Optimized Temperature Effect of Li-Ion Diffusion with Layer Distance in Li(Ni$_x$Mn$_y$Co$_z$)O$_2$ Cathode Materials for High Performance Li-Ion Battery

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Understanding and optimizing the temperature effects of Li-ion diffusion by analyzing crystal structures of layered Li(Ni$_x$Mn$_y$Co$_z$)O$_2$ (NMC) (x + y + z = 1) materials is important to develop advanced rechargeable Li-ion batteries (LIBs) for multi-temperature applications with high power density. Combined with experiments and ab initio calculations, the layer distances and kinetics of Li-ion diffusion of LiNi$_x$Mn$_y$Co$_z$O$_2$ (NMC) materials in different states of Li-ion de-intercalation and temperatures are investigated systematically. An improved model is also developed to reduce the system error of the “Galvanostatic Intermittent Titration Technique” with a correction of NMC particle size distribution. The Li-ion diffusion coefficients of all the NMC materials are measured from -25 to 50 °C. It is found that the Li-ion diffusion coefficient of LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ is the largest with the minimum temperature effect. Ab initio calculations and XRD measurements indicate that the larger Li slab space benefits to Li-ion diffusion with minimum temperature effect in layered NMC materials.

1. Introduction

Li-ion batteries (LIBs) are now widely used in portable electronic industry, plug-in hybrid vehicles (PHEVs), and electric vehicles (EVs) all over the world due to their advantages such as high energy density, high voltage, and long cycle life.[1] As one of the most widely used cathode materials, LiNi$_x$Mn$_y$Co$_z$O$_2$ (labeled as NMC) has been investigated extensively, due to their high reversible capacity, good environmental compatibility, and relatively high Li-ion diffusivity. In the previous works, different kinds of NMC materials with different content ratio of Ni, Co, and Mn have been developed, and their electrochemical properties have also been studied, such as LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (111),[4] LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ (442),[5] LiNi$_{0.42}$Mn$_{0.42}$Co$_{0.16}$O$_2$ (552),[6] LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ (532),[7] LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (622),[8] and LiNi$_{0.7}$Mn$_{0.15}$Co$_{0.15}$O$_2$ (71515).[9] For example, Noh et al. compared the electrochemical properties including the Li-ion diffusion coefficient, capacity retention, and electrochemical stabilities (25 to 55 °C) of layered NMC cathode materials (111), (532), (622), (71515), (811) and LiNi$_{0.85}$Mn$_{0.075}$Co$_{0.075}$O$_2$ at room temperature and found that the Ni content had a great influence on the electrochemical properties.[10]

Solid phase diffusion coefficient ($D_s$) is one of the most important parameters for the active materials of the LIBs, as it determines the charge and discharge rate capability directly. In particular, for high power density applications, fast Li-ion transport in cathode materials is a key factor and must be needed. As a result, many experimental and theoretical works have been devoted to investigating the Li-ion diffusion properties in layered cathode materials.[11,12] However, to the best of our knowledge, there is little work reported to study the relationship between the layer distance and kinetics of Li-ion diffusion in different temperatures of layered NMC cathode materials systematically, which is important for LIBs applied in multi-temperature environments.

At the same time, in order to measure $D_s$ accurately, many methods such as galvanostatic intermittent titration technique (GITT)[13–16] potentiostatic intermittent titration technique (PITT),[14,17] electrochemical impedance spectroscopy,[18] and cyclic voltammetry[19] have been developed in the past decades. Although factors such as the inaccuracy of the assumptions,
the distribution of the NMC particle size, the jitter of the cell voltage, and so on, may cause the measurement errors, however, no better methods can replace these methods mentioned above. Despite the existence of the errors and the disadvantage of long-time waiting, the results measured by GITT are still well accepted by scientists up to now. Besides, it is easier to implement compared with the other methods. Meanwhile, as different previous researches used different experiment conditions, different methods and different instruments, the GITT results always had a few orders of magnitude differences, and it is also difficult to compare the diffusion properties of different NMC materials from previous reported works. Therefore, it is hard to distinguish that which material has the best Li-ion diffusivity.

