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LiNi_{0.5}Mn_{1.5}O₄ Spinel and Its Derivatives as Cathodes for Li-Ion Batteries

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1. Introduction

It is well known that lithium-ion batteries are common in consumer electronics. It is one of the most popular types of rechargeable battery for portable electronics, with the best energy densities, no memory effect, and a slow loss of charge when not in use [1, 2]. Beyond consumer electronics, LIBs are also growing in popularity for military, electric vehicle, and aerospace applications. Its excellent properties originate from its materials including cathode, anode and electrolyte and so on. For cathode materials, there are mainly three kinds of materials which have been widely studied and applied commercially, including layered oxide LiCoO₂, spinel LiMn₂O₄ and olivine LiFePO₄. Among the cathode materials, LiCoO₂ has been used since the invention of LIB [3], while LiMn₂O₄ and LiFePO₄ are considered as promising ones due to less toxicity, low cost, more safety and good electrochemical properties [4, 5]. In term of redox energy level, these materials can be charged and discharged at around 4 V, which limits their energy density. The spinel LiNi_{0.5}Mn_{1.5}O₄ is becoming a research focus recently. The most remarkable property of spinel LiNi_{0.5}Mn_{1.5}O₄ is its discharge voltage plateau at around 4.7 V. In some cases, using LiNi_{0.5}Mn_{1.5}O₄ will lead fewer cells at the battery pack level. For example, hundreds of ordinary lithium ion batteries are needed to meet the requirement of electric vehicle (EV) in the state of start-up, accelerate and climb-up [6] because more energy is needed in this case. If the high voltage cells are utilized, the amount of batteries used for EV can decrease greatly. This chapter gives a detailed introduction on LiNi_{0.5}Mn_{1.5}O₄ spinel and the latest research advances in this area.

2. Structures of LiNi_{0.5}Mn_{1.5}O₄

There are two kinds of crystal structure for spinel LiNi_{0.5}Mn_{1.5}O₄, i.e. face-centered spinel (*Fd3m*) and primitive simple cubic crystal (*P4₃32*). For LiNi_{0.5}Mn_{1.5}O₄ with a face-centered structure (*Fd3m*), the lithium ions are located in the 8a sites of the structure, the manganese and nickel ions are randomly distributed in the 16d sites. The oxygen ions which are cubic-close-packed (ccp) occupy the 32e positions. For LiNi_{0.5}Mn_{1.5}O₄ (*P4₃32*) with a primitive simple cubic structure, the manganese ions are distributed in 12d sites, and nickel ions in 4a sites. The oxygen ions occupy the 24e and 8c positions, while the lithium ions are located in the 8c sites. In this case, the Ni and Mn ions are ordered regularly [7-9]. Whether LiNi_{0.5}Mn_{1.5}O₄ has a structure of face-centered spinel (*Fd3m*) or primitive simple cubic

($P4_332$) depends on its synthetic routes. In synthesizing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, annealing process at 700°C after calcination led to the ordering of Ni and Mn ions, making it transformed from face-centered spinel ($Fd3m$) to primitive cubic crystal ($P4_332$). Schematic drawing of the structures of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is shown in Fig. 1 [10].

