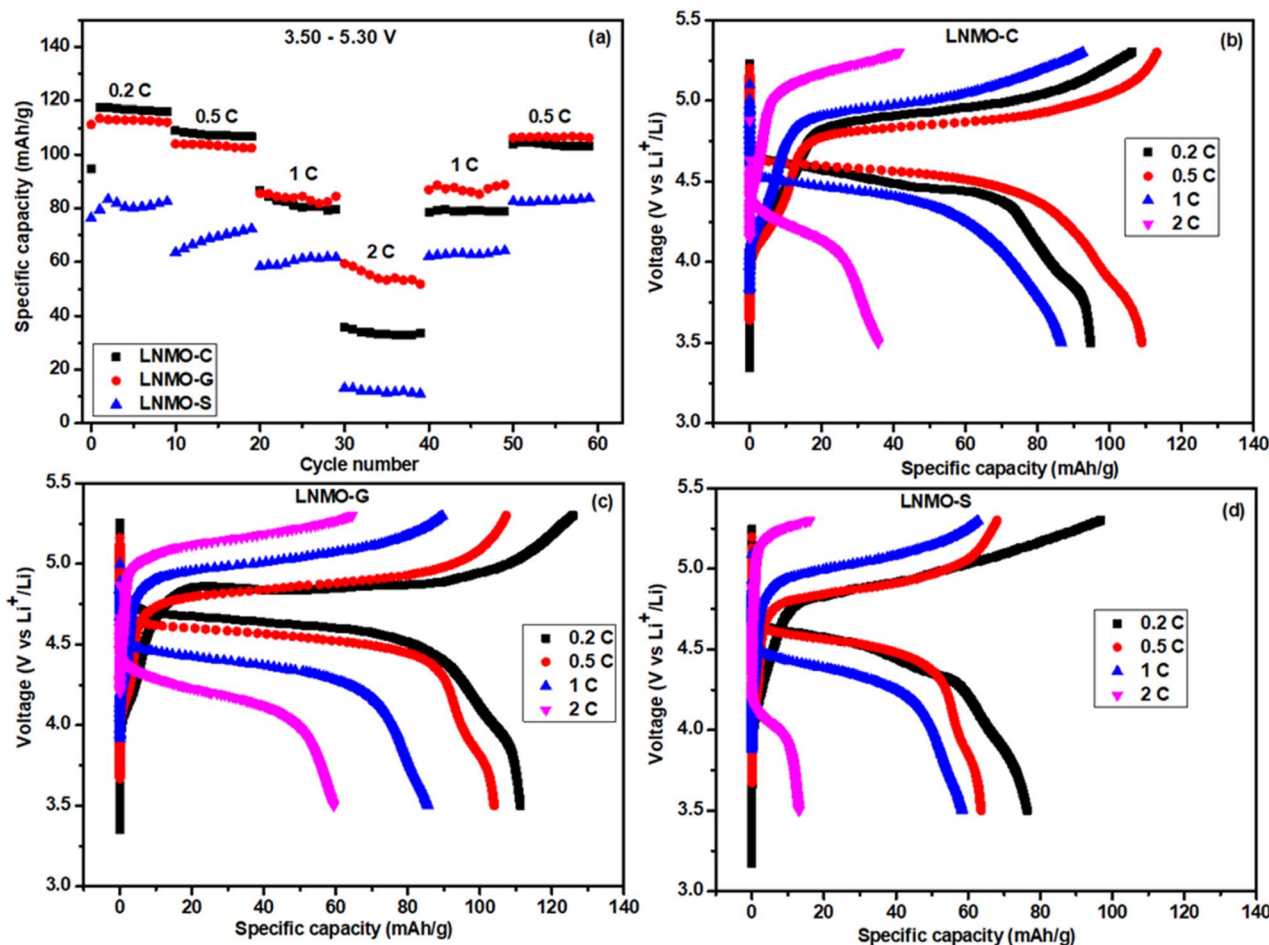


Fig. 9 Rate performance of the LNMO cells (a) and their representative initial charge–discharge curves at different current densities (b–d). The cells were cycled in a voltage range of 3.50–5.30 V at 25 °C.

