

Article

Ti-Doped Co-Free $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ Cathode Materials with Enhanced Electrochemical Performance for Lithium-Ion Batteries

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Abstract: Cobalt-free manganese-based lithium-rich layered oxides (LLOs) have garnered research attention as prospective lithium-ion cathode materials owing to their large specific capacity and low price. However, their large-scale application is hindered by their low Coulombic efficiency, poor cycling performance, voltage attenuation, and structural phase transition. To address these issues, the LLO structure is modified via Ti doping at the manganese site herein. Ti-doped $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10$, and 0.15) is prepared using the high-temperature solid-state method. The Ti-doped $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ is calculated via first principles. The results show that Ti^{4+} doping improves the cycle stability and rate performance of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$. Electrochemical test results show that the sample exhibits enhanced electrochemical performance when the Ti doping amount is 0.05. The discharge specific capacity at 0.1C is $210.4 \text{ mAh}\cdot\text{g}^{-1}$, which reaches $191.1 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles, with a capacity retention rate of 90.7%. This study proves the feasibility of using cheap cobalt-free LLOs as cathode materials for LIBs and provides a novel system for exploiting low-cost and high-performance cathode materials.

Keywords: lithium-rich layered oxide; $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ cathode; Ti doping; Co-free; DFT



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1. Introduction

The increasing energy demands and need for environmental protection and green, sustainable development have necessitated the use of energy-saving, efficient, and eco-friendly lithium-ion batteries (LIBs) as energy-storage materials. In particular, electric vehicles and portable electronic devices require LIBs [1–3]. At present, the low capacity of electrodes hinders their ability to meet the needs of modern life [4–7]; therefore, high-performance cathode materials must be explored to promote the development of LIBs. Lithium-rich layered oxides (LLOs) have recently been characterized by their remarkably high reversible specific capacity resulting from their material properties. Moreover, LLOs have good thermal stability, high working voltage, high-temperature performance, are low-cost, and are resistant to environmental conditions [8–14].

LLOs have garnered considerable research attention since their discovery; however, their commercialization continues to be a challenge [15–21]. This is because (1) they have low Coulombic efficiency due to initial activation; (2) their capacity degrades as the lamellar structure transforms into a spinel-phase structure during cycling; and (3) Li_2MnO_3 has low electrochemical activity, which yields lower rate performance. Studies conducted to mitigate these issues and optimize the performance of LLOs have revealed that ion doping can directly affect the LLO structure and suppress Li and Ni mixing. Ion doping can provide charge compensation during Li deintercalation and increase ionic conductivity, which is beneficial for initiating electrochemical reactions [22–25].

In bulk doping, metal cations or nonmetallic anions with physical and chemical properties similar to those of substituted elements—such as K [26,27], Na [28–30], Mg [31–33], Al [34,35], Mo [36,37], or Cr [38,39]—are used. Ion doping is a relatively simple process and can reduce the material synthesis cost; thus, it is a high-energy, high-efficiency modification method. The Ti–O bond energy is considerably higher than Mn–O and Ni–O bond energies, which can effectively inhibit oxygen loss. An appropriate Ti^{4+} doping amount can reduce the interlayer spacing of LLOs and enhance their structural stability, thereby improving their overall performance. Kou [40] successfully doped Ti^{4+} into the cathode material $\text{Li}_{1.167}\text{Ni}_{0.4}\text{Mn}_{0.383}\text{Co}_{0.05}\text{O}_2$ via co-precipitation. The sample with a doping amount of 0.04 had a discharge specific capacity of $186.6 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1C. Yamamoto [41] successfully prepared Ti-doped $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ and found that Ti and Mn had similar coordination environments; moreover, the modified material retained its high discharge capacity after 100 cycles.

Herein, the Mn sites in $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ were doped with appropriate amounts of Ti^{4+} in the bulk phase. A series of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10$, and 0.15) doped with Ti^{4+} at the Mn sites were synthesized using the high-temperature solid-state method. The samples before and after modification were compared and analyzed via X-ray diffraction (XRD), SEM, and other characterization methods and electrochemical performance tests. The influence of various synthesis conditions on the crystal structure, microstructure, and electrochemical performance of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ was investigated along with the Ti^{4+} doping amount.

2. Results and Discussion

Models of the optimized architecture are shown in Figure 1a. The DFT calculation results are shown in Figure 1b. Before the ion doping (Figure 1b), the peaks of Mn, Ni, and O can be observed on the left side of the Fermi level, indicating that Mn, Ni, and O are hybridized, and all three are involved in the redox reaction. However, after Ti doping (Figure 1c), only Ni and O peaks can be observed on the left side of the Fermi level, indicating that Ni and O hybridized at this time. At the same time, the peaks of Ni and O were enhanced compared with undoped, meaning that the contribution of Ni and O in the redox reaction is increased. Ti does not participate in the redox reaction. Before doping, Mn plays a major role because of the dz^2 electrons on the eg orbital. After the introduction of Ti, the dz^2 electrons on the eg orbital are transferred from the valence band on the left to the conduction band on the right, and Mn^{3+} is converted to Mn^{4+} . It can also be found that the band gap changes from 0.28 eV before doping to 0.65 eV after doping Ti. The possible reason is that the Ti–O bond strength is large, which is not conducive to the Li migration of the Mn layer, so the band gap increases. However, also benefiting from the higher Ti–O bond energy, the Jahn–Teller effect is slightly suppressed after replacing some Mn sites in the lattice, forming a more stable layered structure. From the DFT calculation results, the stability of lattice O in the Ti-doped material is improved during the cycle, showing excellent cycle performance.

The XRD patterns (Figure 2a) show that the diffraction peak positions of materials before and after doping are similar, conforming to the structural characteristic peaks of the layered $\alpha\text{-NaFeO}_2$ phase belonging to the R-3m space group. The diffraction peaks of (006)/(012) and (018)/(110) are split, indicating that all samples have layered crystal structures and high crystallinity. The faint diffraction peaks between 20° and 25° represent the existence of monoclinic Li_2MnO_3 , belonging to the C2/m space group. The peak is thought to be due to the short-range superlattice ordering of Li and Ni atoms in the transition metal layer [42]. No other impurity phases were observed before and after doping, indicating that the doped sample had pure phases. Moreover, the $I_{(003)}/I_{(104)}$ ratio reflects the order of the cation in the material. An $I_{(003)}/I_{(104)}$ ratio of <1.2 indicates a serious ion-mixing phenomenon in the crystal structure of the material [43,44]. The samples doped with 0.05 Ti have an $I_{(003)}/I_{(104)}$ ratio of 1.42, which is considerably higher than that of the undoped material (1.13). This indicates that Ti doping suppresses ion mixing. Figure 2b is

an enlarged diagram of the (003) diffraction peak. The (003) diffraction peaks are offset in the direction of a large angle as the Ti^{4+} amount increases, indicating that Ti^{4+} enters the $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ lattice without affecting the lamellar structure.