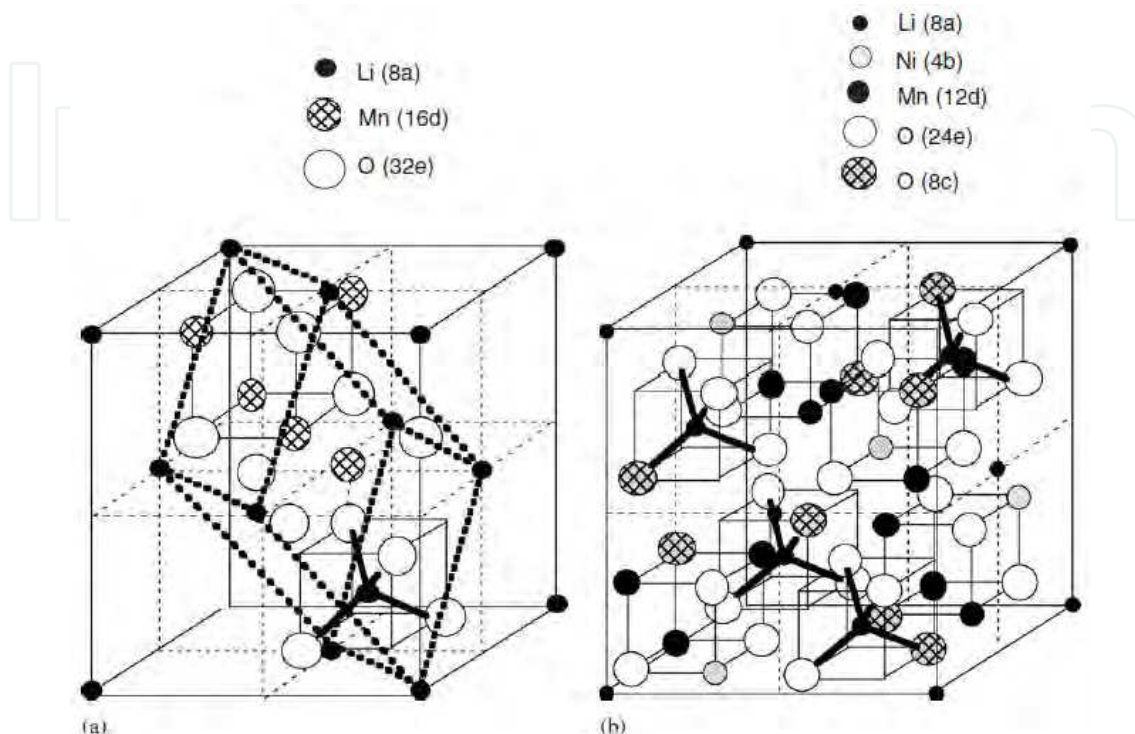


Fig. 1. Schematic drawing of the structures of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel lattice: a) face-centered spinel ($Fd3m$) b) primitive simple cubic ($P4_332$) [10]

Infrared spectroscopy is an effective method to distinguish these two structures. Infrared spectra of ordered ($P4_332$) and disordered ($Fd3m$) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibit different patterns between 650 and 450 cm^{-1} . At this band range, there are apparent spectra at 588 and 430 cm^{-1} for ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The intensity ratio of two bands at 619 and 588 cm^{-1} can be used qualitatively to assess percentage of ordering in spinel which contains both ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [11].

The diffusion path of Li in the spinel structure is a three-dimensional network. Lithium moves from one tetrahedral site to the next through a vacant octahedral site. The activation barriers of migration are greatly influenced by the electrostatic repulsion from the nearest transition metal. Because the distribution of Ni and Mn is different in ordered ($P4_332$) and disordered ($Fd3m$) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the activation barriers for migration of Li will be different from each other. Although the previous studies showed that disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited better cycling performance than ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at high rates [12-13], a recent study shows that the activation barriers for Li ion transportation in ordered ($P4_332$) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be as low as around 300 meV according to first-principles calculation, so the ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can exhibit good cycle ability at high current rates [14].

In the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the high calcination temperature sometimes leads to the reduction of the Mn oxidation state from $+4$ to $+3$, which results in the formation of $Fd3m$ structure. When annealed at 700°C in air after a high-temperature calcination at 1000°C , the

resulting powders does not contain Mn³⁺ [15]. It was reported that LiNi_{0.5}Mn_{1.5}O₄ synthesized under O₂ atmosphere has the cubic spinel structure with a space group of *P*4₃32 instead of *Fd*3m [16, 17].

3. Mechanism of high voltage and insertion/deinsertion

Based on the results obtained with the systems LiMn_{2-y}Ni_yO₄ and LiCr_yMn_{2-y}O₄, Dahn and Sigala [18, 19] previously pointed out that the high voltage originated from the oxidation of nickel and chromium ion. The 4.1 V plateau was related to the oxidation of Mn³⁺ to Mn⁴⁺ and the 4.7 V plateau to the oxidation of Ni²⁺ to Ni⁴⁺. The oxidation of chromium ion could bring about a high voltage of 4.9 V. Yang [20] suggested that a significant amount of Mn⁴⁺ ion in the spinel framework was essential for electrochemical reaction to occur at around 5 V. His view was supported by Kawai [21] who argued that the presence of manganese was necessary to keep the high voltage capacity because manganese-free spinel oxides, such as Li₂NiGe₃O₈, did not show any capacity above 4.5 V. The influence of doping metals including M = Cu [22-24], Co [25], Cr [26-29], Fe [30-32], Al [33, 34], and Zn [35] on the properties of LiM_{0.5}Mn_{1.5}O₄ have been investigated. Among these materials, Ni-doped compound LiM_{0.5}Mn_{1.5}O₄ displays higher capacity and better cycle ability. For spinel LiNi_{0.5}Mn_{1.5}O₄, there is a capacity occurring at 4.6-4.7 V, which can be attributed to a two electron process, Ni²⁺/Ni⁴⁺. While in the 4 V region, the electrode sometimes shows some minor redox behavior, related to the Mn³⁺/Mn⁴⁺ couple. When there are more Mn⁴⁺ and Ni²⁺ in LiNi_{0.5}Mn_{1.5}O₄, then the corresponding capacity at 4 V will be less and that at 5 V will be large. [36, 37].