compared to LNMO-C and LNMO-S can be attributed to its smaller crystallite size and the least cationic disorder (Table 2), which aids shorter diffusion pathways, improved electrolyte contacts and faster Li ion diffusion during cycling. In addition, the superior rate capacity of the LNMO-G sample could also be due to its large particles (Fig. 4). Large particles with a small surface area usually allow thinner and more uniform CEI formation on their surface compared with smaller particles with larger surface areas, thereby favoring Li kinetics. Importantly, the polarization seen in all the cells can be due to the very high voltage window used to test the cells, mostly 3.0–5.3 V, which can lead to decomposition of the electrolyte, formation of CEI and an increase in internal cell impedance.^{47,48} Furthermore, the initial charge–discharge curves of the rate performance test for the LNMO-C cell at different current densities (Fig. 9b) showed normal electrochemical behaviour for CE < 100%. Unlike the CE > 100% recorded for LNMO-C (Fig. 6, 7a and 8a), the difference here was that lower current densities (0.2C and 0.5C) were used to gradually activate the cathode in the initial cycles, which can favour the Mn³⁺ disproportionation reaction. The presence of Jahn–Teller-active Mn³⁺ can result in disproportionation reactions, with Mn²⁺ dissolution ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} +$

Mn⁴⁺) leading to capacity loss^{37,49}. At higher current densities, the electrochemical reactions occur very fast, thereby kinetically limiting the disproportionation reaction and Mn²⁺ dissolution. At a lower current density, the electrochemical rate is slower, and the Mn³⁺ disproportionation reaction can occur more readily, leading to capacity loss and irreversible structural changes, which result in CE < 100%.^{49,50} In essence, the applied current density acts as a kinetic control factor of the Mn³⁺ disproportionation reaction. Therefore, when the rate of electron transfer and ion diffusion within the cathode material is modulated, the reaction can either be promoted or suppressed, thereby impacting the electrochemical performance of these materials, especially the layered oxide cathodes.

Electrochemical impedance spectroscopy (EIS) was performed to determine the Li ion kinetics in the LNMO materials. The Nyquist plots of the uncycled and the cycled (100 cycles) LNMO cells are presented in Fig. 10. The plots show a semicircle and an oblique line (Warburg resistance) at high and low frequencies, respectively. The high-frequency semicircle is attributed to the resistance of Li ion diffusion through the solid electrolyte interphase (SEI) film, referred to as charge transfer resistance (R_{ct}). The impedance to Li-ion diffusion in the active

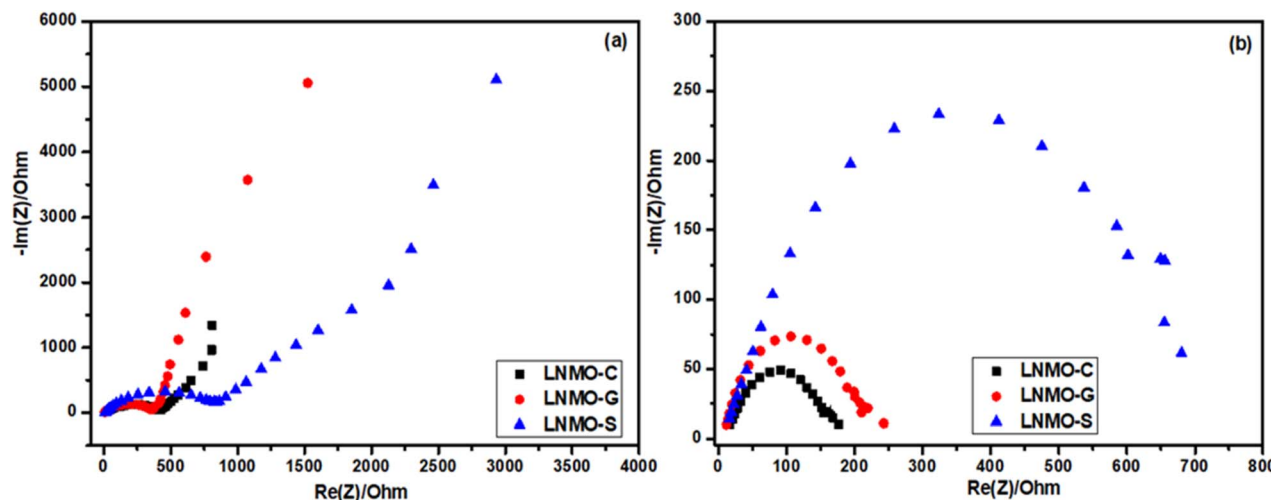


Fig. 10 Nyquist plots of the LNMO cathodes (a) before cycling and (b) after cycling. The cells were cycled (100 cycles) at 1C in a voltage range of 3.50–5.30 V at 25 °C.