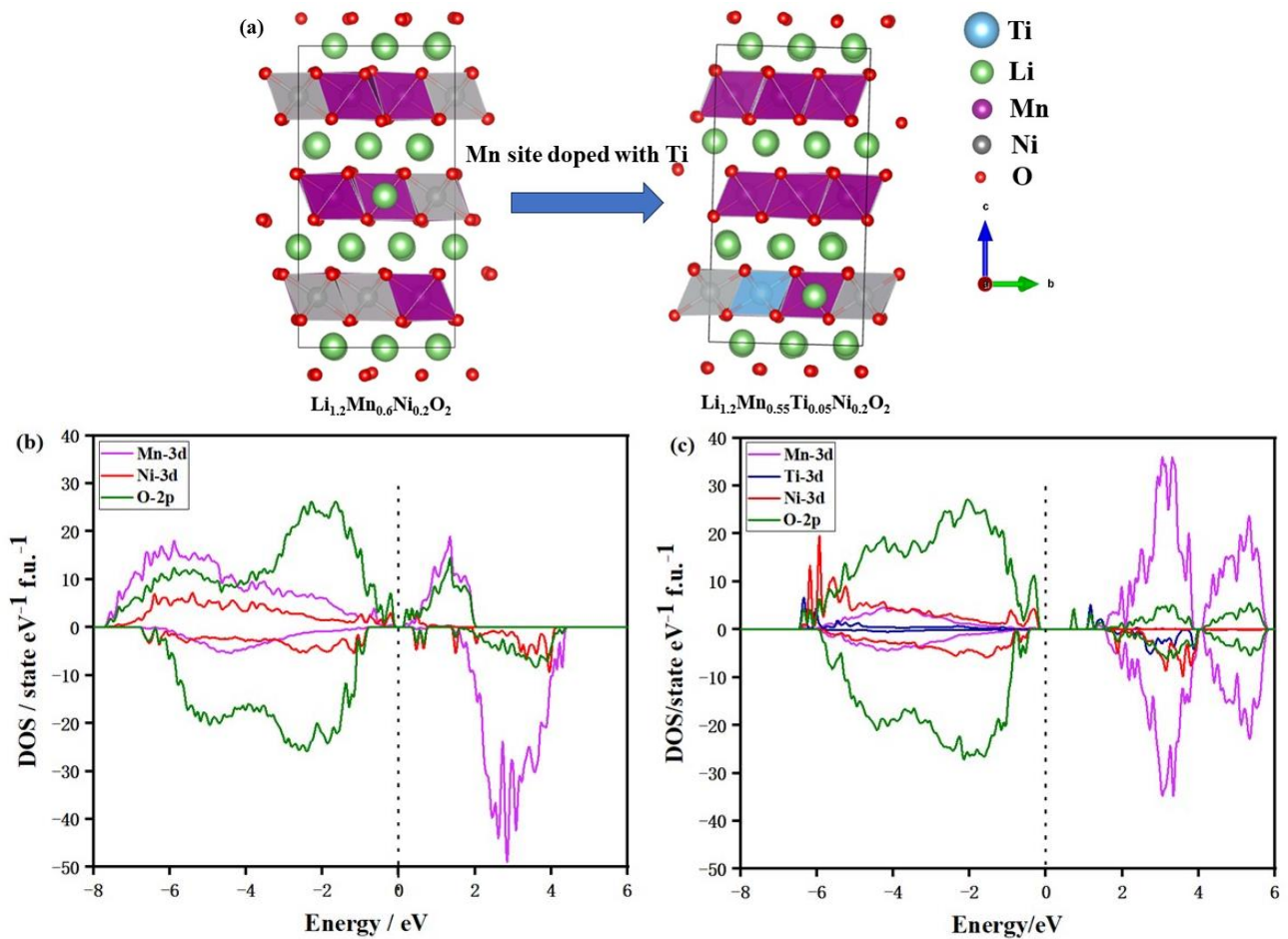


Figure 1. (a) Optimized crystal structure of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$ with Ti^{4+} occupying the Mn^{4+} site; (b) The density of states: $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$; (c) The density of states: $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$ with Ti^{4+} occupying.

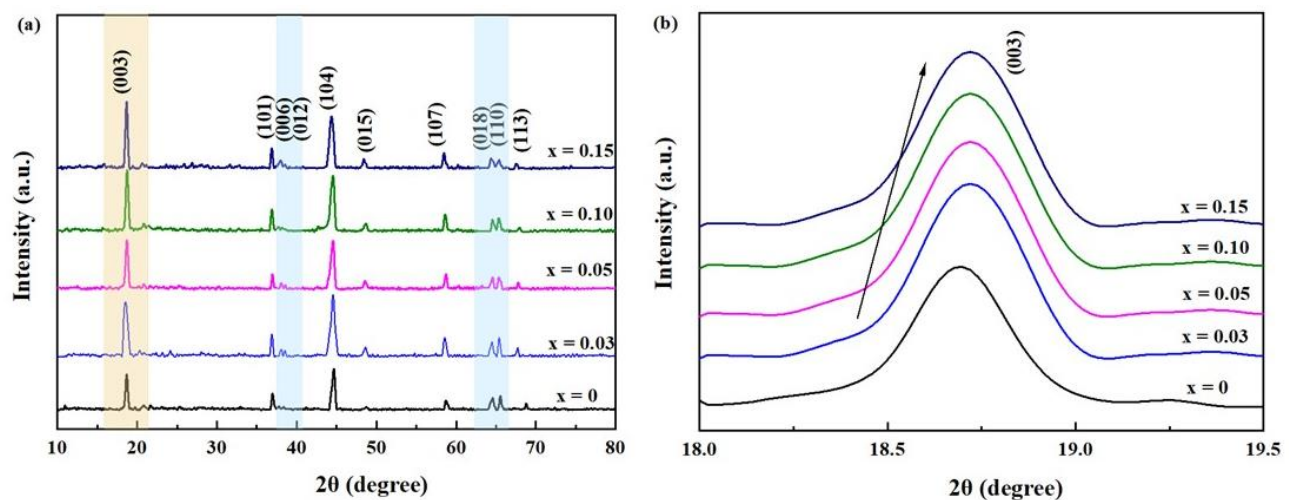


Figure 2. (a) XRD patterns of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$); (b) Amplification diagram of the diffraction peak of (003).

O vacancies cause Mn migration in Li_2MnO_3 , transforming the crystal structure from layered to spinel and causing voltage attenuation [45–47]. To avoid O vacancy generation and Mn migration, the bonding between oxygen and transition metal atoms in Li_2MnO_3 must be enhanced. Figure 3 and Table 1 show the XRD refinement results of the undoped sample and that doped with 0.05 Ti, obtained using the FullProf software (23-November-2023). It can be seen from Table 1 that the incorporation of Ti changes the a and c values and cell volume of the material. This may be because Ti has a larger ionic radius than Mn and Ni, so the incorporation of Ti will increase the lattice length and make the cell volume and lattice spacing increase, which also shows that Ti ions enter the lattice. The doping of Ti increases the cell volume and increases the diffusion ability of lithium ions in the octahedral 3a and 3b channels, thereby further improving its electrochemical performance.

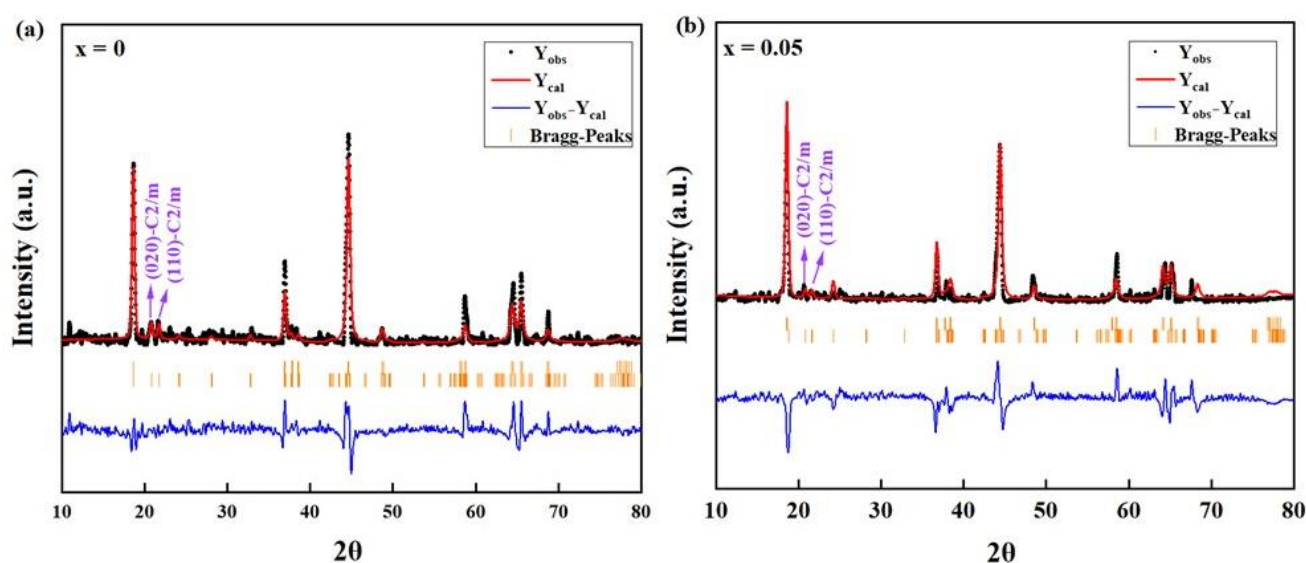


Figure 3. Rietveld refinements for (a) $x = 0$ and (b) $x = 0.05$ $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$.

Table 1. Lattice parameters for samples with $x = 0$ and $x = 0.05$.

Crystal Data	$\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$	$\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$
a (Å)	2.85161	2.86661
c (Å)	14.27338	14.32345
V (Å ³)	100.5166	101.9332
c/a	5.0054	4.9967
R _{wp} (%)	2.48	1.32
R _p (%)	1.54	0.77
R-3m	76.72	79.35
C2/m	23.28	20.65
χ^2 (%)	1.86	1.82

Figure 4 shows the SEM images and particle size distribution of cathode materials doped with different Ti amounts. The particles in the four groups of samples showed irregular block structures and smooth surfaces. The samples with $x = 0.05$ have uniform particle distribution and good morphology, whereas those with $x = 0.03$ and $x = 0.15$ show slight agglomeration. The particle size distribution curve shows that with the increase in Ti^{4+} doping amount, the average particle size of the sample increases first, then decreases, and then increases. When $x = 0, 0.03, 0.05, 0.1$, and 0.15 , the particle sizes are $\sim 2.93, 7.63, 2.79, 3.46$, and $4.21 \mu\text{m}$, respectively. When a small amount of Ti ($x = 0.03$) is introduced, the doping at this time is partially doped, and the doping is not uniform, which may introduce the agglomeration of the material and increase the particle size. With the gradual introduction of Ti^{4+} ($x = 0.05$), the particle size of the sample decreased and dispersed. This

shows that the doping of an appropriate amount of Ti may have a certain degree of dispersion effect on the microscopic particles of the sample, thus reducing the agglomeration between the particles to a certain extent. However, when the doping amount of Ti^{4+} is too large, it may lead to uneven or even abnormal grain growth. Excessive doping ions will accumulate at the grain boundary, affect the migration of the grain boundary, and increase the particle size. Generally speaking, during electrochemical reactions, the uniform particle distribution facilitates Li^+ diffusion, which improves the material properties.

