

Impacts of lithium content on structural and electrochemical properties of nanostructured high-voltage cathode material $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$)

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$\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$) cathode materials were synthesized by the coprecipitation method. We investigated the impacts of the lithium content on the structural change and electrochemical properties of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using Rietveld refinement with X-ray diffraction measurements and charge/discharge tests. Ni_6MnO_8 began to appear when the lithium content was 0.96. Li_2MnO_3 began to appear when the lithium content was 1.0. The contents of the two phases gradually increased with the lithium content in the range of 0.96 to 1.04. $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had the highest contents of Ni_6MnO_8 and Li_2MnO_3 phases. The Ni_6MnO_8 phase was ubiquitous in the samples synthesized at a high temperature. Li_2MnO_3 accompanied Ni_6MnO_8 . When the content of Ni_6MnO_8 reached a certain value, the spinel structure could not sustain more Li in the original crystal lattice, which generated an unstable structure in which excess Li existed in Li_2MnO_3 . The separation of Ni_6MnO_8 promoted extraction of Li_2MnO_3 . The irreversible capacity increased, while the initial Coulombic efficiency decreased with the increase in the Li_2MnO_3 amount.

Keywords: lithium content, $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni_6MnO_8 , Li_2MnO_3

1. INTRODUCTION

The high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compound is a promising cathode material for next-generation lithium-ion batteries, which are mainly studied for high-energy applications owing to their high energy density (650 W h kg^{-1}) at a high operating voltage up to 4.7 V [1,2]. There are two possible

lattice structures for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ depending on the Ni/Mn ordering in the lattice [3–5]. One of them is the primitive simple cubic ($P4_332$). In the $P4_332$ -type $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni and Mn orderly occupy the 4a and 12d octahedral sites, respectively. This spinel is referred to as ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The other is a face-centered spinel ($Fd-3m$), referred to as disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ owing to Ni and Mn randomly distributed at the 16d octahedral sites. Almost all studies focused on the phase-pure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Careful approaches have been employed to avoid the generation of secondary phase. It has been proposed that the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ phase exists in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [6–9]. The high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material can easily produce Li_2MnO_3 in the synthesis process [10]. Our group also reported that the high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material produces Ni_6MnO_8 and Li_2MnO_3 during high-temperature synthesis [11]. Extensive studies have been also carried out on the high-temperature phase transformation mechanism. Even though the structures of the Ni_6MnO_8 and Li_2MnO_3 phases are well accepted, the detrimental effect of the Ni_6MnO_8 and Li_2MnO_3 phases during high-temperature synthesis remains unclear.

In this study, we evaluated the impacts of the lithium content on the structural and electrochemical properties of a nanostructured high-voltage cathode material $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$). X-ray diffraction (XRD) results show that the increase in the lithium content changes the spinel structure from two phases to three phases. The corresponding structural parameters and electrochemical properties are discussed in detail.

2. EXPERIMENTAL METHODS

Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were selected as starting materials. A mixed solution of NiSO_4 and MnSO_4 (molar ratio of Ni/Mn = 0.5:1.5), 0.3-mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, and 1-mol/L Na_2CO_3 at pH of 7.8 was fed dropwise into a continuously stirred tank reactor at a rate of 0.5 mL/min using a peristaltic pump. A relatively fine needle was used to control the droplet size to a volume of 0.01 mL. After vigorous stirring for 10 h, the $\text{Ni}_{0.5}\text{Mn}_{1.5}(\text{CO}_3)_2$ precursor was collected and washed four times with distilled water to remove residual sodium and sulfate radicals, and then filtered and dried. Finally, we synthesized $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples with various lithium contents x of 0.96, 0.98, 1.0, 1.02, and 1.04. These samples were prepared at 900 °C in air for 10 h.

The structure of the resultant $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was characterized by powder XRD (D/Max2500PC, Japan) with Cu K_α radiation, graphite monochromator, tube voltage of 30 kV, tube current of 100 mA, and step size of 0.02° in the range of 10° to 120° . The morphologies and microstructures of the samples were studied using field-emission scanning electron microscopy (FESEM, Nova Nano SEM450, USA). The as-synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, carbon black, and polyvinylidene fluoride were mixed at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone to form a slurry. The slurry was coated onto an aluminum foil, and then dried in a vacuum oven at 120 °C for 12 h. The electrolyte was a 1-M LiPF_6 solution in ethylene carbonate:dimethyl carbonate:ethyl methyl carbonate with a volume ratio of 1:1:1. A Cellgard2400 membrane was used as an electrode separator. The synthesized cathode materials were used to fabricate CR2016 coin cells with a metallic lithium plate as a counter electrode. Charge/discharge tests were performed in a voltage range of 3.5–4.9 V with a battery test system (LAND-CT2001A, China).

Electrochemical impedance spectroscopy was performed using an impedance analyzer (Zahner Elektrik IM6, Germany) in a frequency range of 100 mHz to 100 kHz with an amplitude of 10 mV.