Here, we combined with experiments and ab initio calculations to investigate the Li-ion diffusion of NMC materials in different temperatures at the different states of Li-ion de-intercalation systematically for the first time. The $D_\text{Li}$ values of a series of different NMC materials (111, 442, 552, 532, 622, and 71515) at different temperatures from $-25 \degree C$ (248 K) to 50 $\degree C$ (323 K) are measured by using the improved GITT method, which is developed to employ an improved model to reduce the system error of GITT method with a correction of NMC particle size distribution. After comparing the kinetics properties of different NMC materials, it is found that 622 shows the highest Li-ion diffusivity with the minimum temperature dependence. Furthermore, both ab initio calculations and X-ray diffraction (XRD) measurements suggest that the Li slab space of the NMC layered material plays a great role on the Li-ion diffusion property versus temperature.

2. Results and Discussion

Figure 1a shows the Scanning electron microscope (SEM) of 622. As the form of different NMC materials is very similar, we take 622 as an example. The spherical particles are the secondary particles which consist of a lot of primary particles with a small grain for each of them. Besides, the SEM indicates that the secondary particles size is heterogeneous and most secondary particles have a diameter about 5–20 µm, as shown in Figure 1b.

Figure 2a-c shows the Li-ion diffusion coefficient ($D_\text{Li}$) versus different state of Li-ion de-intercalation ($\delta$) of Li$_{1-\delta}$(Ni$_{0.5}$Mn$_{0.5}$Co$_2$)$_2$O$_2$ ($0 \leq \delta \leq 1$) at 50, 25, and 0 $\degree C$, respectively. The Li-ion diffusion coefficients of all the NMC materials are in the range of about $1-10 \times 10^{-11}$ cm$^2$ s$^{-1}$. The diffusion coefficient of 622 is the largest among all the NMC materials we tested no matter at which temperature, while 111 is the smallest at 25 and 0 $\degree C$. The Li-ion diffusion coefficient increases with the temperature (Figure 2d). At the high temperature of 50 $\degree C$, the diffusion coefficient becomes greater than that at 25 $\degree C$. Meanwhile, the diffusion coefficient at low temperatures (0 and $-25 \degree C$) is less than that at 25 $\degree C$ (Figure 2b). According to the equation between the diffusion coefficient and the temperature (see Equation (8) in Experimental Section), lower temperature means smaller diffusion coefficient. With the rise of the temperature, Li-ions can diffuse more easily.

For the same material, the $\delta$ dependence increases as the temperature decreases. At 50 $\degree C$, the $\delta$ dependence of the Li-ion diffusion coefficient of all the NMC materials is very small, while the Li-ion diffusion coefficient changes a lot with $\delta$ at 0 $\degree C$. That is because $\delta$ is not the only factor that affects the Li-ion diffusion coefficient. When the Li-ion diffusion coefficient is large enough, the temperature dominates the mechanism instead of $\delta$. Meanwhile, the Li-ion diffusion coefficient increases with the increase of $\delta$. Interestingly, we found that the temperature fluctuation and the $\delta$ dependence of 622 diffusion coefficient were the smallest at 25 $\degree C$, while the variations of the other NMC materials are much larger. This implied that 622 has the largest applied range for different temperatures.

To further study 622 temperature effect of Li-ion diffusion coefficient, $D_\text{Li}$ versus temperatures from $-25$ to 50 $\degree C$ is shown in Figure 2d, indicating that the increase of the Li-ion diffusion coefficient is less than an order of magnitude. The diffusion coefficient of 622 still has $2 \times 10^{-11}$ cm$^2$ s$^{-1}$ at $-25 \degree C$. Therefore, in a certain temperature range (such as $-25$ to 50 $\degree C$), 622 can keep a relatively larger Li-ion diffusion coefficient. Hence, from the perspective of the experiment results, intuitively, 622 is the most promising NCM material for multi-temperature applications with higher Li-ion diffusivity and lower temperature effect. The rate capabilities of all the NMC materials were also tested, as shown in Figure 2e,f. We can see that the rate capability of 622 is the best, with the least capacity loss among all the NMC materials from 1 to 5 C, as it is shown in Figure 2e. Though the capacity of 71515 (147 mAh g$^{-1}$) is larger than that of 622 (142 mAh g$^{-1}$) at 1 C, the capacity of 622 (107 mAh g$^{-1}$) becomes larger than that of 71515 (105 mAh g$^{-1}$) at 5 C. Figure 2f shows the rate capability of 622 and 71515 at 0 $\degree C$, and note that the capacity of 622 (55 mAh g$^{-1}$) is much bigger than that of 71515 (19 mAh g$^{-1}$) at 5 C.

