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Impact of lithium excess on the structural and electrochemical properties of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ high-voltage cathode material †

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LiNi$_{0.5}$Mn$_{1.5}$O$_4$-based cathode materials are synthesized by one-step nonaqueous co-precipitation method. Appropriate excess lithium ions can extrude transition metal ions out of tetrahedral 8a sites, which could have a higher effect on the rate performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ than the well-known factor, i.e. cationic order degree in 16d octahedral sites.

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is a promising cathode material for lithium-ion batteries as it offers a high operating voltage of ~4.7 V arising from Ni$^{3+/4+}$ couple instead of Mn$^{3+/4+}$ couple of spinel LiMn$_2$O$_4$. It possesses two similar crystal structures. One with a random distribution of Mn$^{4+}$ and Ni$^{2+}$ ions in the octahedral 16d sites displays the disordered phase with the space group of P6$_3$m. Another belongs to the space group of P4$_{3}21$ with an order arrangement of Mn$^{4+}$ and Ni$^{2+}$. The real structure of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ contains both two phases. Factors influencing the performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ mainly reported are cationic order degree in octahedral 16d sites and surface planes. Generally the material with lower cationic order degree is thought to have better rate performance because of its higher Li-ion diffusion coefficient.

Changing annealing conditions is a traditional way to control cationic order because Mn$^{4+}$ derived from oxygen vacancies hinders this order degree. Whittingham et al. prepared disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with high-rate capability by increasing Mn$^{3+}$ concentration. Meanwhile some other methods such as varying Ni/Mn ratio, doping and polymer-assisted method also could be actualized to control cationic order with no need for further annealing. However a common phenomenon, namely some extent of transition metal ions (Ni$^{2+}$ and/or Mn$^{4+}$) occupy in the tetrahedral 8a sites instead of original Li$^+$ ions, usually is overlooked. Means applied to control cationic order degree in octahedral 16d sites could even enhance this staggered arrangement. Though the mixing effect between lithium ions and transition ions in cathode materials with layered structure has been proven to be unfavorable to rate ability, its effect on the performance of spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has not received enough attention.

In an attempt to clarify the role of tetrahedral 8a sites occupation, a simple method was carried out: appropriate excess lithium ions can extrude transition ions out of tetrahedral 8a sites without causing morphology and structure change but an increase of cationic order degree in 16d octahedral sites. Li excess could improve the cycle ability by suppress the Jahn-Teller effect of spinel LiMn$_2$O$_4$, while Li$_2$MnO$_3$ derived from Li-rich for the ternary layered cathodes have a great influence on the electrochemical capability. Nevertheless, impact of lithium excess on LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is lack of study. Following characterizations would provide results that avoiding the transition metal ions occupation in tetrahedral 8a sites by Li excess is beneficial to mobility of Li$^+$. The diffusion channel of Li$^+$, 8a-16c-8a, is liable to be blocked by transition metal ions in tetrahedral 8a sites, as shown in Fig. 1.

In this work, one-step nonaqueous co-precipitation method (Fig. 1 Schematic illustration of (a) Li$^+$ diffusion channel and (b) Li$^+$ diffusion channel been blocked in spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ structure.)

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S1, ESIf) was applied to precipitate Li4+, Ni3+ and Mn4+ at the same time to prepare Li10+xNi8−xMn1.5O4 (x=0, 0.01, 0.03, 0.05). For the reasonable comparative analysis of these two factors (tetrathedral 8a sites occupation and cationic order degree in 16d octahedral sites) influencing the rate performance, keeping identical morphologies for all samples is the prerequisite. It can be found that all the samples display regular, small octahedral grains with a size distribution of 200-500 nm. (Fig. S2, ESIf).

As shown in Fig. 2. The XRD peaks of LiNi0.5Mn1.5O4 and Li10Ni0.45Mn1.5O4 coincide well with spinel structure. The lack of any superstructure diffraction peaks, which derives from the ordering of transition ions in the octahedral 16d sites, reveals that these two samples have a relatively low degree of cationic order.22 However, increasing Li amount changes the structure from disordered to ordered phase, as revealed by the existence of superstructure diffraction peaks such as (110), (210), (320) and (410) peaks.23 It’s worth noting that peaks of superstructure for Li10Ni0.45Mn1.5O4 are weaker than those of Li10Ni0.45Mn1.5O4. Of particular note, a diffraction peak appears at 2θ=30.9°, which was indexed as the (220) diffraction of the spinel compounds. The appearance of the (220) diffraction peak for Li10Ni0.45Mn1.5O4 indicates that there must be some transition metal ions occupying the tetrahedral 8a sites replacing of the original Li+ ions.24 The weak diffraction peaks marked by asterisks possibly are from Li2Ni1.45O.25 This common impurity is only observed in LiNi0.5Mn1.5O4 and Li10Ni0.45Mn1.5O4. Arrebola et al considered that based on the crystal field model, in spinel structure Ni2+ ions have a strong tendency to occupy octahedral 16d positions; therefore Mn was forced to occupy tetrahedral 8a positions. And the radius of Mn4+ (0.53 Å) is closer to Li+ (0.59 Å) than Ni2+ (0.69 Å), thus it can be speculated that excess lithium ions could extrude Mn ions out of tetrahedral 8a positions to suppress the formation of Ni-rich impurity.