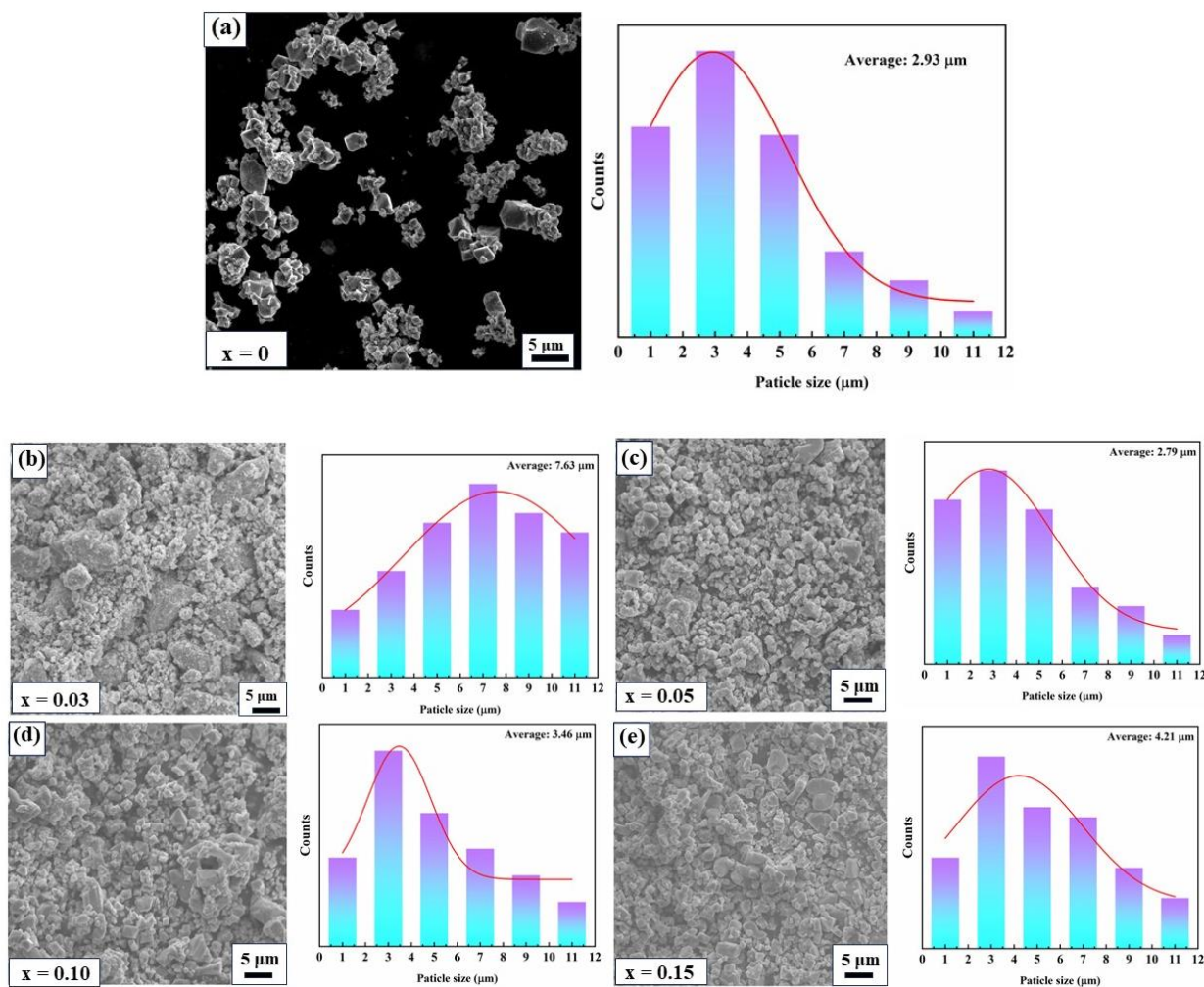


Figure 4. SEM images and particle size distribution of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$: (a) $x = 0$; (b) $x = 0.03$; (c) $x = 0.05$; (d) $x = 0.10$; (e) $x = 0.15$ (The blue column represents the percentage of the content corresponding to each particle size; the red line is a normal distribution curve based on Gaussian function fitting).

EDS surface scanning analysis was performed to determine the elemental distribution of Ti-doped cathode materials ($x = 0.05$). Figure 5 shows that Ti, Mn, and Ni are uniformly dispersed across the grain surfaces of samples.

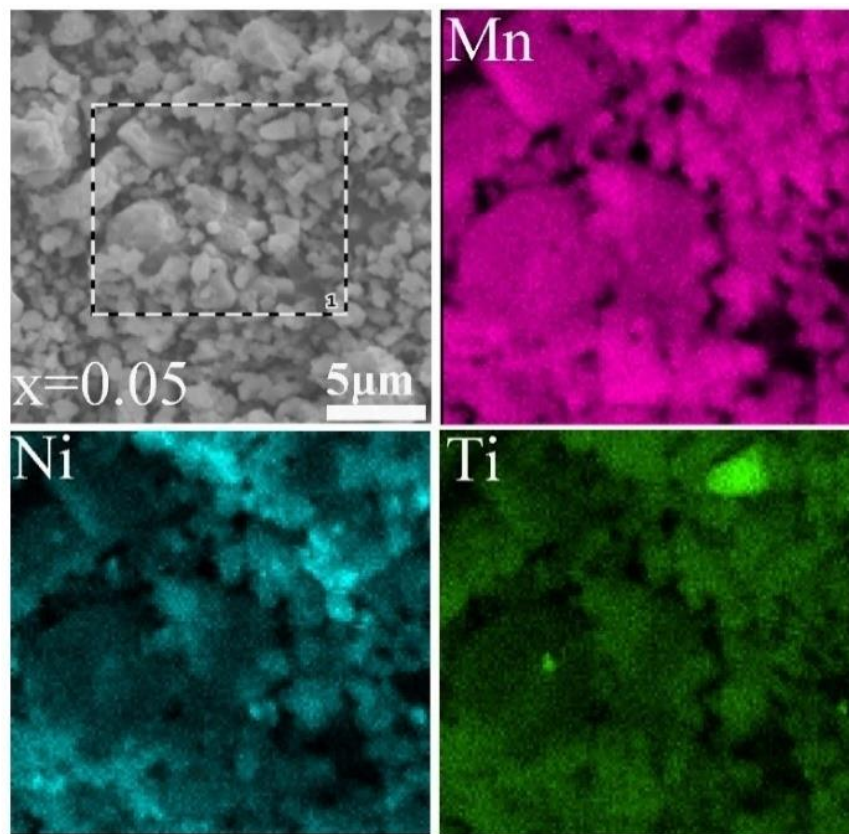


Figure 5. EDS mappings of $x = 0.05$ sample.

XPS was performed on $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$ to determine the impact of transition metal valence states on the particle surface after Ti doping. Figure 6a shows the XPS spectra of samples with $x = 0$ and $x = 0.05$, which reveal the existence of Li, Ni, Mn, Ti, and O. Figure 6b shows that the $\text{Mn}2p_{3/2}$ and $\text{Mn}2p_{1/2}$ peaks appear at ~ 642.1 and ~ 653.9 eV, respectively, which proves that Mn has a valence state of +4. The binding energies of $\text{Ni}2p_{1/2}$ and $\text{Ni}2p_{3/2}$ are located at around ~ 872.5 and ~ 854.9 eV, respectively, as shown in Figure 6c; the difference in their binding energies is ~ 17.6 eV, demonstrating that Ni has the oxidation valence state of +2.

Figure 6d shows the XPS spectra of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$, with O1s peaks at ~ 529.3 and ~ 531.3 eV. They are regarded as lattice oxygen and oxygen vacancies present on the sample surface. Compared with that of the undoped samples, the peak intensity at ~ 531.3 eV of the doped sample considerably increases. This indicates the presence of a large number of oxygen vacancies on its surface, which suppress O_2 production and restrains the crystal structure transformation during long-term cycling, thereby positively influencing the cycling and kinetic performances of the material [48–50]. Figure 6e shows the XPS spectrum of the dopant, Ti. Ti has binding energies of ~ 464 and ~ 458 eV, confirming its positively tetravalent oxidation state. XRD and XPS results confirmed the successful doping of Ti^{4+} into $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, which did not change the oxidation states of Mn and Ni.