Among all NMCs, 532 is one of most widely used cathode materials in LIB applications. Here, we compare the Li-ion diffusion coefficients and related temperature effect of 622 and 532 in the following study. According to Equation (8) in the Experimental Section, if we take logarithm on both sides of the equation at the same time, we can plot the logarithm of the Li-ion diffusion coefficient versus the reciprocal of the temperature, in which the slope of the new straight line corresponds to the absolute value of $E_a$, as shown in Equation (1).

Figure 1. a) SEM of 622, b) the particle size distribution of Li(Ni$_{0.5}$Mn$_{0.5}$Co$_2$)$_2$O$_2$. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. www.MaterialsViews.com
E_a (eV) is the activation energy for diffusion, \( k \) (eV K\(^{-1}\)) is the Boltzmann constant, and \( D_0 \) is the diffusion coefficient when the temperature goes to infinite.

The calculation and GITT results of 532 and 622 at \( \delta = 0.33 \) are shown in Figure 3a,b, respectively, in which all curves show almost linear and the slope of 532 is slightly larger than that of 622, suggesting that the value of \( E_a \) of 532 is larger so as to be easier to be affected by the temperature. Note that the Li-ion diffusion coefficient of calculation is 1–2 orders of magnitude larger than that of GITT, which is mainly attributed to the systematic error which exists between the experiment and the calculation (see Section 4.1). Although the value of the slope from calculation is much bigger than that of measurement, the variation trends of the Li-ion diffusion coefficients of 532 and 622 by measurement and calculation are same.

The question is why the Li-ion diffusion coefficient of 622 is larger than that of 532 and other NMCs to be the largest with the minimum temperature effect in all the NMC materials. The mechanism is investigated according to relationship of layer distance structure versus Li-ion diffusion property by combination with the experimental measurements and ab initio calculations as below.

As shown in Equation (1), the Li-ion diffusion coefficient is related to the effective activation energy \( E_a \). As indicated in our previous work,\(^{[12]}\) there are two kinds of Li-ion diffusion pathways in such layered structures, namely, Li-ion diffuses from one octahedral site to next site through the oxygen dumbbell or an intermediate tetrahedral site, in which Li-ions tend to choose oxygen dumbbell hopping at the early stage of
charging (delithiation), and tetrahedral site hopping (TSH) begins to dominate when more than 1/3 Li-ions ($\delta > 0.33$) are extracted (Figure 4). The size of the oxygen dumbbell or the tetrahedral site (strain effect) as well as the electrostatic interaction between Li-ion in the activated state and the transition metal cation would contribute to the activation energy. As a result, the activation energy of Li-ions along this pathway is closely associated with the size of Li–O tetrahedrons and octahedrons. The oxygen atoms from upper and under layer would affect the diffusion barrier of Li. Li-ions that diffuse in narrow pathway are under larger forces, which leads to higher activation energy. In Figure 4b (TSH route), Li-ion diffuses from position 1 to position 3. When Li-ion is in position 2, the distance of Li and O atoms affects the work that the system has to do to transfer the Li-ion across this O atoms tetrahedron. Smaller Li slab space would decrease the size of the O atoms tetrahedron, while the energy barrier of this diffusion pathway would increase. The distance between these two O atoms is closely associated with the activation energy of this pathway. As a result, the activation barrier for Li-ion diffusion depends on the Li slab space (a type of the strain effect) and the kind of transition metals and their valence states. Previous studies$^{[12]}$ and Kang$^{[20]}$ reported that more Ni content with low valence state and large Li slab space are beneficial for Li-ion diffusion. Especially, the activation barrier is sensitive to the Li slab space. When Li slab space increases by 0.1 Å, activation energy along this pathway rises by 100 meV.$^{[20]}$ Here, the Ni$^{3+}$ content is the same for 532 and 622 at $\delta = 0.33$ and 0.5. Therefore, the difference of Li-ion diffusion coefficients between the two kinds of materials must come from the difference of Li slab spaces.

As shown in Figure 4a, Li slabs and transition metal oxide slabs are distributed alternatively, in which $d_1$ is the thickness of transition metal oxide slab, and $d_2$ is the Li slab space, $d_{001}$ is the distance of (001) plane. The relationship between $d_1$ and $d_2$ is given as $d_1 + d_2 = d_{001}$.