XPS results show that the Mn valence state in Li10Ni0.5Mn1.5O4 is between +3 and +4, and Mn valence state increases with excess Li (Fig. S3, ESI††). The formation of oxygen vacancies could be suppressed by slow cooling process and then manganese has to take the responsibility to balance charge. In the light of spectral lines of manganese oxide, both of the manganese 2p3/2 and 2p1/2 regions can be deconvoluted into two peaks. The peaks at 642.0 and 643.3 eV of the Mn2p3/2 spectrum arise from Mn3+ and Mn4+.

Fig. 3 (a) Raman spectra of Li10Ni0.5Mn1.5O4 samples, and (b) Intensity ratio of (400)/(311) XRD peaks.

Fig. 2 XRD patterns of the four Li10Ni0.5Mn1.5O4 samples: (a) full range, (b) enlarged region to show the superstructure reflections arising from the Mn3+ and Ni4+ ordering in the 16d octahedral sites and (c) enlarged region to show the change of lattice parameter. Asterisks refer to the reflections arising from Li2Ni1.45O impurity phase.
Fig. 4 HRTEM images (a1 to d1) and electron diffraction patterns in the [100] (a2 to d2) and [110] (a3 to d3) zones of (a) LiNi0.8Mn1.2O4, (b) Li1.01Ni0.49Mn1.5O4, (c) Li1.01Ni0.46Mn1.5O4 and (d) Li1.01Ni0.45Mn1.5O4.

The high resolution electron microscopies are compared in Fig. 4 along with their diffraction patterns in the [100] and [110] zones. Fig. 4 (a1) to (d1) show the HRTEM images of the lattice fringe, of which $d_{(111)}$ measured is ~0.47 nm, corresponding to the (111) interplanar distance. Only a representative spinel diffraction pattern can be observed in the [100] and [110] zones for Li1.0xNi0.5−xMn1.5O4 (x=0, 0.01, 0.03), while Li1.0xNi0.46Mn1.5O4 exhibits superlattice diffraction as shown in Fig.4 (d2 and d3). The electron diffraction patterns show that the increasing Li amount introduces more ordered phase (or decreases disordered phase) content as well.

Galvanostatic cycling tests were conducted at a current density of 1.01 $\text{mA cm}^{-2}$ (0.1 C) from 3.5 to 5.0 V, as shown in Fig. 5(a). All the cathodes exhibited two typical plateaus: long and distinct flat plateau around 4.7 V attributed to Ni$^{3+/2+}$, Mn$^{3+/4+}$ redox reaction, another short plateau around 4.0 V arising from Mn$^{3+/4+}$ redox process. The voltage plateau of 4.0 V indicates that a small number of manganese remained as Mn$^{4+}$, because the oxidation state of manganese is fixed at +4 only in the ideal structure. The length fraction of plateau at 4.0 V decreases by increasing the Li fraction. This trend can be accounted for by considering that an increase in Li amount results in a decrease of Mn$^{3+}$ concentration, in accord with the XRD, XPS and TEM. Besides, it is worth noting that the charge plateau of LiNi0.8Mn1.2O4 and Li1.01Ni0.46Mn1.5O4 samples around 4.7 V splitting to two plateaus corresponding to Ni$^{3+/4+}$ and Ni$^{4+/2+}$ couples individually in Fig.5(a), while these two plateaus overlapped for Li1.01Ni0.49Mn1.5O4 and Li1.01Ni0.45Mn1.5O4. It has been reported that the narrower separation between the two voltage plateaus indicates a higher degree of cationic ordering. A more detailed analysis is further possible with the dQ/dV plots (Q = specific capacity and V = voltage). The two dQ/dV peaks in the 4.7 V region indicate respectively the two-step oxidation or reduction for the Ni$^{4+/2+}$ redox couple. The inset of Fig. 5(b) is the dQ/dV plots in 4V region of the spinel cathodes, also showing that the intensity of peak in the 4.0 V regions reduces by increasing the Li fraction.