3. RESULTS AND DISCUSSION

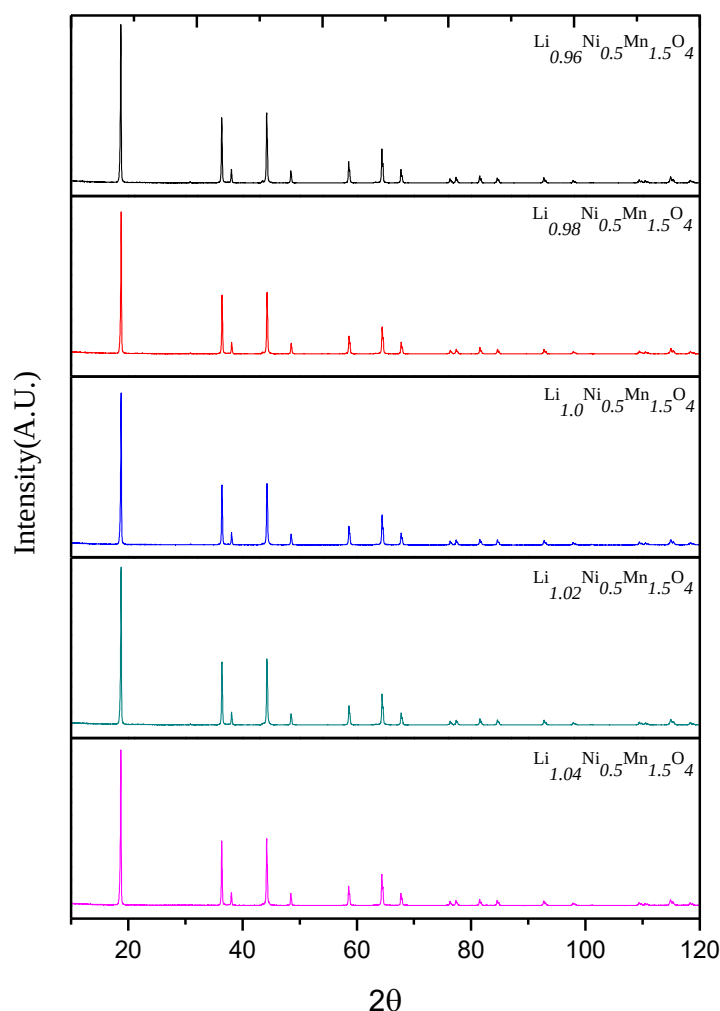


Figure 1. XRD patterns of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ products ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$).

As shown in Figure 1, the XRD peaks of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples are in agreement with the cubic spinel structure. All prepared $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials could be indexed with the Fd-3m unit cell corresponding to a disordered spinel. In addition to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, decomposition products, including the Ni_6MnO_8 and Li_2MnO_3 phases, appear in the final powder [11]. In the beginning, when the lithium content was 0.96, the weak peaks at 37.5° , 43.7° , and 63.3° corresponding to Ni_6MnO_8 were observed [12]. When the lithium content increased to 0.98, the intensities of the weak peaks at 37.5° , 43.7° , and

63.3° increased, which indicates that the Ni_6MnO_8 phase content increased. After the lithium content increased to 1.0, Li_2MnO_3 phase peaks began to appear at 36.7° and 65.4°, and the Ni_6MnO_8 phase content continued to increase. When the lithium content further increased to 1.02, the other weak peak at 68.8° corresponding to Li_2MnO_3 began to appear, which indicates that the Li_2MnO_3 phase content increased. At the end, when the lithium content was 1.04, the peak at 68.8° was more obvious. Notably, the weak peak corresponding to Ni_6MnO_8 and Li_2MnO_3 increased with the lithium content, which indicates that the contents of the Ni_6MnO_8 and Li_2MnO_3 phases increased with the lithium content.