Gao [38] put forward an explanation for the origin of high voltage. As an electron is removed from Mn³⁺, it is removed from Mn eg (↑) which has an electron binding energy at around 1.5-1.6 eV, and this accounts for the 4.1V plateau. When there are no more electrons left on Mn eg (↑) (all Mn are Mn⁴⁺), electrons are removed from Ni eg (↑↓) which has an electron binding energy of about 2.1 eV, and the voltage plateau moves up to 4.7 V because of the increased energy needed to remove electrons.

Terada [39] studied the mechanism of the oxidation reaction during Li deintercalation by measuring the *in situ* XAFS spectra of Li_{1-x}(Mn_yM)₂O₄ (M=Cr, Co, Ni). It is found from the Ni K-edge XAFS analysis that Ni in Li_{1-x}Mn_{1.69}Ni_{0.31}O₄ experiences three distinct valence states during Li deintercalation, Ni²⁺, Ni³⁺ and Ni⁴⁺. The X-ray absorption near-edge structures (XANES) of Mn and M shows that the high voltage (~5 V) in the cathode materials is due to the oxidation of M³⁺ to M⁴⁺ (M = Cr, Co), and M²⁺ to M⁴⁺ (M = Ni). The origin of the low voltage (3.9-4.3 V) is ascribed to the oxidation of Mn³⁺ to Mn⁴⁺.

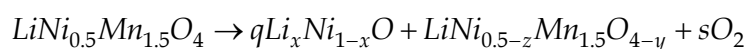
Ariyoshi [40] reported that the reaction at *ca.* 4.7 V consisted of two cubic/cubic two-phase, *i.e.* □ [Ni_{1/2}Mn_{3/2}]O₄ was reduced to Li[Ni_{1/2}Mn_{3/2}]O₄ via □_{1/2} [Ni_{1/2}Mn_{3/2}]O₄. The flat voltage at 4.7 V consists of two voltages of 4.718 and 4.739 V. The reaction of Li[Ni_{1/2}Mn_{3/2}]O₄ to Li₂[Ni_{1/2}Mn_{3/2}]O₄ proceeds into a cubic/tetragonal two-phase reaction with the reversible potential at 2.795 V.

4. Synthesis of LiNi_{0.5}Mn_{1.5}O₄

There are mainly two kinds of methods to synthesize electrode materials for lithium ion batteries, *i.e.* solid-state reaction method and wet chemical method. Solid-state reaction

method is simple and suitable for mass production. However, it is difficult to obtain pure products by this method. Some impurities containing nickel oxide usually exist in the products. Among the impurities, $\text{Li}_x\text{Ni}_{1-x}\text{O}$ is also related to the loss of oxygen at high temperatures. The capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared through solid-state reaction is about only 120 mAh g^{-1} [41]. Fang [42] prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by an improved solid-state reaction. He used appropriate amounts of Li_2CO_3 , NiO and electrolytic MnO_2 as reactants. After being thoroughly ball-milled, the mixed precursors were heated up to 900°C , then directly cooled down to 600°C and heated for 24 h in air. The heating and cooling rates were about 30°C/min and 10°C/min , respectively. The product could deliver 143 mAh g^{-1} at $5/7\text{C}$ and still retained 141 mAh g^{-1} after 30 cycles. Fang also synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using a one-step solid-state reaction at 600°C in air. The prepared product delivered up to 138 mAh g^{-1} , and the capacity retained 128 mAh g^{-1} after 30 cycles [43]. Recently Chen employed a mechanical activated solid state reaction from stoichiometric amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MnO_2 and Li_2CO_3 to prepare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Its reversible capacity was about 145 mAh g^{-1} and remained 143 mAh g^{-1} after 10 cycles [44]. Other solid-state reaction reports have also been reported [45-56]. Wet chemical methods make the reactions take place among reactants at the molecular level. It is common that after precursors are obtained by wet method, less energy or lower reaction temperature are needed to turn the precursors into final products. Wet chemical methods include coprecipitation method [57-60], polymer-pyrolysis method [61, 62], ultrasonic-assisted co-precipitation (UACP) method [63, 64], sol-gel method [65-67], radiated polymer gel method [68], sucrose-aided combustion method [69], spray-drying method [70], emulsion drying method [71], composite carbonate process [72], molten salt method [73, 74], mechanochemical process [75], poly (methyl methacrylate) (PMMA)- assisted method [76] ultrasonic spray pyrolysis [77], polymer-assisted synthesis [78], combinational annealing method [79], pulsed laser deposition [80], electrophoretic deposition [81], spin-coating deposition [82], carbon combustion synthesis [83], soft combustion reaction method [84], pulsed laser deposition [85], spray drying and post-annealing [86], rheological method [87], polymer-mediated growth [88], self-reaction method [89], internal combustion type spray pyrolysis [90, 91], a chloride-ammonia coprecipitation method [92], a novel carbon exo-templating method [93], flame type spray pyrolysis [94], self-combustion reaction (SCR) [95] and so on. Comparing to solid-state reaction method, the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are much improved by these methods.