The XRD patterns of the six NMC materials we tested are shown in Figure 5a. The materials have a highly crystalline layered structure, with diffraction peaks corresponding to the R-3m space group. The splitting of the (108), (110) and (006), (102) peaks indicated well-ordered $\alpha$-NaFeO$_2$ structure. The (003) peaks of different NMCs are almost at the same 2$\theta$. Based the (003) peaks of XRD, we can find that the distances of (001) plane ($d_{001}$, the layer distance of NMC shown in Figure 4a) of all the NMCs are almost same around 4.74 (±0.01) Å at $\delta = 0$ as shown in Table 1, in which chemical lithium de-intercalation is used to control $\delta$. Figure 5b,c shows the XRD of 532 and 622 at different $\delta$, respectively. As $\delta$ increases, the (003) peak shifts as shown in the inset graphs. A summary of distances of (001) planes of all the NMCs with different $\delta$ by XRD is shown in Figure 5a.

![Figure 4](https://www.materialsviews.com/)

Figure 4. a) Lattice of NMC layered structure. Green atoms, Li; red atoms, O; silver/purple/blue atoms, Ni/Mn/Co transition metals. b) Tetrahedral site pathway and c) oxygen dumbbell pathway for Li-ion diffusion in NMC layered structure.
Table 1, in which displacements of the (001) peaks shift to lower diffraction angles, meaning that the (001) plane distances of all the NMCs increase with Li-ion de-intercalation process (increasing δ). Note that the (001) plane distances of 622 increase more than that of 532 with the increasing δ.

By using ab initio calculation models, the (001) plane distances and Li slab spaces of different NMCs are calculated as shown in Tables 2 and 3, respectively. Note that measured (001) plane distances of 333, 442, and 552 around 4.74 (±0.01) Å are a little bit larger than those of calculation around 4.68 (±0.02) Å, in which x(Ni) = y(Mn) in Li(Ni\text{x}Mn\text{y}Co\text{z})O\text{2}. However, measured and calculated (001) plane distances of NMC 532, 622, 715 are very close around 4.73–4.78 Å at δ = 0 (see Tables 1 and 2), in which x(Ni) > y(Mn) in Li(Ni\text{x}Mn\text{y}Co\text{z})O\text{2}. The difference of transition metal oxide slab is caused by ionic radius of Ni, Co, and Mn. According to Equation (2), when transition metal oxide slab is smaller, Li slab would share larger space. The calculation data of transition metal oxide slabs at δ = 0, 0.33, and 0.5 is shown in Table 3. (110) plane distance measured by XRD at δ = 0, 0.1, 0.25, and 0.5 can indirectly indicate distances of transition metal oxidation octahedral inside their slabs as shown in Table S4 (Supporting Information).

In our experiments, we found that with the increase of δ, d\text{001} of all NMCs become bigger (see Table 1), and the calculations also show that d\text{001} increases with δ (Table 2). However, transition metal oxide slabs (d\text{1}) of NMCs decrease with the increase of δ because the Ni ionic radius decreases during the Ni oxidation from Ni\text{2+} to Ni\text{3+}, or Ni\text{3+} to Ni\text{4+}. d\text{1} and d\text{2} of NMC materials are calculated, as shown in Table 3, in which the transition slab space (d\text{1}) decreases as the increasing of δ. According to Equation (2), Li slab space increases with the increasing of δ, which is consistence with the variation of d\text{2} in Table 3. Note that d\text{1} of 111 is the smallest. That is because in NMC111, the content of Mn\text{4+} and Co\text{3+} is the largest among all the NMC materials. Due to the smaller size of Mn\text{4+} (53 pm) and Co\text{3+} (54.5 pm) compared with Ni\text{3+} (60 pm) and Ni\text{2+} (69 pm), NMC111 has the smallest transition slab space (d\text{1}). These calculation and measurement data indicate that transition metal oxide slab (d\text{1}) of 622 is the smallest among all the NMC materials except 111, while the Li slab (d\text{2}) of 622 is largest comparing to that of 532 and 715 (see Table 3).

The question is why the layer distance (d\text{001}) and the Li slab (d\text{2}) of 622 at various Li-ion de-intercalation(δ) are larger than that of other NMCs. As Ni content rises in NMC material

**Figure 5.** a) XRD of NMC materials. XRD of b) 532 and c) 622 after chemical lithium de-intercalation. The data in the dashed line box is magnified in the inset graph.
Table 1. The distance of (001) plane of a series of NMC materials analyzed from XRD. The value of the error is 0.01 Å.