material is responsible for the oblique line, referred to as Warburg resistance.^{51,52} The original (ohmic) impedance (R_e) of the battery is represented by the intercept on the real axis in the high-frequency region.⁵³ Table 4 presents the R_{ct} and R_e values for all LNMO cells obtained from the EIS data. Before cycling, LNMO-C, LNMO-G, and LNMO-S cells exhibited R_e values of 21.04, 6.25, and 8.56 Ω . After 100 cycles, the R_e values of the LNMO-G and LNMO-S cells increased to 11.72 and 13.85 Ω , respectively while that of LNMO-C reduced to 17.21 Ω . The LNMO-G cathode material gave the least R_e , while the LNMO-C material showed the highest value, before and after cycling. Moreover, the LNMO-C, LNMO-G, and LNMO-S cells gave R_{ct} values of 401.73, 360.01, and 832.46 Ω before cycling, which decreased to 176.31, 242.80, and 681.48 Ω , respectively, after 100 cycles. During cycling, the stabilized SEI promotes Li ion kinetics to varying degrees in all the LNMO materials. The LNMO-G material had the least R_{ct} (360.01 Ω) before cycling, indicating better electroconductivity, which can be connected to its better rate capability and capacity retention compared to the LNMO-C and LNMO-S materials. The LNMO-S cell had the highest R_{ct} values before and after cycling, explaining its poor electrochemistry. This impedance in the LNMO-S material can be attributed to its high cationic disorder and lower crystallinity coupled with its morphology (irregular particles and rough surface), leading to anisotropic strain and an inhomogeneous and thicker CEI, which would hinder Li ion diffusion in the material.⁵⁴ The very high R_{ct} values of LNMO-S account for its very low discharge capacities and rate capability loss at high

currents (especially at >1C rates), seen in the rate capability analysis (Fig. 9a).⁵⁴ These results show that the type of fuel utilized during the synthesis of the LNMO material influences its structural and electrochemical performance.

The LNMO synthesized *via* glycine-mediated sol-gel combustion gave superior electrochemical performance compared with those synthesized using citric acid- or sucrose-mediated sol-gel combustion. Furthermore, the effect of Ag doping in LNMO was exploited to optimize the structural and electrochemical performance of the LNMO cathode materials. Therefore, the Ag-doped LNMO (LNMAO) cathode was synthesized by the glycine-mediated sol-gel combustion method by replacing 0.03 mole of Mn with Ag to obtain a nominal stoichiometry of the $\text{LiNi}_{0.5}\text{Mn}_{1.47}\text{Ag}_{0.03}\text{O}_4$ material. The elemental analysis of LNMAO (Table S3) showed a stoichiometric ratio close to the nominal ratio and that of LNMO-G, in which 0.04 mole of Ag was doped. In addition, the EDS spectra of LNMAO (Fig. S1b) showed a characteristic Ag peak at 3 keV, showing that Ag was doped at the transition metal sites of the LNMAO material.⁵⁵ The TG-DTG, XRD, Raman spectroscopy and electrochemical results are given in Fig. 11. The TG-DTG results (Fig. 11a) showed four major exothermic peaks compared to the three exothermic peaks observed in LNMO-G (Fig. 1b). The extra peak can be attributed to the presence of Ag in the LNMAO material. At 350 °C, LNMAO combustion showed a total mass loss of about 50%, whereas LNMO-G combustion gave about 77% total mass loss at about the same temperature. This indicates that Ag doping reduced mass loss during the combustion

Table 4 Impedance data from the EIS spectra of the LNMO cathodes before and after cycling

Sample	LNMO-C		LNMO-G		LNMO-S	
	Before cycling	After 100 cycles	Before cycling	After 100 cycles	Before cycling	After 100 cycles
R_e (Ω)	21.04	17.21	6.25	11.72	8.56	13.85
R_{ct} (Ω)	401.73	176.31	360.01	242.80	832.46	681.48