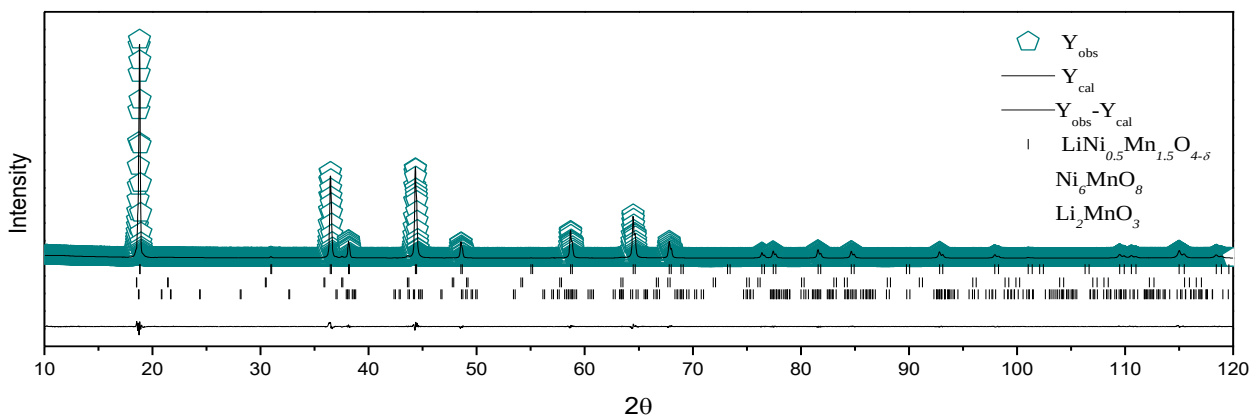
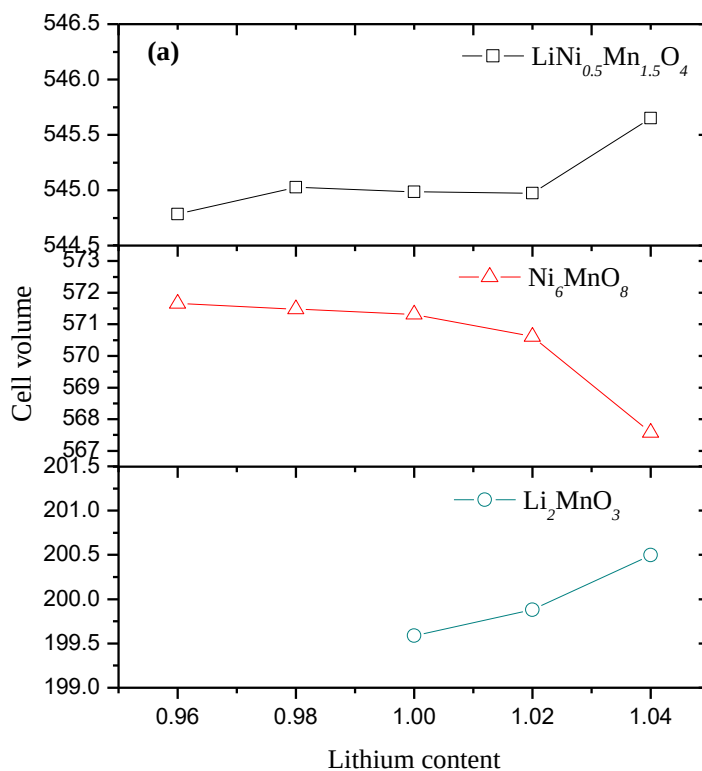


Figure 2. Rietveld refinement of the XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.



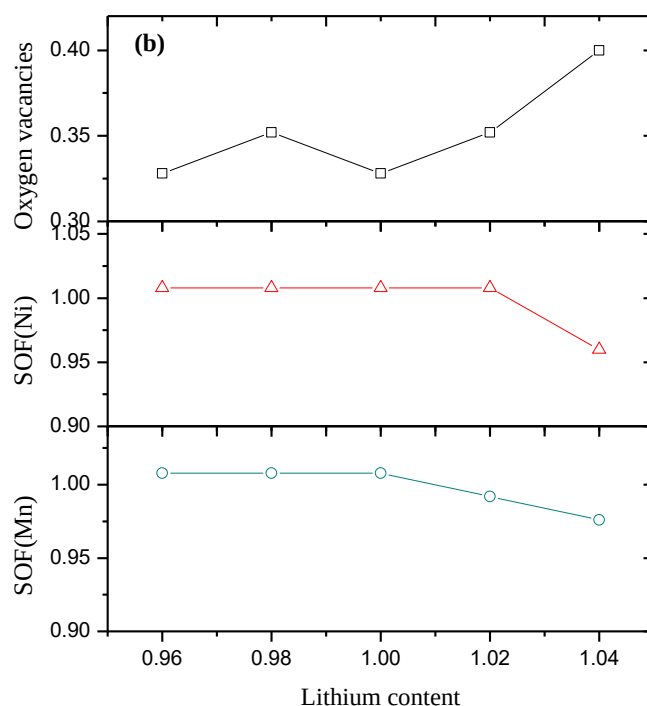


Figure 3. (a) Variations in the unit cell volumes of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni_6MnO_8 , and Li_2MnO_3 phases as a function of the lithium content. (b) Change in the number of oxygen vacancies and variation in the occupancy of Ni, Mn in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the lithium content increases.

Among the five samples, $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had the highest contents of Ni_6MnO_8 and Li_2MnO_3 phases. The Ni_6MnO_8 phase was ubiquitous in the samples synthesized at high temperatures. Li_2MnO_3 was accompanied by Ni_6MnO_8 . Li_2MnO_3 appears only when the content of Ni_6MnO_8 reaches a certain value. Thus, the increase in the lithium content changes the spinel structure from two phases to three phases. In the Li-poor (x of 0.96 and 0.98) samples, Li_2MnO_3 was not produced owing to the lower lithium content. However, in the Li-rich (x of 1.0, 1.02, and 1.04) samples, when a sufficient Ni_6MnO_8 was produced, the spinel structure could not sustain more Li in the original crystal lattice, which generated an unstable structure in which excess Li existed in Li_2MnO_3 . The separation of Ni_6MnO_8 promotes the extraction of Li_2MnO_3 .