<table>
<thead>
<tr>
<th>δ (°C)</th>
<th>(001) plane distance [Å]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>333 442 552 532 622 71515</td>
</tr>
<tr>
<td>0.1</td>
<td>4.729 4.751 4.745 4.753 4.735 4.734</td>
</tr>
<tr>
<td>0.25</td>
<td>4.773 4.777 4.783 4.769 4.754 4.757</td>
</tr>
<tr>
<td>0.5</td>
<td>4.819 4.810 4.812 4.799 4.839 4.828</td>
</tr>
</tbody>
</table>

Table 2. The (001) plane distance in different NMC with δ = 0, 0.33, and 0.5 from ab initio calculations.

<table>
<thead>
<tr>
<th>δ (°C)</th>
<th>(001) plane distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>333 442 552 532 622 71515</td>
</tr>
<tr>
<td>0</td>
<td>4.664 4.705 4.686 4.766 4.785 4.768</td>
</tr>
<tr>
<td>0.33</td>
<td>4.672 4.721 4.708 4.778 4.792 4.781</td>
</tr>
<tr>
<td>0.5</td>
<td>4.678 4.729 4.717 4.788 4.797 4.787</td>
</tr>
</tbody>
</table>

Table 3. Transition slab space (d₁) and Li slab space (d₂) in ab initio calculation with δ = 0, 0.33, and 0.5.

<table>
<thead>
<tr>
<th>δ (°C)</th>
<th>d₁ [Å]</th>
<th>d₂ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(Calculated)</td>
<td>0.040 0.091 0.076 0.154 0.084 0.215</td>
</tr>
<tr>
<td>0.33</td>
<td>0.032 0.080 0.046 0.099 0.076 0.120</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.028 0.073 0.033 0.069 0.065 0.096</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>(Calculated)</td>
<td>0.264 0.261 0.260 0.261 0.270 0.253</td>
</tr>
<tr>
<td>0.33</td>
<td>0.260 0.261 0.262 0.267 0.276 0.261</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.265 0.265 0.268 0.279 0.273 0.269</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. The average activation energy of Li-ions in different NMC.

<table>
<thead>
<tr>
<th>δ (°C)</th>
<th>Average activation energy [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>514 495 503 475 484</td>
</tr>
<tr>
<td>0.5</td>
<td>471 457</td>
</tr>
</tbody>
</table>

The height of Li–O octahedrons is used to indicate the Li slab space. So the size of Li–O octahedrons and tetrahedrons along the Li-ions diffusion pathway is closely associated with the activation energy of Li-ions. For example, if the size of Li–O octahedrons reduces, the interaction between Li atoms and O atoms would increase. Therefore, Li-ions in 622 can diffuse easily due to the larger size of Li–O octahedrons and tetrahedrons than other NMC materials. On the other hand, Li slab space changes with the δ variation. Li-ions diffusion is accompanied by electrons transfer and redox of transition metal ions, and Li slab gets larger in the early stage of charging process due to the removal of O²⁻–Li⁺–O²⁻ bonds across the slab, which is consistent with the variation of d₁ in Table 3. The activation energies of Li-ions diffusion of 532, 622 are calculated when δ = 0.33 and 0.5 along TSH pathway with Ni atom nearby as shown in Table 4, along which diffusion pathways with Ni atom are the advantageous pathways with low activation energy in NMC materials.[12] Obviously, the activation energy of 622 is much lower than that of 532 due to the larger layer distances.

Temperature effects of Dₛ in NMC materials are shown in Figure 2, in which the variation of Dₛ at 0 °C is larger than those at 50 °C indicating that the Li-ion diffusion is more likely to rely on the Li slab space at low temperature, because the thermal motion of Li-ions is one of the factors that facilitate the diffusion process. Ions at high temperature can diffuse spontaneously even self-destruct. It can be concluded that Dₛ is dominated by the increase of δ at low temperature such as 0 °C. When the temperature rise exceeds a threshold value, Dₛ becomes not so sensitive to δ and the variation of Dₛ is smaller when δ increases. Interestingly, the curve of Dₛ versus δ variation is flatter for 622 compared to other NMC materials (Figure 2b) at each temperature. The spacing between Li slabs is one of the important factors that affects the activation energy.[12,20] If the spacing is enlarged, the energy barrier will be lowered, so Li-ions can migrate more easily to lead to less sensitive to the Li slab space variation during the de-intercalation process. Therefore, 622 is the most promising NMC materials, for it has a larger Li-ion diffusion coefficient, the minimum temperature dependence, a better thermal adaptability and a smaller δ dependence.