In order to study the effect of excess lithium on diffusion of Li$^+$ in the cathodes, the electrochemical impedance spectroscopy was performed. Fig. 5(c) displays the Nyquist plots of the spinel electrodes before cycling. All EIS contain one semicircle in the high- and medium-frequency regions and an inclined line in the low frequency zone. The diffusion coefficient ($D_{li}$) of lithium ion can be calculated from the plots in the low-frequency region using the equation:

$$D_{li} = \frac{(RT)^2}{2n^2F^2C_L\sigma^2}$$

where the implications of $T$ is the kelvin degree, $R$ the universal gas constant, $n$ the number of electrons per molecule during reaction, $A$ the superficial area, $F$ the Faraday’s constant, $C_L$ the lithium ion concentration, $\omega$ the angular frequency, and $\sigma$ is the Warburg factor. The $Z(\omega)^{-0.5}$ plots to calculate $\sigma$ is presented in Fig. 5(d). A linear characteristic could be seen for both profiles. The calculated lithium ion diffusion coefficient of Li1.03Ni0.47Mn1.5O4 is higher than other three samples, which is calculated as 3.159×10$^{-13}$ cm$^2$ s$^{-1}$ and close to that measured by CV. Interestingly, though Li1.03Ni0.47Mn1.5O4 exhibits higher degree of cationic ordering than LiNi0.5Mn1.5O4 and Li0.91Ni0.49Mn1.5O4, it exhibits better lithium ion diffusion capability, implying that well-known factor, cationic order degree in 16d octahedral sites, does not dominates the Li$^+$ transport for these three samples.

The cycle and rate performances (Fig. 6) are in good agreement with EIS results. At 25 $^\circ$C, the LiNi0.5Mn1.5O4, Li1.01Ni0.49Mn1.5O4, Li1.03Ni0.47Mn1.5O4 and Li1.03Ni0.45Mn1.5O4 samples delivered initial specific capacities of 105.9, 114.8, 123.7 and 88.1 mAh g$^{-1}$ at a 5 C rate and retained 93.4%, 95.0%, 95.7% and 96.0% after 300 cycles, respectively. It can be seen that the coulombic efficiency of the initial cycle for all the samples is relatively low because the batteries were charged at 0.1C, and then discharged at 5 C, but it became higher and stable in the following cycles. The Li-excess samples exhibited higher coulombic efficiency resulting in better cycle performance. The cycle ability is comparable with LiNi0.5Mn1.5O4 nanotubes synthesized by self-templating method, which delivered a discharge capacity of 85 mAh g$^{-1}$ at 5 C even after 550 cycles. At a high rate of 30 C, the discharge capacity of Li1.03Ni0.47Mn1.5O4 can still reach 90.1 mAh g$^{-1}$, corresponding to
Li samples (LiNi$_{1-x}$Mn$_x$O$_2$) were used to improve the discharge capacity at high C-rates. The LiNi$_{0.5}$Mn$_{0.5}$O$_2$ electrode displays a discharge capacity of 114.2 mAh g$^{-1}$ at 10C-rates. In contrast, the rate behaviour of LiNi$_{0.4}$Mn$_{0.6}$O$_2$ is worse, presenting a discharge capacity of only 87.3 mAh g$^{-1}$ when the current density increases to 10C.

Many researchers have reported that high degree of cationic ordering would deteriorate rate performance for its limited lithium diffusion. In this study, the LiNi$_{0.5}$Mn$_{0.5}$O$_2$ electrode with the highest order degree indeed shows the worst rate capability. Compared to the LiNi$_{0.5}$Mn$_{0.5}$O$_2$ to LiNi$_{0.4}$Mn$_{0.6}$O$_2$, it can be found that LiNi$_{0.5}$Mn$_{0.5}$O$_2$ with higher degree of cationic ordering delivers lower rate ability. This could be because degree of cations ordering play a leading role for this two samples, in agreement with the general view. However, for the first three samples (LiNi$_{0.5}$Mn$_{0.5}$O$_2$, LiNi$_{0.4}$Mn$_{0.6}$O$_2$, LiNi$_{0.3}$Mn$_{0.7}$O$_2$), excess lithium improved the rate ability obviously, indicating the transport of lithium ions could be enhanced by unhindered diffusion channel even with a more ordered arrangement of nickel and manganese ions in 16d octahedral sites.

In conclusion, octahedral grains of LiNi$_{0.5}$Mn$_{0.5}$O$_2$-based materials are synthesized through a one-step co-precipitation method. A series of samples with increasing degree of cationic ordering in 16d octahedral sites (harmful to mobility of Li$^+$) were prepared, of which the amount of transition metal ions in tetrahedral 8a sites reduces (beneficial for Li$^+$ diffusion). The improved performance of LiNi$_{0.4}$Mn$_{0.6}$O$_2$ might be attributed to appropriate excess lithium ions that can preferentially occupy the tetrahedral 8a sites, extruding transition metal ions out of tetrahedral 8a positions to keep Li$^+$ ions diffusion channel unobstructed. However, when the lithium excess is too much, it will result in obvious enhancement of the order degree in octahedral 16d sites, which is widely accepted as a negative factor for the rate capacity.

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Notes and references

Li$_{1+x}$Ni$_{0.5-x}$Mn$_{1.5}$O$_4$, made via a novel one-step co-precipitation route, undergoes a disordered-to-ordered phase change. Transition metal ions in tetrahedral sites could influence performance more than the cationic ordering in octahedral site does.