We refined the XRD data in Figure 2 to determine the structures of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and any other phases generated during high-temperature sintering. Table 1 shows the calculated lattice parameters. Figure 3(a) shows the variations in the unit cell volumes of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni_6MnO_8 , and Li_2MnO_3 phases as a function of the lithium content. Figure 3(b) shows the change in the number of oxygen vacancies and variations in the Site Occupation Factor of Ni, Mn (SOF) as the lithium content increases. In general, the unit cell volumes of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Li_2MnO_3 phases exhibited an increasing trend. The change in the unit cell volume of the Ni_6MnO_8 phase exhibited a decreasing trend with the increase in the lithium content. The content of oxygen vacancies started to increase when the lithium content reached 1.0. The SOFs of Ni and Mn started to decrease when the lithium content exceeded 1.02 and 1.0, respectively. These results agree well with the variations in the unit cell parameters of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The increase in the content of oxygen vacancies and decreases in the contents of Ni, Mn in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ lead to lattice expansion.

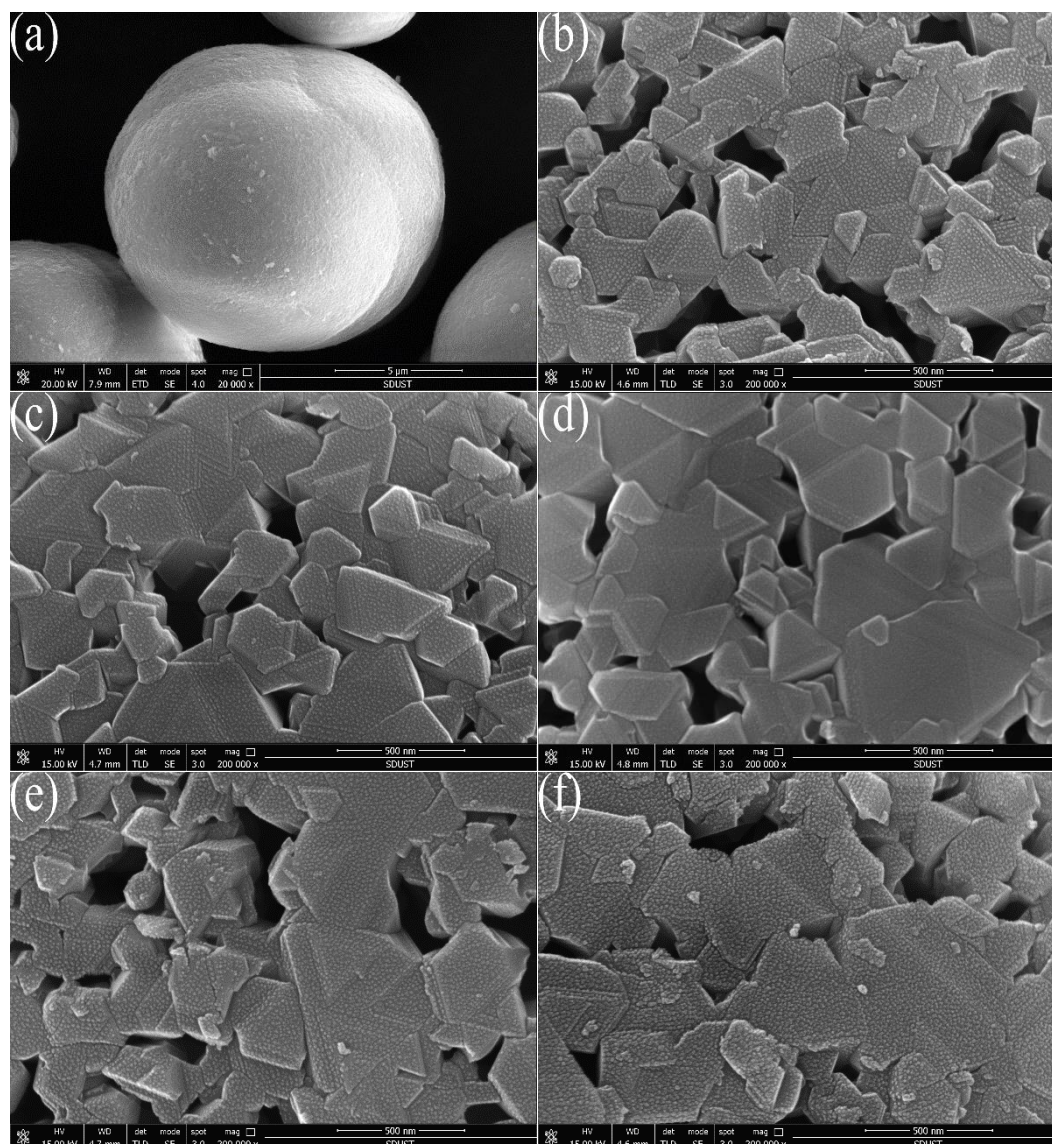


Figure 4. (a) SEM image of the precursor under a low magnification, which indicates a single particle size. (b, f) SEM images of the synthesized $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$) samples with various lithium contents under a high magnification, respectively.