3. Conclusion
Li-ion diffusion properties versus layer distance for a series of NMC materials at different temperatures are studied systematically for the first time. Among all the NMC materials, the Li-ion diffusion coefficient of NMC622 is the largest with a smaller fluctuation with the temperature. Our experimental measurements
and ab initio calculations suggest that the large Li slab space accounts for the large Li-ion diffusivity with lower the activation energy along the diffusion pathway. This study reveals that a large Li slab space would facilitate the Li-ion diffusion with less temperature dependence and also predicts that 622 is the most promising materials for LIBs applied in multi-temperature environments.

4. Experimental Section

The series of NMC were synthesized by the co-precipitation method followed by solid-state reaction.[16] The 3%–5% excess of lithium was added in order to make the molar ratio for Li / (Ni + Mn + Co) around unity. The sintering procedure was done at 800 °C for 8–12 h and then the sample was quickly cooled down to the room temperature. The synthesis conditions for these NMC cathode materials (111, 442, 552, 532, 622, and 71515) were the same, so the influence of the synthesis temperature to the d-space and diffusion properties is little. Electrochemical experiments were performed using cells consisting of cathode electrode made of NMC, anode electrode of metal Li and electrolyte of EC: DEC.

Electrochemical measurements were carried out by MACCOR battery test cabinet (Model MC-16 Battery Test System, 5 V, 5 A). The electrochemical cells are consisted of NMC and Li metal as the positive electrode and negative electrode, respectively. The electrolyte was LiPF$_6$ in EC: DEC mixture solvent. During the GITT experiments, the cells were kept in a thermotank (RKS-80L, 220 V, 50 Hz) to guarantee that the temperature was constant during the measurements. Prior to the measurements, all the cells were activated by 3 charge/discharge cycles, and then they were charged again to 4.35 V for the GITT measurements. During the GITT measurements, the cells were repeatedly discharged for 15 min at 0.05 C and rested for 45 min, until the voltage reached 3.3 V. SEM (ZEISS SUPRA 55) and laser particle analyzer (Mastersizer3000E) were used to determine the homogeneity and distribution of the particle diameters. X-ray diffraction (DB Advance) was used to measure the spacing between layer distances of the NMC materials at different state of Li-ion deintercalation of Li$_{1-x}$(Ni$_{0.52}$Mn$_{0.24}$Co$_{0.24}$)O$_2$ (0 ≤ δ ≤ 1). Element analysis by Inductive Coupled Plasma Emission Spectrometer atomic emission spectrometer (ICP-aes: JY2000–2) was used to measure the amount of Li after the chemical lithium deintercalation which was handled by stirring the NMC powders in a series of different concentration acetonitrile solution of NO$_3$BF$_3$ for 24 h.

Accuracy Improvement of GITT: As the cell is discharged at a constant current, the voltage is a function of time. Assuming that the diffusion in each solid NMC particle is a 1D diffusion process,[16] and neglecting the double-layer charging process, the charge-transfer process, and the phase transformation,[13,14] the $D_i$ can be calculated by Fick’s law through Equation (3).

$$D_i = \frac{4}{\pi} \left( \frac{V_i}{\Delta V} \right)^2 \left( \frac{\Delta V}{\Delta V} \right)^2 \left( \frac{\tau}{\tau} \right) \left( \frac{L^2}{D_i} \right)$$

where $(F / 96485 \text{ C mol}^{-1})$ is the Faraday constant, $S (\text{cm}^2)$ is the interfacial area between the electrode and the electrolyte of the cell, $J (\text{A})$ is the applied current in the GITT experiment, $L (\text{cm})$ is the diffusion distance, $z_a$ is the charge number ($z_a = 1$ for Li-ions), and $V_{t_0} (\text{cm}^3 \text{ mol}^{-1})$ is the molar volume of the NMC materials, respectively. The values of $\frac{dE}{d\delta}$ and $\frac{dE}{dV}$ can be extracted from the relationships of $E$ versus $\delta$ and $E$ versus $V$, respectively. For simplicity, we also approximated that the NMC particles were all spherically shaped with particle size distribution to get the average radius of $R_i$.[16] This approximation was fairly reasonable, as the SEM image shown in Figure 1a. We ignored the porosity of the NMC materials. As the secondary particle is composed of primary particles which are closely packed (Figure 1a), the porosity is small. So we treat the secondary particle as a solid sphere.