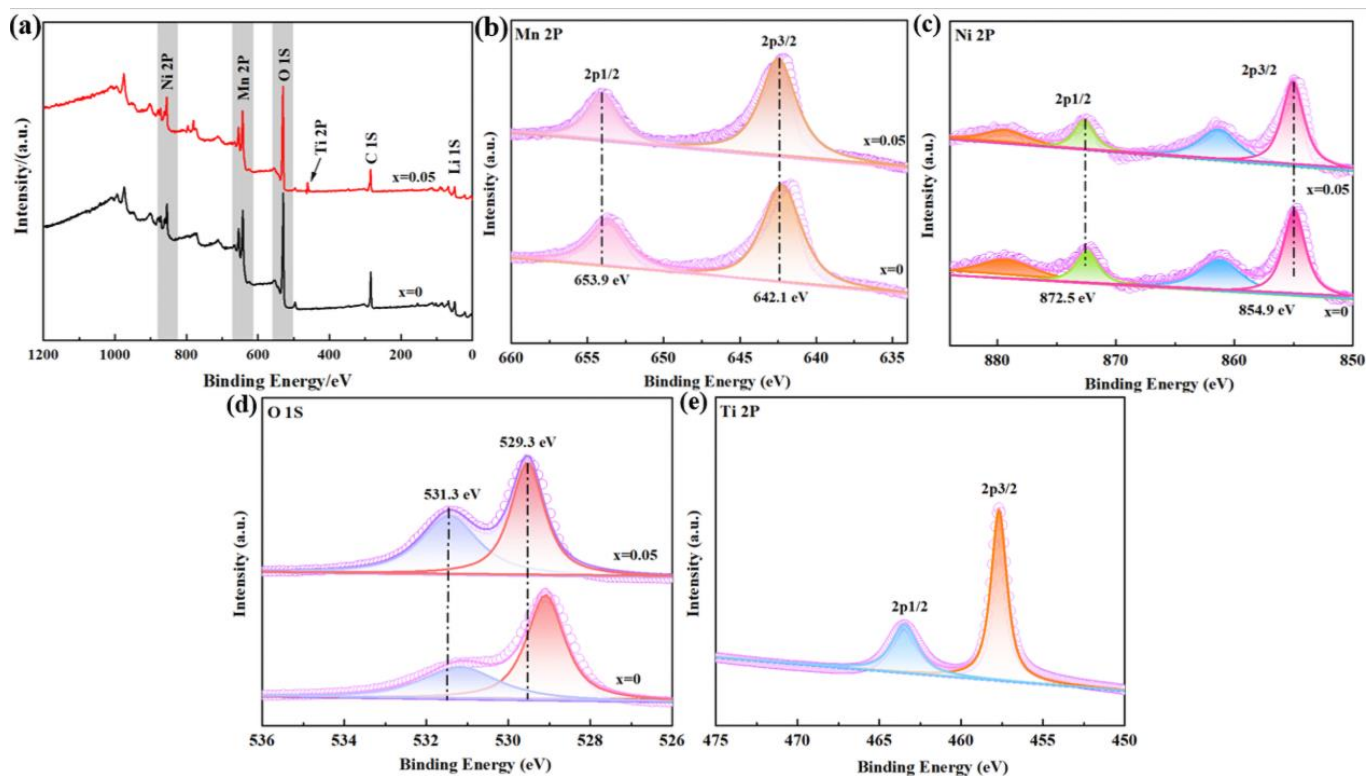


Figure 6. XPS spectra of $x = 0$ and $x = 0.05$ samples: (a) full spectrum; (b) Mn 2p spectrogram; (c) Ni 2p spectrogram; (d) O 1s spectrogram; (e) Ti 2p spectrogram.

Figure 7 shows the CV test results for five sample groups. Three oxidation peaks appeared in all samples, and the peak at ~ 3.1 V corresponded to Mn^{4+} reduction. Mn^{4+} reduction balances the decrease in oxygen during the initial charging process. The appearance of the Mn reduction peak in the subsequent cycle indicates that it is involved in the electrochemical reaction. The oxidation peak around 4.0 V corresponds to the oxidation of Ni^{2+} to Ni^{4+} , accompanied by the detachment of Li^+ from the Li layer. The reduction peak around 4.5 V corresponds to O^{2-} , which diminishes as the Ti doping amount increases, indicating that the addition of Ti reduces the loss of oxygen. The coincidence degree of the CV curves of the original sample and the sample with $x = 0.03$ gradually decreases, indicating the poor cyclic reversibility of the cathode material. The CV curves of the samples with $x = 0.05, 0.10$, and 0.15 have a high coincidence degree, indicating that Ti doping enhances the cycling stability. Moreover, the potential discrepancy in the oxidation and reduction peaks can reflect the reversibility of the electrode reaction and polarization level. The sample containing $x = 0.05$ exhibited a minimum difference and less capacity loss, indicating that an appropriate Ti doping amount reduces electrochemical polarization and facilitates the de-embedding of Li^+ .

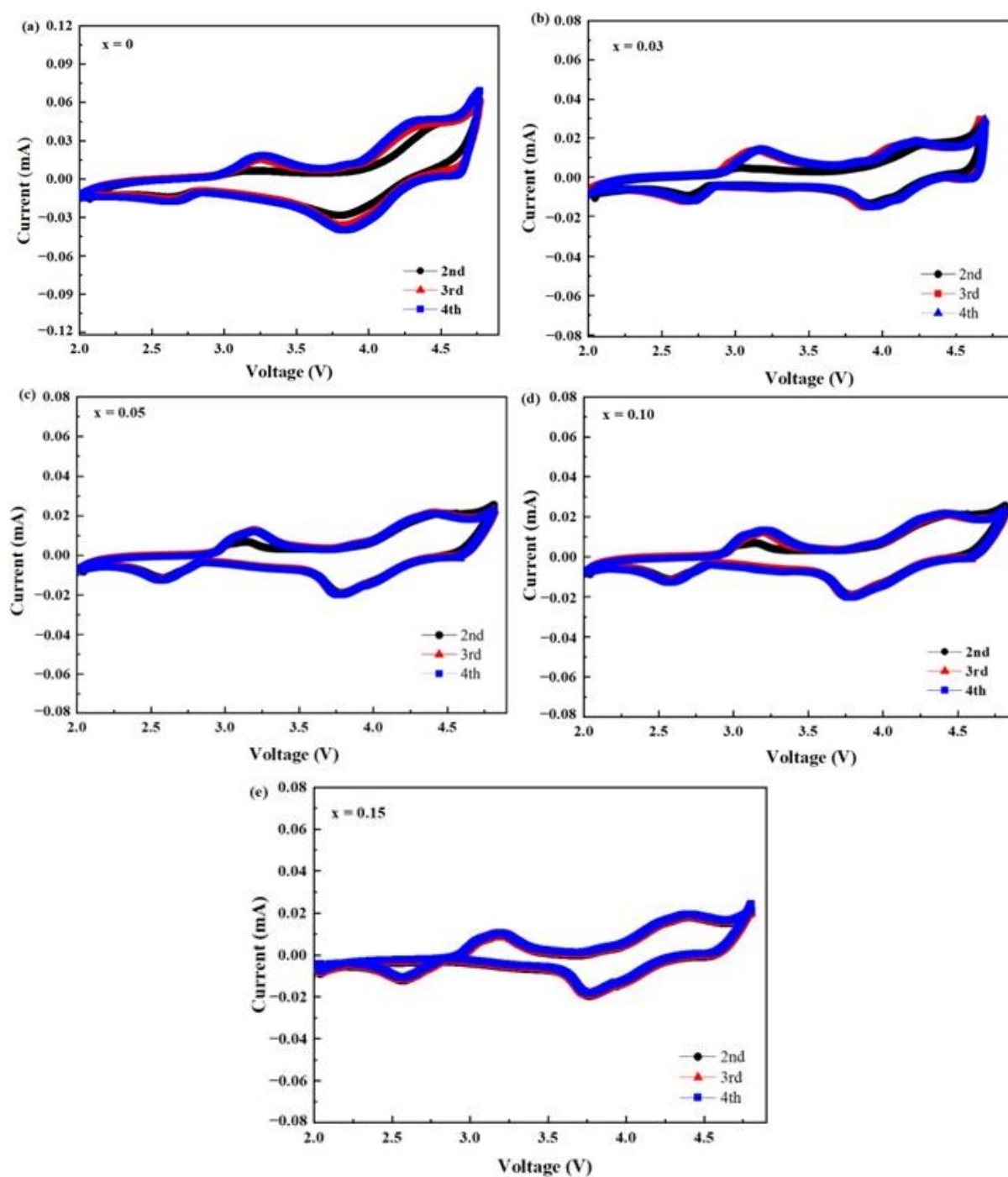


Figure 7. CV curves of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ samples: (a) $x = 0$; (b) $x = 0.03$; (c) $x = 0.05$; (d) $x = 0.10$; (e) $x = 0.15$.

Charge–discharge tests were performed on the five cathode materials, as illustrated in Figure 8. The original and Ti-doped modified samples show the charge–discharge properties of LLO. The first charge curve of all cathode materials is divided into two parts. When the charging voltage is <4.5 V, the oblique line region corresponds to the continuous release of Li^+ from the Li layer and the oxidation of Ni^{2+} to Ni^{4+} . When the charging voltage is >4.5 V, the other region corresponds to the activation of Li_2MnO_3 . Li^+ detachment was accompanied by oxygen release and irreversibly detached as Li_2O . Samples with $x = 0.03, 0.05, 0.10$, and 0.15 had discharge specific capacities of 128.2, 193.9, 163.6, and 159.6 $\text{mAh}\cdot\text{g}^{-1}$, respectively. Furthermore, the discharge curves of samples with

$x = 0.10$ and 0.15 show a small platform at ~ 2.6 V, resulting from a spinel phase generated by Li^+ on the material surface [41]. Results indicate that the sample with $x = 0.05$ has the largest first charge–discharge specific capacity, which decreases with increasing Ti doping amount.