Figure 4 shows SEM images of the precursor and corresponding $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$) products. As shown in Figure 4(a), the precursor exhibited an excellent spherical morphology and particle size of $\sim 13 \mu\text{m}$ [13]. The precursor powder was homogeneous without agglomerated particles. The spherical morphology and diameter of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ products were unchanged after the high-temperature calcination. To evaluate the microstructures of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ products, Figure 4(b)–(f) show the surface morphologies of single particles of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$

products under a high magnification as a function of the Li content. In general, the primary particles of the obtained $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples consisted of discrete particles with clear and smooth surface facets, which implies a high crystallinity, consistent with the XRD results. These results indicate that the lithium content does not significantly alter the morphology of the pristine compound. With the increase in the lithium content, the primary particle size gradually increased. All samples contained regular small octahedral grains with a size distribution in the range of 150–700 nm, which enhanced the electrochemical performance by decreasing the lithium ion diffusion length [14] and increasing the effective surface area in contact with the electrolyte. The microparticles composed of aggregated nanoparticles are desired to form three-dimensional channels for ion diffusion [15]. In the process of electrode reaction, this type of particles also leads to a high loading and can better accommodate the volume change and reduce the electrode tension upon cycling [16]. Therefore, we expect that $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with this morphology will have a good electrochemical performance.

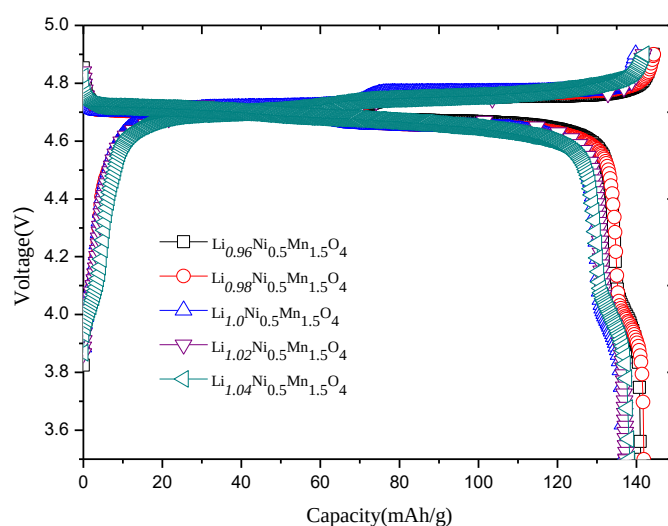


Figure 5. Fifth charge–discharge curves of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02$, and 1.04) tested against a Li metal anode at a rate of 0.1 C between 3.5 and 4.9 V .

The voltage–capacity curves at the fifth cycle of the tested cells in the range of 3.5 to 4.9 V at a rate of 0.1 C are presented in Figure 5. Two separated voltage plateaus are observed in the region of 4.7 V , attributed to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$. A shoulder centered at 4.0 V developed in all electrochemical profiles, which is commonly attributed to the oxidation of Mn^{3+} in the spinel structure [17]. The samples with x of $0.96, 0.98, 1.0, 1.02$, and 1.04 exhibited discharge capacities of $141.1, 141.9, 136.7, 137.4$, and 138.3 mA h g^{-1} , respectively. The capacities of the Li-poor samples were slightly larger than those of the Li-rich samples, because the large concentration of the rocksalt phase, which is largely inactive and partially coats the spinel phase, results in a poor electrochemistry. Therefore, the minimization of the Ni_6MnO_8 and Li_2MnO_3 phases is necessary to enhance the electrochemical properties.

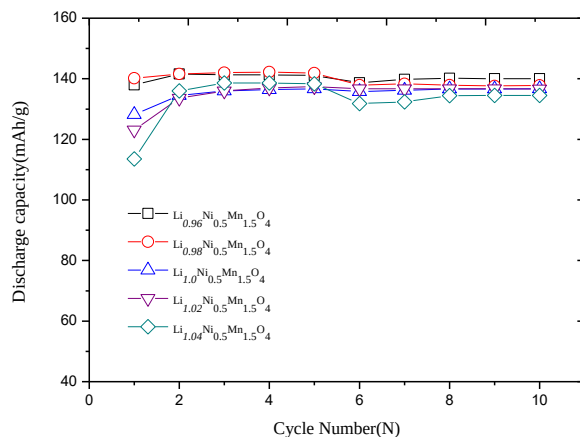


Figure 6. Cycle performances of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$).