As we used fairly low current rate (0.05 C) for GITT,[14] Equation (3) can be simplified as

$$D_i = \frac{4}{\pi} \left( \frac{R_i}{2} \right)^2 \left( \frac{\Delta V}{\Delta V} \right)^2 \left( \frac{\tau}{\tau} \right) \left( \frac{L^2}{D_i} \right)$$

where $\tau (s)$ is the duration time for each discharge step, and the values of $\Delta V$, and $\Delta V_i$ can be extracted from Figure 6, respectively. According to Equation (4), $D_i$ is proportional to the square of $R_i$. It is important to find a reasonable value of $R_i$ to reduce the errors caused by the particle distribution. As for the particle equivalent radius ($R_i$), the current $I$ in Equation (3) should be proportional to the total mass of the active particles, and therefore should be proportional to the total volume, assuming that the density is constant. While the interfacial area $S$ in Equation (3) equals to the sum of the active particles surface area. Thus, the particle equivalent radius, $R_i$, should follow

$$R_i = \frac{\text{Average Mass}}{\text{Total Mass}} \times \frac{1}{1}$$

where $V$ and $S$ are the average volume and the average surface area of the particles, respectively, and $R$ is the radius of each NMC particle. Figure 1b shows the particle size distribution of 622 measured by the laser particle analyzer. The relationship between the volume percent and the logarithm of the particle diameter ($2\delta$) basically obeys Gaussian distribution. Over 99% of the 622 particles diameter is between 4.5 and 31.1 μm. Take the cubic and square of $R_i$, and calculate their average value $R_i^3$ and $R_i^2$ respectively according to the distribution. Therefore, $R_i$ of 622 equals to 8.2 μm (or the equivalent diameter is 16.4 μm), based on Equation (5). Besides, Figures S6 and S7 (Supporting Information) show the SEM pictures and the particle size distribution of all the NMC samples that we test, respectively. The particle size is heterogeneous, but the distribution approximates to the Gaussian distribution. For Li$_{1-x}$(Ni$_{0.52}$Mn$_{0.24}$Co$_{0.24}$)O$_2$, GITT is accurate to extract $D_i$ if $0.2 < \delta < 0.5$, out of which the assumption of GITT is no longer valid.[16] The discharge pulse can no longer be treated as a delta function, resulting large measurement errors.

Due to the factors such as the inaccurate of the assumptions, the distribution of the NMC particle size, the jitter of the cell voltage, and so on, the GITT measurement still has its model errors. For example, the size of the NMC particles is heterogeneous, so it has a distribution. According to Equation (4), the error in spherical particle radius $R_i$ affects $D_i$. Usually, $R_i$ is smaller than actual radius. Besides, at the beginning and ending of the discharge, the voltage is unbalanced after 30 min rest. Despite these errors, no better method than GITT has been developed. As a result, previous studies reported that diffusion coefficient for NMC materials is usually in the range of $10^{-8}$ and $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ in GITT and PITT test.[10,22]
As a result of diffusion between Li-ions position, the diffusion coefficient depends on the barrier energy between Li-ions, as it is shown in Equation (8)

$$D_i = D_0 e^{-\frac{E_b}{kT}}$$  \hspace{1cm} (8)

It should be noticed that $E_b$ is effective activation energy instead of actual activation energy to describe some energy barrier along diffusion pathways. In NMC materials, there is no observable structure displacement below 600 K. As in Equation (8), log($D_i$) is linear to 1/$T$, to compare the results from first-principle calculation with experimental results, linear fitting was applied to reach the diffusion coefficient at room temperature.

Also, cNEB method was performed to investigate the migration barrier of Li-ions in NMC layered materials.\[c] cNEB was a complementary to NEB method. In this work, cNEB was applied in a 3 × 3 × 1 supercell with five images as intermediate states. A series of images along the migration pathway were fully relaxed with a spring constant as constraint condition. Total energy of these series of intermediate states were calculated to describe the migration barrier along this pathway.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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