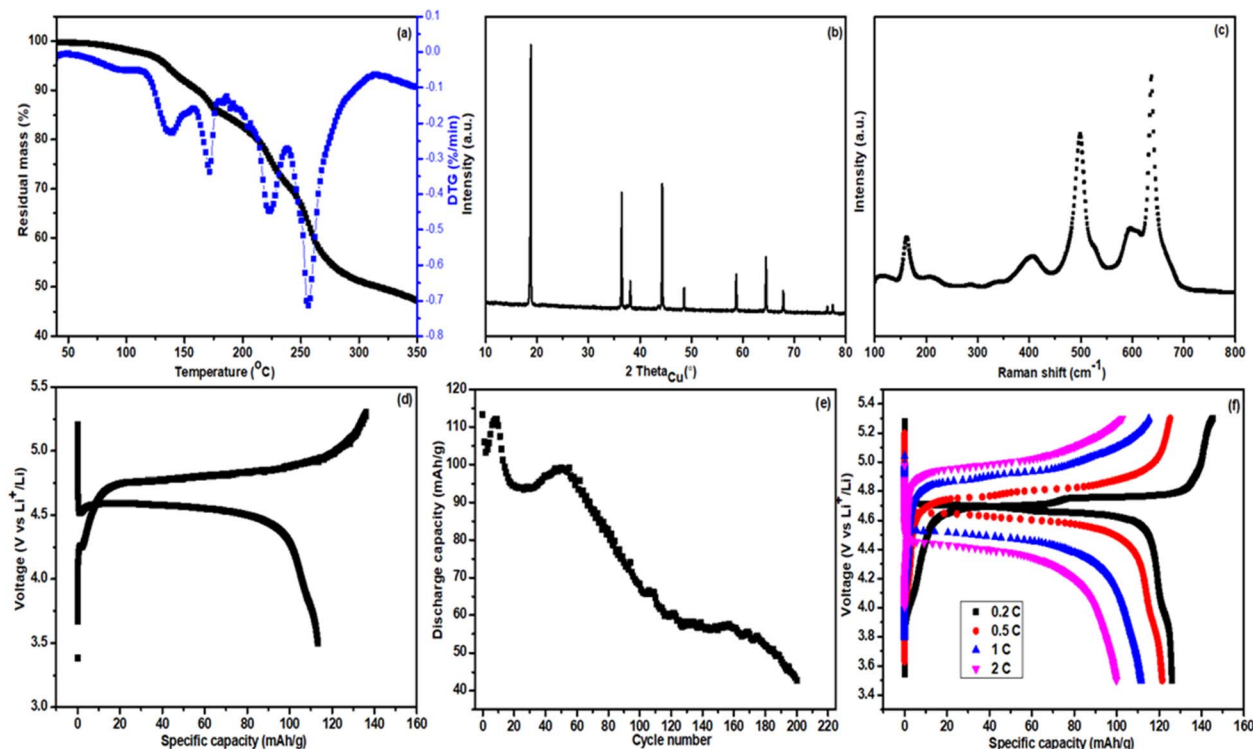


Fig. 11 LNMAO characterization: (a) TG/DTG of the precursor gel, (b) XRD, (c) Raman spectra, (d) initial charge–discharge curve, (e) cycling stability, and (f) representative initial charge–discharge curves at different current densities. The cells were cycled in a voltage range of 3.50–5.30 V at 25 °C.

process. The lower mass loss observed for the LNMAO precursor is likely due to the catalytic effect of Ag and the enhancement of thermal stability by reducing the volatile organic content in the precursor, thereby improving the combustion characteristics compared with the LNMO-G precursor.^{23,24}