The cycling performances obtained after completion of five charge–discharge cycles at 0.1 C and 0.2 C are shown in Figure 6. All $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials exhibited good cycling performances. The $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{0.98}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{1.02}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples delivered initial specific capacities of 138, 140.2, 128.2, 123.1, and 113.5 mA h g^{-1} at a rate of 0.1 C. The capacity of $\text{Li}_{0.98}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was slightly higher than that of $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 0.1 C owing to the higher lithium content. However, at 0.2 C, the capacity of $\text{Li}_{0.98}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was slightly lower than that of $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The advantage of the vacancies is reflected at a high discharge rate. The Li vacancies can improve the stability of the structure. The comparison of $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{1.02}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows that the $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode exhibited the highest discharge capacity at 0.1 C. The capacity of Li_2MnO_3 may be released. Electrochemical properties of Li_2MnO_3 have been studied [18,19]. Experimental results show that the material is electrochemically active beyond 4.5 V vs. Li/Li^+ in layered lithium-rich manganese-based materials [20]. At 0.2 C, the capacity of $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sharply decreased. This result corresponds to the low cycling performance of Li_2MnO_3 . The Coulombic efficiencies of the initial cycle were 91.1%, 90%, 90.1%, 86.3%, and 87.1%, respectively. The Coulombic efficiencies of the initial cycle for the Li-rich samples ($x = 1.02$ and 1.04) were lower than those of the Li-poor samples ($x = 0.96$ and 0.98). The poor Coulombic efficiency indicates that the Ni_6MnO_8 phase as a considerable fraction of these samples is electrochemically inactive. The Ni_6MnO_8 and Li_2MnO_3 phases not only reduce the overall capacity of the electrode but also isolate the spinel domains from direct contact with the electrolyte. Further studies are required on the role of the Ni_6MnO_8 and Li_2MnO_3 phases in the spinel material.

Initial charge/discharge values are shown in Table 2 to study the initial Coulombic efficiencies of these samples. The voltage plateau of each sample varies with the composition change. As the amount of Li_2MnO_3 increases, the discharge voltage plateau starts to shift to a lower voltage. In addition, the initial discharge capacities decrease as the amount of Li_2MnO_3 increases. To the best of our knowledge, the irreversible capacity loss is due to the extraction of lithium as “ Li_2O ” upon charging from Li_2MnO_3 in layered materials [21, 22]. The content of Li_2MnO_3 in the Li-poor samples is lower than that in the Li-rich samples, which results in a lower irreversible capacity loss and higher Coulombic efficiency.

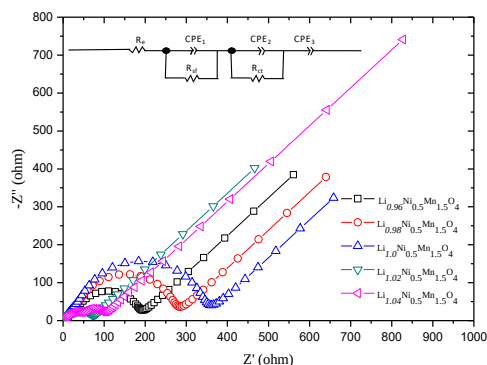


Figure 7. Electrochemical impedance spectroscopy of the synthesized $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02$, and 1.04).

Figure 7 shows Nyquist plots of the spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes ($x = 0.96, 0.98, 1.0, 1.02$, and 1.04) after cycling at 0.1 C . All electrochemical impedance spectra contain one semicircle in the high- and medium-frequency regions and inclined line in the low-frequency zone. There is no semicircle associated with the $R_{\text{SEI}}/C_{\text{SEI}}$ parallel circuit, because the graphite or other carbonaceous material content is very low on the thin film electrode, which leads to a smaller R_{SEI} [23]. The fitting equivalent circuit is shown in the inset of Figure 7. In this circuit, R_s is the electrolyte resistance, which corresponds to the high-frequency intercept at the real axis, R_{ct} is the charge transfer resistance [24], R_{sf} is the resistance of the Solid Electrolyte Interface film (SEI), and C_{dl} is the capacitance of the double electric layer. The lithium ion diffusion coefficient of $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is minimized, as it has the highest content of the Ni_6MnO_8 and Li_2MnO_3 phases. $\text{Li}_{1.02}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had larger R_{sf} values than that of $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, likely because the Ni_6MnO_8 and Li_2MnO_3 phases were coated on the surface of the cathode material, which resulted in a high SEI film resistance. The comparison of $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{0.98}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows that $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had the smallest R_{ct} of $150.2\ \Omega$, which corresponds to its excellent electrochemical performance.

Table 1. Structural parameters of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ products ($x = 0.96, 0.98, 1.0, 1.02$, and 1.04).

Overall composition: $\text{Li}_{0.96}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$						
site	atom	x	y	z	SOF	B_{iso}
Phase 1 Composition: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Vol: 544.784 (0.010) Cell: 8.16723(8)						
8a	Li	0.37500(0)	0.37500(0)	0.37500(0)	0.96(0)	0.435(210)
16d	Ni	0.00000(0)	0.00000(0)	0.00000(0)	0.25(0)	0.388(21)
16d	Mn	0.00000(0)	0.00000(0)	0.00000(0)	0.75(0)	0.388(21)
32e	O	0.23721(14)	0.23721(14)	0.23721(14)	0.918(0)	0.391(71)
Phase 2 Composition: Ni_6MnO_8 Vol: 571.658 (0.078) Cell: 8.2994(7)						
24d	Ni	0.00000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
4a	Mn	0.00000(0)	0.00000(0)	0.00000(0)	1.0 (0)	0.500(0)
8c	O	0.25000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)