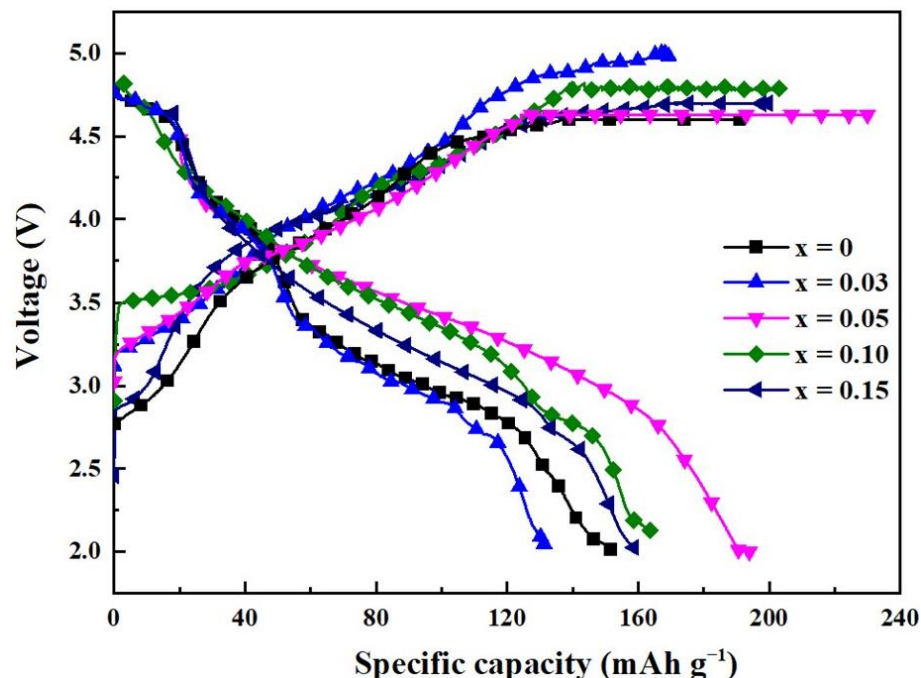


Figure 8. The first cycle charge/discharge profiles of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$).

Figure 9 shows the rate performance test results of all samples. Table 2 shows the discharge specific capacity of all samples. The discharge specific capacities of the samples with $x = 0.05$ were $204.3, 174.2, 141.4$, and $110.7 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1\text{C}, 0.2\text{C}, 0.5\text{C}$, and 1C , respectively. The corresponding discharge capacities of the undoped samples under the same conditions were $151.7, 120.6, 89.2$, and $64.3 \text{ mAh}\cdot\text{g}^{-1}$, respectively. When going back to 0.1C again, the samples with $x = 0.05$ and 0.10 had discharge specific capacities of 198.9 and $176.7 \text{ mAh}\cdot\text{g}^{-1}$, with high capacity retentions of 97.3% and 88.8% , respectively. Moreover, the discharge specific capacity first increases and then decreases with increasing Ti doping amount. The discharge specific capacities of the sample with $x = 0.15$ are only 92.7 and $67.5 \text{ mAh}\cdot\text{g}^{-1}$ at 0.5C and 1C , respectively, with severe capacity loss; it also shows considerable capacity decay in subsequent cycles.

Table 2. The discharge capacity of the $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ at different current densities.

Current Density Sample Specific Capacity/ $\text{mAh}\cdot\text{g}^{-1}$	0.1C	0.2C	0.5C	1C
$\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$	151.7	120.6	89.2	64.3
$\text{Li}_{1.2}\text{Mn}_{0.57}\text{Ti}_{0.03}\text{Ni}_{0.2}\text{O}_2$	129.2	97.2	67.7	40.9
$\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ti}_{0.05}\text{Ni}_{0.2}\text{O}_2$	204.3	174.2	141.4	110.7
$\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.10}\text{Ni}_{0.2}\text{O}_2$	180.6	148.4	116.3	91.4
$\text{Li}_{1.2}\text{Mn}_{0.45}\text{Ti}_{0.15}\text{Ni}_{0.2}\text{O}_2$	166.2	125.8	92.7	67.5

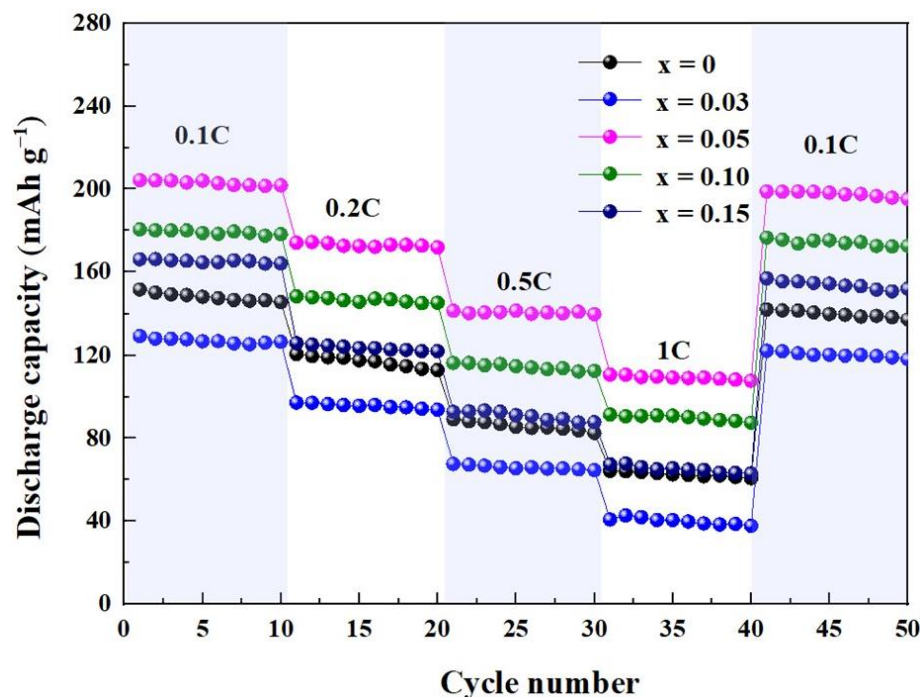


Figure 9. The rate performance of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$).

Figure 10a shows the charge–discharge performance test results of all samples at 0.1C for 100 cycles. The samples with $x = 0.03, 0.05$, and 0.10 showed enhanced cycling performance compared to the undoped sample. However, the discharge performance rapidly deteriorated with excessive Ti doping due to changes in the material structure. The first discharge specific capacities of the samples with $x = 0, 0.03, 0.05, 0.10$, and 0.15 were $150.9, 131.6, 210.4, 177.7$, and $165.1 \text{ mAh}\cdot\text{g}^{-1}$, respectively; after 100 cycles, the discharge specific capacities decreased to $113.6, 86.2, 191.1, 144.3$, and $128.2 \text{ mAh}\cdot\text{g}^{-1}$, respectively; the capacity retention values were $75.2\%, 65.5\%, 90.7\%, 81.2\%$, and 77.6% , respectively.

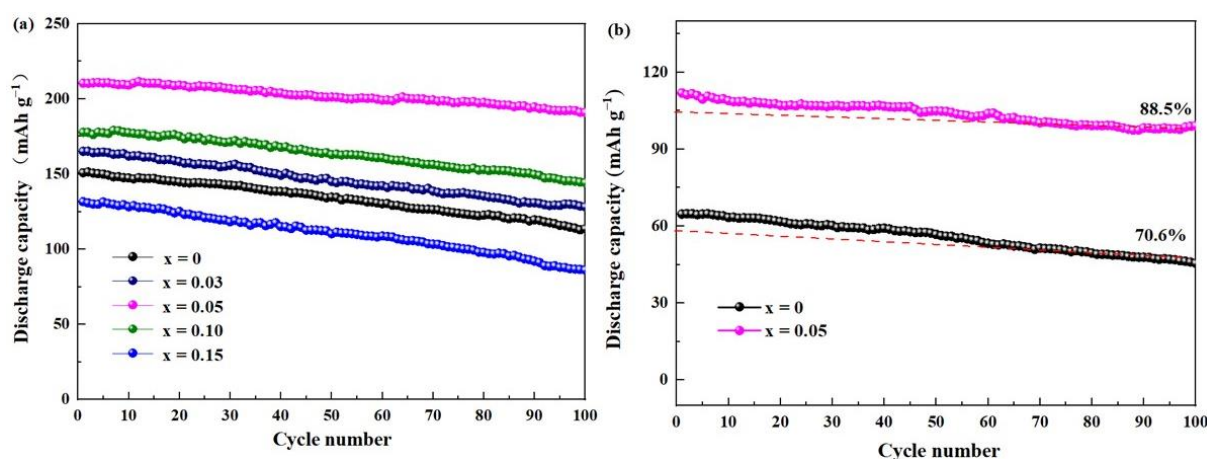


Figure 10. The cycle performance of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$: (a) $x = 0, 0.03, 0.05, 0.10, 0.15$; (b) $x = 0, 0.05$.

To further investigate the influence of Ti doping on the electrochemical properties of LLOs, samples with $x = 0.05$ and undoped samples were subjected to a cycling test at 1C. The initial discharge specific capacity of the doped sample was considerably high (Figure 10b), and the capacity retention after 100 cycles was 88.5% , considerably higher than that of the original material (70.6%). This indicates that the sample with $x = 0.05$ has a good cycling performance at a high magnification.

Figure 11 shows the changes in the discharge medium voltage of the doped samples during the 0.1C charge–discharge cycle. The median voltage of the undoped sample decreased from 3.521 to 3.014 V after 100 cycles, with a voltage attenuation of 0.507 V. The discharge voltage attenuation values of samples with $x = 0.03$, 0.05, 0.10, and 0.15 were 0.531, 0.357, 0.365 and 0.443 V, respectively. Ti doping can effectively alleviate voltage attenuation during the charge–discharge cycle, thereby inhibiting the structural evolution of LLOs and improving their cycling stability. The sample with $x = 0.05$ has a smaller voltage attenuation value, indicating that it has a more stable operating voltage.