The XRD peaks of all LNMAO could be indexed to a cubic spinel-type structure with space group $Fd\bar{3}m$, as presented in Fig. 11b. The samples showed no impurity peaks that are normally associated with ordered LNMO, thus confirming that Ag was successfully doped in LNMO. The sharp peaks observed in the XRD patterns indicate the crystalline nature of all the synthesized samples.¹² The $I_{(311)}/I_{(400)}$ ratio for LNMAO was 1.01, suggesting comparable stability and cationic order with the LNMO-G sample.^{30,31} The calculated lattice parameters (a), cell volume (V) and average crystalline size (D) for LNMAO were 8.167 Å, 544.68 Å³ and 55.47 nm, respectively, similar to the values obtained for the undoped materials (Table 2). This shows that Ag doping did not affect the pristine structural properties of the LNMO material. The Raman spectra of the LNMAO materials (Fig. 11c) showed similar peaks to the undoped LNMO materials, revealing disordered LNMO structures. The LNMAO sample presented irregular shapes, rough surfaces and large particles size, as seen in the SEM image (Fig. S2).

The effect of Ag doping on the electrochemical performance of LNMO cells was evaluated. The first discharge capacity of LNMAO cells was 114 mA h g⁻¹, with a corresponding coulombic efficiency of 88.46% (Fig. 11d), which is comparable to the initial discharge capacity of LNMO-G (115 mA h g⁻¹) and

higher than those of the other undoped LNMO cells. However, the LNMAO cell recorded poorer cycling stability (Fig. 11e), with a capacity retention of 34.78% after 200 cycles. The average capacities of the LNMAO material were 128, 120, 110, and 100 mA h g⁻¹ at 0.2C, 0.5C, 1C, and 2C, respectively (Fig. 11f). This result suggests that the LNMAO cell gave a better rate capability than LNMO-G (Fig. 9c). This indicates that Ag doping enhances the rate capability of the LNMO material. The Nyquist plots of the uncycled and the cycled (after 100th cycle) LNMAO cells are presented in Fig. S3. The uncycled and cycled LNMAO materials displayed R_e values of 4.42 and 9.94 Ω, respectively, which are smaller than those of the LNMO-G material, which gave 6.25 and 11.72 Ω, respectively. Moreover, compared with the LNMO-G sample, the LNMAO material recorded a lower R_{ct} value of 248.37 Ω, which reduced to 137.00 Ω after 100 cycles (Table S3). These EIS results show that the Ag doping reduces the impedance and thereby increases Li ion kinetics in the LNMAO material. These results agree with previous studies, which show that cation doping of LNMO cathode materials improves electrochemical kinetics by enhancing lithium-ion diffusion, reducing charge transfer resistance, and potentially improving structural stability. This leads to better rate capability and cycling performance, making it a promising approach for enhancing the performance of high-voltage lithium-ion batteries.^{3,8,9} Overall, the synthesis method adopted in this study yields LNMO cathodes with promising electrochemical performance that are comparable to the performances obtained

via synthesis approaches previously reported in the literature (Table S5).

4. Conclusion

In this study, different fuels (citric acid, glycine and sucrose) were used to optimize the structure and electrochemical performance of LNMO cathode materials obtained by the SCS method. The structural analyses show that the LNMO-G material gave the highest crystallinity and the least crystallite size and cationic disorder compared with the LNMO-C and LNMO-S samples. The LNMO-C cell gave higher discharge capacities and CE > 100% at a current density of 1C between 3.5–4.98 V, which can be attributed to the increased $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox activity induced by the citric acid-mediated SCS. The LNMO-G cell demonstrated high-voltage performance, recording the highest first discharge capacity of 115.83 mA h g⁻¹ with a capacity retention of 80.06% after 200 cycles when cycled at 1C between 3.50 and 5.30 V. In addition, the LNMO-G cell delivered the best rate capability compared with the LNMO-C and LNMO-S cells. The EIS analyses show that the LNMO-G material displayed the least charge transfer resistance and ohmic resistance among the synthesized LNMO materials, which improved the Li ion kinetics in this material. The LNMO-S cell displayed poorer rate capability and very high impedance values, which increased polarization in the cell with cycling because of interfacial structural instability. These results show that the fuel type influences the structural and electrochemical performance of the LNMO cathodes obtained by SCS. Finally, Ag doping specifically improved the rate capability of the LNMO-G material (LNMAO), which was reflected in the material's reduced impedance.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article are provided within this article and the supplementary information (SI). Supplementary information: standard thermodynamics data and calculations, EDS spectra, additional SEM and EIS data are provided. See DOI: <https://doi.org/10.1039/d5se01296a>.

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