24e	O	0.15130(657)	0.00000(0)	0.00000(0)	1.0(0)	0.500(0)
Agreement parameters: R_p : 7.44 R_{wp} : 11.4						

Overall composition: $\text{Li}_{0.98}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$						
site	atom	x	y	z	SOF	B_{iso}
Phase 1 Composition: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Vol: 545.027(0.010) Cell: 8.16844(9)						
8a	Li	0.37500(0)	0.37500(0)	0.37500(0)	0.98(0)	0.799(225)
16d	Ni	0.00000(0)	0.00000(0)	0.00000(0)	0.25(0)	0.457(22)
16d	Mn	0.00000(0)	0.00000(0)	0.00000(0)	0.75(0)	0.457(22)
32e	O	0.23739(14)	0.23739(14)	0.23739(14)	0.912(1)	0.508(74)
Phase 2 Composition: Ni_6MnO_8 Vol: 571.484(0.083) Cell: 8.2985(7)						
24d	Ni	0.00000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
4a	Mn	0.00000(0)	0.00000(0)	0.00000(0)	1.0 (0)	0.500(0)
8c	O	0.25000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
24e	O	0.15343(674)	0.00000(0)	0.00000(0)	1.0(0)	0.500(0)
Agreement parameters: R_p : 7.67 R_{wp} : 11.6						

Overall composition: $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$						
site	atom	x	y	z	SOF	B_{iso}
Phase 1 Composition: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Vol: 544.984(0.009) Cell: 8.16823(8)						
8a	Li	0.37500(0)	0.37500(0)	0.37500(0)	1.0 (0)	0.648(194)
16d	Ni	0.00000(0)	0.00000(0)	0.00000(0)	0.25(0)	0.276(21)
16d	Mn	0.00000(0)	0.00000(0)	0.00000(0)	0.75(0)	0.276(21))
32e	O	0.23783(15)	0.23783(15)	0.23783(15)	0.918(0)	0.299(63)
Phase 2 Composition: Ni_6MnO_8 Vol: 571.313(0.071) Cell: 8.2977(6)						
24d	Ni	0.00000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
4a	Mn	0.00000(0)	0.00000(0)	0.00000(0)	1.0 (0)	0.500(0)
8c	O	0.25000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
24e	O	0.83657(535)	0.00000(0)	0.00000(0)	1.0(0)	0.500(0)
Phase 3 Composition: Li_2MnO_3 Vol: 199.587(0.117) Cell: $a = 4.9368(19)$ $b = 8.528(3)$ $c = 5.0055(16)$ $\alpha = 90.00000$ $\beta = 108.71(3)$ $\gamma = 90.00000$						
2c	Li	0.00000(0)	0.00000(0)	0.50000(0)	1.0(0)	1.000(0)
4h	Li	0.00000(0)	0.66411(3169)	0.50000(0)	1.0(0)	1.000(0)
2b	Li	0.00000(0)	0.50000(0)	0.00000(0)	1.0(0)	1.000(0)
4g	Mn	0.00000(0)	0.15953(432)	0.00000(0)	1.0(0)	0.500(0)
4i	O	0.38349(1982)	0.00000(0)	0.09929(2491)	1.0(0)	0.500(0)
8j	O	0.21663(1307)	0.35618(801)	0.13926(1294)	1.0(0)	0.500(0)
Agreement parameters: R_p : 7.07 R_{wp} : 10.4						

Overall composition: $\text{Li}_{1.02}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$						
site	atom	x	y	z	SOF	B_{iso}
Phase 1 Composition: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Vol: 544.881(0.009) Cell: 8.16771(8)						
8a	Li	0.37500(0)	0.37500(0)	0.37500(0)	1.00(0)	0.925(210)
16d	Ni	0.00000(0)	0.00000(0)	0.00000(0)	0.25(0)	0.298(20)
16d	Mn	0.00000(0)	0.00000(0)	0.00000(0)	0.75(0)	0.298(20)

32e	O	0.23768(13)	0.23768(13)	0.23768(13)	0.9(0)	0.247(65)
16d	Li	0.00000(0)	0.00000(0)	0.00000(0)	0.02(0)	0.298(20)
Phase 2 Composition: Ni ₆ MnO ₈ Vol: 571.995(0.088) Cell: 8.3010(7)						
24d	Ni	0.00000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
4a	Mn	0.00000(0)	0.00000(0)	0.00000(0)	1.0 (0)	0.500(0)
8c	O	0.25000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
24e	O	0.83416(647)	0.00000(0)	0.00000(0)	1.0(0)	0.500(0)
Phase 3 Composition: Li ₂ MnO ₃ Vol: 200.365(0.066) Cell: $a = 4.9270(9)$ $b = 8.5283(15)$ $c = 5.0293(10)$ $\alpha = 90.00000$ $\beta = 108.536(18)$ $\gamma = 90.00000$						
2c	Li	0.00000(0)	0.00000(0)	0.50000(0)	1.0(0)	1.000(0)
4h	Li	0.00000(0)	0.64926(1659)	0.50000(0)	1.0(0)	1.000(0)
2b	Li	0.00000(0)	0.50000(0)	0.00000(0)	1.0(0)	1.000(0)
4g	Mn	0.00000(0)	0.17058(190)	0.00000(0)	1.0(0)	0.500(0)
4i	O	0.43858(1090)	0.00000(0)	0.08133(1173)	1.0(0)	0.500(0)
8j	O	0.19692(726)	0.31281(351)	0.12917(616)	1.0(0)	0.500(0)
Agreement parameters: R_p : 7.19 R_{wp} : 11.0						