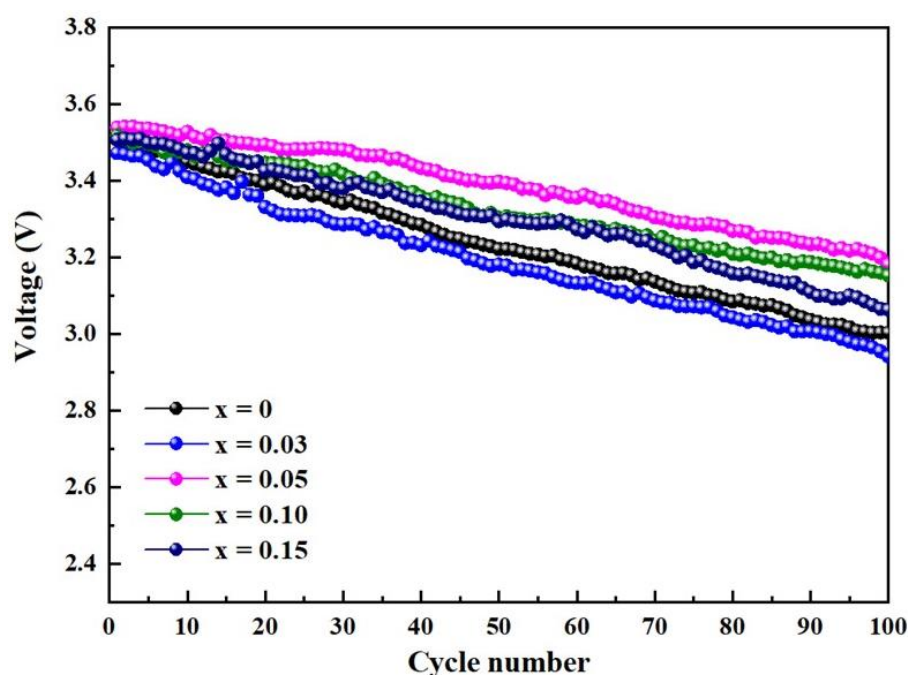


Figure 11. Mean voltage of the $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$).

To further understand the kinetic properties of Ti-doped materials, electrochemical impedance tests were performed on all samples (Figure 12a). All samples have the same electrochemical impedance spectra, with arcs in the high-frequency region (charge transfer impedance between the electrode and electrolyte) and diagonal lines in the low-frequency region (related to the diffusion of the Li ions in the active material). For the low-frequency test, an equivalent circuit was built based on the impedance spectrum (Figure 12a), where R_s is the resistance of the solution, R_{ct} is the resistance to charge transfer, and W is the Warburg impedance. The R_s values of samples with $x = 0, 0.03, 0.05, 0.10$, and 0.15 are 12.6, 11, 13.5, 13.1, and 14 Ω , respectively. The R_{ct} values of samples with $x = 0, 0.03, 0.05, 0.10$, and 0.15 are 351.5, 464.4, 257.2, 302.5, and 452.4 Ω , respectively (Figure 12b). The Li^+ diffusion coefficient (D) of the electrode materials can be computed according to the following formula [51]:

$$D_{\text{Li}^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{\text{Li}}^2 \sigma^2}$$

where R is the gas constant, $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T is the absolute temperature, $T = 298 \text{ K}$; A is the surface area of the electrode, $A = 0.785 \text{ cm}^2$; n is the number of electrons; F is the Faraday constant, $F = 96,485 \text{ C} \cdot \text{mol}^{-1}$; and C is the potassium ion concentration in the electrode; and σ is the Warburg coefficient, which can be obtained from the slope between Z_{re} and $\omega^{-1/2}$, as shown in Table 3. The σ and Li^+ diffusion coefficients of the prepared samples are listed in this table. It can be seen that the Li^+ diffusion coefficient of the sample with $x = 0.05$ is slightly higher than that of other samples.

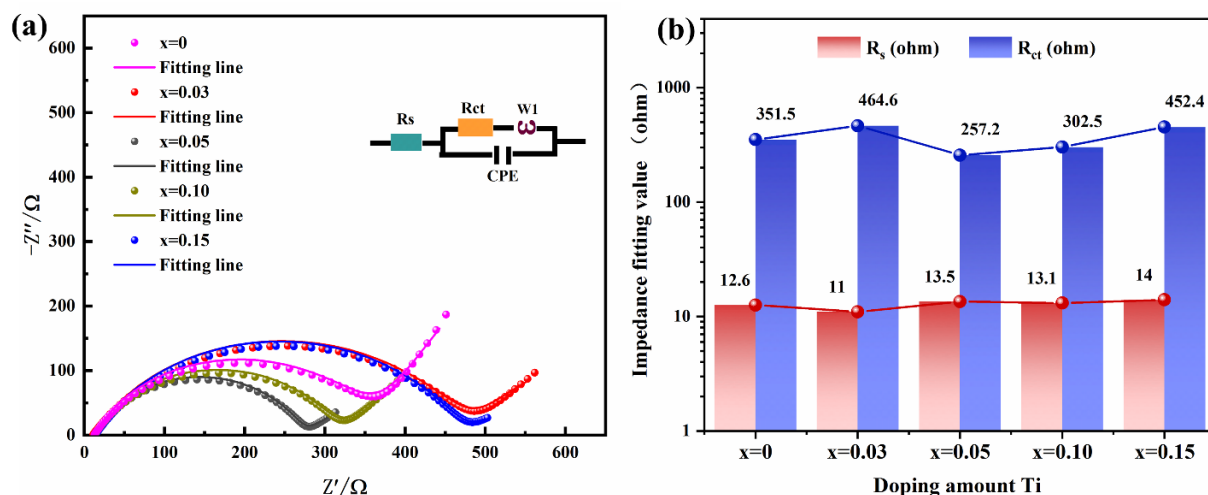


Figure 12. (a) Nyquist plots for the $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$); (b) Electrochemical properties of materials from EIS.

Table 3. The σ and Li^+ diffusion coefficients of the $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$.

Sample	$x = 0$	$x = 0.03$	$x = 0.05$	$x = 0.10$	$x = 0.15$
σ ($\Omega \text{ s}^{-1/2}$)	23.00	20.22	9.08	18.09	12.01
D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$)	2.72×10^{-10}	3.52×10^{-10}	1.74×10^{-10}	4.39×10^{-10}	9.96×10^{-10}

The sample with $x = 0.05$ has the smallest charge transfer impedance and the largest Li^+ diffusion coefficient than the other samples. This indicates that doped LLOs have high electronic and ionic conductivity and a high Li-ion diffusion rate, which enhance their diffusion kinetics. This also somewhat explains the increase in the rate and cycling performance of the cathode material after Ti doping.

3. Experimental Methods

3.1. Preparation of Ti-Doped $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ Cathode Material

According to the stoichiometric ratio of $\text{Li}_{1.2}\text{Mn}_{0.6-x}\text{Ti}_x\text{Ni}_{0.2}\text{O}_2$ ($x = 0, 0.03, 0.05, 0.10, 0.15$), Li_2CO_3 , MnO_2 , TiO_2 , and NiO were placed in a ball mill tank and mixed at a speed of 200 r/min for 3 h to fully mix. After the reaction, the uniformly milled sample was calcined in a muffle furnace. The specific process parameters were as follows: the temperature was increased to 900 °C with a rate of 15 °C increase per minute, followed by a constant sintering at the same temperature for 12 h, and then slowly cooled. It was sieved and milled to obtain samples with different Ti doping amounts.

3.2. Materials Characterization

The composition and structure of the samples were analyzed using XRD (Rigaku, Toshima, Tokyo, Japan). The diffraction target is Cu $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) and the data were acquired at an operating voltage of 40 kV, tube current of 300 mA, and $2\theta = 10^\circ\text{--}80^\circ$. Samples were analyzed for overall morphology by field-emission scanning electron microscopy (FE-SEM, ZEISS SUPRA55, Oberkochen, Germany). X-ray photoelectron spectroscopy (XPS) was tested on an ESCALAB 250 XI spectrometer to obtain valence information of the surface element compounds.

3.3. Electrochemical Measurements

A total of 80% active substance, 10% acetylene black, and 10% binder were weighed and ground. N-methyl pyrrolidone was added dropwise and ground until well-mixed. It was coated on clean aluminum foil and dried. The dried electrode sheets were cut into tiny

discs of about 5 mm radius and continued drying. The 1 mol L^{−1} LiPF₆ solution (EC–EMC–DMC volume ratio of 1:1:1) was selected as the electrolyte to complete the assembly of the half-cell in a glove box.

Charge and discharge performance and rate performance of the samples were analyzed by Land CT2001A Battery Test System (Wuhan Shenglan Electronic Technology Co., Ltd., Wuhan, China). Solartron 1260 + 1287 electrochemical impedance analyzers (British Powerstrong Precision Measurement Co., Ltd., Shanghai, China) were adopted for cyclic voltammetry (CV) testing and electrochemical impedance spectroscopy (EIS) testing. The voltage window range was 2–4.8 V, the scanning rate was 0.1 mV·s^{−1}, and the cycle test occurred 3 times.

3.4. Computational Method

Computation is based on density function theory (DFT) and implemented using the VASP6.3.2 software package. A pseudopotential derived from the projected affixed wave (PAW)-based method is used, and a switched association function is PBE54 in the generalized gradient approximation (GGA). A 3 × 3 × 1 supercell is used in the calculation, and the Monkhorst-pack K-space grid point is 3 × 3 × 2. The plane wave was chosen to have a truncation energy of 450 eV and a Gaussian spread of 0.05 eV, and the force convergence criterion is set to −0.02, indicating that the force of each atom is less than 0.02 eV. Considering the strong Coulomb interactions of d electrons in transition metals, the GGA + U method is used to deal with the U_{eff} of exchange-correlation energy for Mn, Ni, and Ti, which are set to 3.9, 5.4, and 4.2 eV, respectively.