Overall composition: Li _{1.04} Ni _{0.5} Mn _{1.5} O ₄						
site	atom	x	y	z	SOF	B_{iso}
Phase 1 Composition: LiNi _{0.5} Mn _{1.5} O ₄ Vol: 545.043(0.009) Cell: 8.16852(8)						
8a	Li	0.37500(0)	0.37500(0)	0.37500(0)	1.0(0)	0.157(183)
16d	Ni	0.00000(0)	0.00000(0)	0.00000(0)	0.25(0)	0.187(21)
16d	Mn	0.00000(0)	0.00000(0)	0.00000(0)	0.75(0)	0.187(21)
32e	O	0.23826(15)	0.23826(15)	0.23826(15)	0.9(0)	0.193(65)
16d	Li	0.00000(0)	0.00000(0)	0.00000(0)	0.024(0)	0.187(21)
Phase 2 Composition: Ni ₆ MnO ₈ Vol: 569.532(0.072) Cell: 8.2891(6)						
24d	Ni	0.00000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
4a	Mn	0.00000(0)	0.00000(0)	0.00000(0)	1.0 (0)	0.500(0)
8c	O	0.25000(0)	0.25000(0)	0.25000(0)	1.0(0)	0.500(0)
24e	O	0.83192(442)	0.00000(0)	0.00000(0)	1.0(0)	0.500(0)
Phase 3 Composition: Li ₂ MnO ₃ Vol: 199.763(0.074) Cell: $a = 4.9367(11)$ $b = 8.5280(17)$ $c = 5.0143(11)$ $\alpha = 90.00000$ $\beta = 108.86(2)$ $\gamma = 90.00000$						
2c	Li	0.00000(0)	0.00000(0)	0.50000(0)	1.0(0)	1.000(0)
4h	Li	0.00000(0)	0.61736(1417)	0.50000(0)	1.0(0)	1.000(0)
2b	Li	0.00000(0)	0.50000(0)	0.00000(0)	1.0(0)	1.000(0)
4g	Mn	0.00000(0)	0.14964(236)	0.00000(0)	1.0(0)	0.500(0)
4i	O	0.46567(1904)	0.00000(0)	0.06052(1600)	1.0(0)	0.500(0)
8j	O	0.22367(1299)	0.31988(414)	0.19236(819)	1.0(0)	0.500(0)
Agreement parameters: R_p : 7.59 R_{wp} : 11.0						

Table 2. Initial charge/discharge values of Li_xNi_{0.5}Mn_{1.5}O₄ ($x = 0.96, 0.98, 1.0, 1.02$, and 1.04).

Sample	Discharge capacity (mAh/g)	Initial Coulombic efficiency (%)	Specific energy (Wh/kg)	Average discharge voltage (V)
0.96	138.0	91.1%	639.4	4.6333
0.98	140.2	90.0%	649.2	4.6305

1.0	128.2	90.1%	590.8	4.6084
1.02	123.1	86.3%	561.2	4.5593
1.04	113.5	87.1%	517.4	4.5586

4. CONCLUSIONS

$\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.96, 0.98, 1.0, 1.02, \text{ and } 1.04$) materials were synthesized by the coprecipitation method. The impacts of the lithium content on the structural and electrochemical properties of the nanostructured high-voltage cathode material $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were analyzed through XRD characterization, Rietveld refinement, SEM, electrochemical performance tests, and electrochemical impedance spectroscopy. The Ni_6MnO_8 phase appeared when the lithium content was 0.96. The Ni_6MnO_8 phase content increased with the lithium content up to 0.98. When the lithium content increased to 1.0, Li_2MnO_3 began to appear and the Ni_6MnO_8 phase content continued to increase. When the lithium content further increased to 1.02 and 1.04, the phase contents of Ni_6MnO_8 and Li_2MnO_3 still increased. The phase contents of Ni_6MnO_8 and Li_2MnO_3 increased with the lithium content. $\text{Li}_{1.04}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had the highest contents of Ni_6MnO_8 and Li_2MnO_3 phases. Ni_6MnO_8 was present in the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples synthesized at a high temperature. The emergence of Li_2MnO_3 was accompanied by Ni_6MnO_8 . When the content of Ni_6MnO_8 reached a certain value, the spinel structure could not sustain more Li in the original crystal lattice, which generated an unstable structure in which excess Li existed in Li_2MnO_3 . The separation of Ni_6MnO_8 promoted the extraction of Li_2MnO_3 . Therefore, the lithium content can adjust the type and content of the phases in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compounds. As the amount of Li_2MnO_3 increased, the irreversible capacity increased, while the initial Coulombic efficiency decreased.

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