4. Conclusions

Herein, a series of LLOs doped with Ti⁴⁺ was prepared using the high-temperature solid-state method. DFT calculations show that when Ti is doped to replace a part of Mn, the Jahn–Teller effect is weakened and a stable layered structure is formed. Moreover, the cycling performance of the material is improved. Li_{1.2}Mn_{0.55}Ti_{0.05}Ni_{0.2}O₂ showed the optimum electrochemical performance among all the samples. After 100 charge–discharge cycles at 0.1C, the discharge specific capacity decreased from 210.4 to 191.1 mAh·g^{−1}, with a high capacity retention of 90.7%; this value was considerably higher than that of the original sample (150.9 mAh·g^{−1}, 75.2%). Thus, a suitable Ti doping amount restrains the irreversible release of oxygen from LLOs and provides them with a stable structure.

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References

- Lu, J.; Chang, Y.L.; Song, B.; Xia, H.; Yang, J.R.; Lee, K.S.; Lu, L. High Energy Spinel-Structured Cathode Stabilized by Layered Materials for Advanced Lithium-Ion Batteries. *J. Power Sources* **2014**, *271*, 604–613. [\[CrossRef\]](#)
- Nitta, N.; Wu, F.; Lee, J.T.; Yushin, G. Li-Ion Battery Materials: Present and Future. *Mater. Today* **2015**, *18*, 252–264. [\[CrossRef\]](#)
- Li, P.; Luo, S.; Zhang, L.; Liu, Q.; Wang, Y.; Lin, Y.; Xu, C.; Guo, J.; Cheali, P.; Xia, X. Progress, Challenges, and Prospects of Spent Lithium-Ion Batteries Recycling: A Review. *J. Energy Chem.* **2024**, *89*, 144–171. [\[CrossRef\]](#)
- Sclar, H.; Maiti, S.; Sharma, R.; Erickson, E.M.; Grinblat, J.; Raman, R.; Talianker, M.; Noked, M.; Kondrakov, A.; Markovsky, B.; et al. Improved Electrochemical Behavior and Thermal Stability of Li and Mn-Rich Cathode Materials Modified by Lithium Sulfate Surface Treatment. *Inorganics* **2022**, *10*, 39. [\[CrossRef\]](#)
- Jung, Y.S.; Cavanagh, A.S.; Dillon, A.C.; Groner, M.D.; George, S.M.; Lee, S.-H. Enhanced Stability of LiCoO₂ Cathodes in Lithium-Ion Batteries Using Surface Modification by Atomic Layer Deposition. *J. Electrochem. Soc.* **2009**, *157*, A75. [\[CrossRef\]](#)
- Yamada, A.; Hosoya, M.; Chung, S.-C.; Kudo, Y.; Hinokuma, K.; Liu, K.-Y.; Nishi, Y. Olivine-Type Cathodes: Achievements and Problems. *J. Power Sources* **2003**, *119–121*, 232–238. [\[CrossRef\]](#)
- Zhao, H.; Liu, S.; Liu, X.; Tan, M.; Wang, Z.; Cai, Y.; Komarneni, S. Orthorhombic LiMnO₂ Nanorods as Cathode Materials for Lithium-Ion Batteries: Synthesis and Electrochemical Properties. *Ceram. Int.* **2016**, *42*, 9319–9322. [\[CrossRef\]](#)
- Niketic, S.; Yim, C.-H.; Zhou, J.; Wang, J.; Abu-Lebdeh, Y. Influence of Ti Substitution on Electrochemical Performance and Evolution of LiMn_{1.5-x}Ni_{0.5}Ti_xO₄ (x = 0.05, 0.1, 0.3) as a High Voltage Cathode Material with a Very Long Cycle Life. *Inorganics* **2022**, *10*, 10. [\[CrossRef\]](#)
- Gyu Kim, M.; Jo, M.; Hong, Y.-S.; Cho, J. Template-Free Synthesis of Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O₂ Nanowires for High Performance Lithium Battery Cathode. *Chem. Commun.* **2009**, *2*, 218–220. [\[CrossRef\]](#)
- Wang, H.; Zhan, F.; Zhan, H.; Ming, X. Improve the Midpoint Voltage and Structural Stability of Li-Rich Manganese-Based Cathode Material by Increasing the Nickel Content. *Catalysts* **2022**, *12*, 584. [\[CrossRef\]](#)
- Gao, J.; Kim, J.; Manthiram, A. High Capacity Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-V₂O₅ Composite Cathodes with Low Irreversible Capacity Loss for Lithium Ion Batteries. *Electrochem. Commun.* **2009**, *11*, 84–86. [\[CrossRef\]](#)
- Lee, Y.; Kim, M.G.; Cho, J. Layered Li_{0.88}[Li_{0.18}Co_{0.33}Mn_{0.49}]O₂ Nanowires for Fast and High Capacity Li-Ion Storage Material. *Nano Lett.* **2008**, *8*, 957–961. [\[CrossRef\]](#) [\[PubMed\]](#)
- Liu, J.; Reeja-Jayan, B.; Manthiram, A. Conductive Surface Modification with Aluminum of High Capacity Layered Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ Cathodes. *J. Phys. Chem. C* **2010**, *114*, 9528–9533. [\[CrossRef\]](#)
- Wang, Q.Y.; Liu, J.; Murugan, A.V.; Manthiram, A. High Capacity Double-Layer Surface Modified Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ Cathode with Improved Rate Capability. *J. Mater. Chem.* **2009**, *19*, 4965. [\[CrossRef\]](#)
- Li, Y.; Ben, L.; Yu, H.; Zhao, W.; Liu, X.; Huang, X. Stabilizing the (003) Facet of Micron-Sized LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ Cathode Material Using Tungsten Oxide as an Exemplar. *Inorganics* **2022**, *10*, 111. [\[CrossRef\]](#)
- Zhou, L.Z.; Xu, Q.J.; Liu, M.S.; Jin, X. Novel Solid-State Preparation and Electrochemical Properties of Li_{1.13}[Ni_{0.2}Co_{0.2}Mn_{0.47}]O₂ Material with a High Capacity by Acetate Precursor for Li-Ion Batteries. *Solid State Ion.* **2013**, *249–250*, 134–138. [\[CrossRef\]](#)
- Lei, Y.; Ni, J.; Hu, Z.; Wang, Z.; Gui, F.; Li, B.; Ming, P.; Zhang, C.; Elias, Y.; Aurbach, D.; et al. Surface Modification of Li-Rich Mn-Based Layered Oxide Cathodes: Challenges, Materials, Methods, and Characterization. *Adv. Energy Mater.* **2020**, *10*, 2002506. [\[CrossRef\]](#)
- Guo, B.; Zhao, J.; Fan, X.; Zhang, W.; Li, S.; Yang, Z.; Chen, Z.; Zhang, W. Aluminum and Fluorine Co-Doping for Promotion of Stability and Safety of Lithium-Rich Layered Cathode Material. *Electrochim. Acta* **2017**, *236*, 171–179. [\[CrossRef\]](#)
- Dogan, F.; Croy, J.R.; Balasubramanian, M.; Slater, M.D.; Iddir, H.; Johnson, C.S.; Vaughey, J.T.; Key, B. Solid State NMR Studies of Li₂MnO₃ and Li-Rich Cathode Materials: Proton Insertion, Local Structure, and Voltage Fade. *J. Electrochem. Soc.* **2014**, *162*, A235. [\[CrossRef\]](#)
- Hu, E.; Yu, X.; Lin, R.; Bi, X.; Lu, J.; Bak, S.; Nam, K.-W.; Xin, H.L.; Jaye, C.; Fischer, D.A.; et al. Evolution of Redox Couples in Li- and Mn-Rich Cathode Materials and Mitigation of Voltage Fade by Reducing Oxygen Release. *Nat. Energy* **2018**, *3*, 690–698. [\[CrossRef\]](#)
- Xu, J.; Deshpande, R.D.; Pan, J.; Cheng, Y.-T.; Battaglia, V.S. Electrode Side Reactions, Capacity Loss and Mechanical Degradation in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2015**, *162*, A2026–A2035. [\[CrossRef\]](#)
- He, W.; Yuan, D.; Qian, J.; Ai, X.; Yang, H.; Cao, Y. Enhanced High-Rate Capability and Cycling Stability of Na-Stabilized Layered Li_{1.2}[Co_{0.13}Ni_{0.13}Mn_{0.54}]O₂ Cathode Material. *J. Mater. Chem. A* **2013**, *1*, 11397. [\[CrossRef\]](#)
- Venkatraman, S.; Choi, J.; Manthiram, A. Factors Influencing the Chemical Lithium Extraction Rate from Layered LiNi_{1-y-z}Co_yMn_zO₂ Cathodes. *Electrochem. Commun.* **2004**, *6*, 832–837. [\[CrossRef\]](#)
- Chen, Z.; Qin, Y.; Amine, K.; Sun, Y.-K. Role of Surface Coating on Cathode Materials for Lithium-Ion Batteries. *J. Mater. Chem.* **2010**, *20*, 7606. [\[CrossRef\]](#)
- Ding, Z.; Xu, M.; Liu, J.; Huang, Q.; Chen, L.; Wang, P.; Ivey, D.G.; Wei, W. Understanding the Enhanced Kinetics of Gradient-Chemical-Doped Lithium-Rich Cathode Material. *ACS Appl. Mater. Interfaces* **2017**, *9*, 20519–20526. [\[CrossRef\]](#)
- Li, Q.; Li, G.; Fu, C.; Luo, D.; Fan, J.; Li, L. K⁺-Doped Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂: A Novel Cathode Material with an Enhanced Cycling Stability for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10330–10341. [\[CrossRef\]](#) [\[PubMed\]](#)

27. Zheng, Z.; Guo, X.-D.; Zhong, Y.-J.; Hua, W.-B.; Shen, C.-H.; Chou, S.-L.; Yang, X.-S. Host Structural Stabilization of $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ through K-Doping Attempt: Toward Superior Electrochemical Performances. *Electrochim. Acta* **2016**, *188*, 336–343. [\[CrossRef\]](#)
28. He, W.; Liu, P.; Qu, B.; Zheng, Z.; Zheng, H.; Deng, P.; Li, P.; Li, S.; Huang, H.; Wang, L.; et al. Uniform Na^+ Doping-Induced Defects in Li- and Mn-Rich Cathodes for High-Performance Lithium-Ion Batteries. *Adv. Sci.* **2019**, *6*, 1802114. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Lim, S.N.; Seo, J.Y.; Jung, D.S.; Ahn, W.; Song, H.S.; Yeon, S.-H.; Park, S.B. Rate Capability for Na-Doped $\text{Li}_{1.167}\text{Ni}_{0.18}\text{Mn}_{0.548}\text{Co}_{0.105}\text{O}_2$ Cathode Material and Characterization of Li-Ion Diffusion Using Galvanostatic Intermittent Titration Technique. *J. Alloys Compd.* **2015**, *623*, 55–61. [\[CrossRef\]](#)
30. Qing, R.; Shi, J.; Xiao, D.; Zhang, X.; Yin, Y.; Zhai, Y.; Gu, L.; Guo, Y. Enhancing the Kinetics of Li-Rich Cathode Materials through the Pinning Effects of Gradient Surface Na^+ Doping. *Adv. Energy Mater.* **2016**, *6*, 1501914. [\[CrossRef\]](#)
31. Makhonina, E.; Pechen, L.; Medvedeva, A.; Politov, Y.; Rummyantsev, A.; Koshtyal, Y.; Volkov, V.; Goloveshkin, A.; Eremenko, I. Effects of Mg Doping at Different Positions in Li-Rich Mn-Based Cathode Material on Electrochemical Performance. *Nanomaterials* **2022**, *12*, 156. [\[CrossRef\]](#)
32. Xiang, Y.; Li, J.; Wu, X.; Liu, Z.; Xiong, L.; He, Z.; Yin, Z. Synthesis and Electrochemical Characterization of Mg-Doped Li-Rich Mn-Based Cathode Material. *Ceram. Int.* **2016**, *42*, 8833–8838. [\[CrossRef\]](#)
33. Xu, H.; Deng, S.; Chen, G. Improved Electrochemical Performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ by Mg Doping for Lithium Ion Battery Cathode Material. *J. Mater. Chem. A* **2014**, *2*, 15015–15021. [\[CrossRef\]](#)
34. Jafta, C.J.; Ozoemena, K.I.; Mathe, M.K.; Roos, W.D. Synthesis, Characterisation and Electrochemical Intercalation Kinetics of Nanostructured Aluminium-Doped $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ Cathode Material for Lithium Ion Battery. *Electrochim. Acta* **2012**, *85*, 411–422. [\[CrossRef\]](#)
35. Iftexhar, M.; Drewett, N.E.; Armstrong, A.R.; Hesp, D.; Braga, F.; Ahmed, S.; Hardwick, L.J. Characterization of Aluminum Doped Lithium-Manganese Rich Composites for Higher Rate Lithium-Ion Cathodes. *J. Electrochem. Soc.* **2014**, *161*, A2109–A2116. [\[CrossRef\]](#)
36. Park, J.-H.; Lim, J.; Yoon, J.; Park, K.-S.; Gim, J.; Song, J.; Park, H.; Im, D.; Park, M.; Ahn, D.; et al. The Effects of Mo Doping on $0.3\text{Li}[\text{Li}_{0.33}\text{Mn}_{0.67}]\text{O}_2 \cdot 0.7\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ Cathode Material. *Dalton Trans.* **2012**, *41*, 3053. [\[CrossRef\]](#)
37. Ji, X.; Xu, Y.; Feng, H.; Wang, P.; Zhou, Y.; Song, J.; Xia, Q.; Tan, Q. Surface $\text{LiMn}_{1.4}\text{Ni}_{0.5}\text{Mo}_{0.1}\text{O}_4$ Coating and Bulk Mo Doping of Li-Rich Mn-Based $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ Cathode with Enhanced Electrochemical Performance for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 47659–47670. [\[CrossRef\]](#)
38. Lee, E.; Sun Park, J.; Wu, T.; Sun, C.-J.; Kim, H.; Stair, P.C.; Lu, J.; Zhou, D.; Johnson, C.S. Role of $\text{Cr}^{3+}/\text{Cr}^{6+}$ Redox in Chromium-Substituted Li_2MnO_3 - $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ Layered Composite Cathodes: Electrochemistry and Voltage Fade. *J. Mater. Chem. A* **2015**, *3*, 9915–9924. [\[CrossRef\]](#)
39. Song, B.; Zhou, C.; Wang, H.; Liu, H.; Liu, Z.; Lai, M.O.; Lu, L. Advances in Sustain Stable Voltage of Cr-Doped Li-Rich Layered Cathodes for Lithium Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A1723–A1730. [\[CrossRef\]](#)
40. Kou, Y.; Han, E.; Zhu, L.; Liu, L.; Zhang, Z. The Effect of Ti Doping on Electrochemical Properties of $\text{Li}_{1.167}\text{Ni}_{0.4}\text{Mn}_{0.383}\text{Co}_{0.05}\text{O}_2$ for Lithium-Ion Batteries. *Solid State Ion.* **2016**, *296*, 154–157. [\[CrossRef\]](#)
41. Yamamoto, S.; Noguchi, H.; Zhao, W. Improvement of Cycling Performance in Ti Substituted $0.5\text{Li}_2\text{MnO}_3$ - $0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ through Suppressing Metal Dissolution. *J. Power Sources* **2015**, *278*, 76–86. [\[CrossRef\]](#)
42. Lu, Z.; MacNeil, D.D.; Dahn, J.R. Layered Cathode Materials $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ for Lithium-Ion Batteries. *Electrochem. Solid-State Lett.* **2001**, *4*, A191. [\[CrossRef\]](#)
43. Zhu, H.; Li, J.; Chen, Z.; Li, Q.; Xie, T.; Li, L.; Lai, Y. Molten Salt Synthesis and Electrochemical Properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Cathode Materials. *Synth. Met.* **2014**, *187*, 123–129. [\[CrossRef\]](#)
44. Santhanam, R.; Rambabu, B. High Rate Cycling Performance of $\text{Li}_{1.05}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Materials Prepared by Sol–Gel and Co-Precipitation Methods for Lithium-Ion Batteries. *J. Power Sources* **2010**, *195*, 4313–4317. [\[CrossRef\]](#)
45. Xu, B.; Fell, C.R.; Chi, M.; Meng, Y.S. Identifying Surface Structural Changes in Layered Li-Excess Nickel Manganese Oxides in High Voltage Lithium Ion Batteries: A Joint Experimental and Theoretical Study. *Energy Environ. Sci.* **2011**, *4*, 2223. [\[CrossRef\]](#)
46. Gu, M.; Belharouak, I.; Zheng, J.; Wu, H.; Xiao, J.; Genc, A.; Amine, K.; Thevuthasan, S.; Baer, D.R.; Zhang, J.G.; et al. Formation of the Spinel Phase in the Layered Composite Cathode Used in Li-Ion Batteries. *ACS Nano* **2013**, *7*, 760–767. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Gao, Y.; Wang, X.; Ma, J.; Wang, Z.; Chen, L. Selecting Substituent Elements for Li-Rich Mn-Based Cathode Materials by Density Functional Theory (DFT) Calculations. *Chem. Mater.* **2015**, *27*, 3456–3461. [\[CrossRef\]](#)
48. Qian, D.; Xu, B.; Chi, M.; Meng, Y.S. Uncovering the Roles of Oxygen Vacancies in Cation Migration in Lithium Excess Layered Oxides. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14665–14668. [\[CrossRef\]](#)
49. Okamoto, Y. Ambivalent Effect of Oxygen Vacancies on Li_2MnO_3 : A First-Principles Study. *J. Electrochem. Soc.* **2011**, *159*, A152. [\[CrossRef\]](#)
50. Kubota, K.; Kaneko, T.; Hirayama, M.; Yonemura, M.; Imanari, Y.; Nakane, K.; Kanno, R. Direct Synthesis of Oxygen-Deficient $\text{Li}_2\text{MnO}_{3-x}$ for High Capacity Lithium Battery Electrodes. *J. Power Sources* **2012**, *216*, 249–255. [\[CrossRef\]](#)

-
51. Zheng, J.; Yan, P.; Estevez, L.; Wang, C.; Zhang, J.-G. Effect of Calcination Temperature on the Electrochemical Properties of Nickel-Rich $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ Cathodes for Lithium-Ion Batteries. *Nano Energy* **2018**, *49*, 538–548. [[CrossRef](#)]

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