As for the impurity phase of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ in product, it is believed that they come from the loss of oxygen at high temperatures. The tetravalent manganese (Mn^{4+}) is unstable at high temperatures and can be converted to trivalent (Mn^{3+}) so that oxygen may partially evolve out of the lattice to form $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-y}$. When x value becomes large, this phase becomes unstable and may decompose into two phases, i.e., $\text{LiNi}_{0.5-z}\text{Mn}_{1.5}\text{O}_{4-y}$ and $\text{Li}_x\text{Ni}_{1-x}\text{O}$. The overall reaction process can be depicted as follows:



To get rid of the impurities, an annealing process after the high temperature treatment is usually necessary. It is acknowledged that impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$ can deteriorate the electrochemical properties of products. However, so far there have not been special researches about how the impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$ affects the electrochemical performances of

products. In order to further investigate the effect of impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compounds were synthesized by solid state reaction method. Fig. 2 (a) and (b) show the XRD patterns of two products. One $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1) was synthesized at 850 °C for 12 h, and the other $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2) was synthesized at 850 °C for 12 h and then annealed at 600 °C for 12 h. The reference material $\text{Li}_{0.26}\text{Ni}_{0.72}\text{O}$ is also illustrated in Fig. 2 (a). It can be seen that there are small peaks at 37.5°, 43.6° and 63.3° in the patterns of two products, illustrating that there was a secondary phase $\text{Li}_x\text{Ni}_{1-x}\text{O}$. The intensity of the impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$ peaks decreased due to the annealing process.

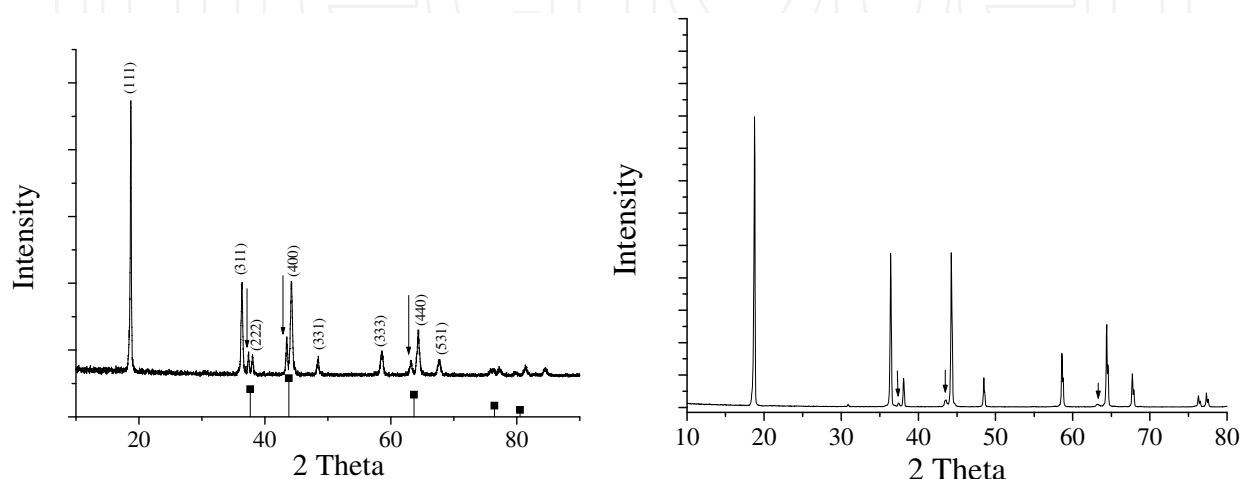


Fig. 2. a) XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1) and $\text{Li}_x\text{Ni}_{1-x}\text{O}$
b) XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2)

Figure 3 (a) shows the charge-discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1) which was synthesized without annealing process. Its discharge capacities were 121.5 mAh g⁻¹ at 0.2 C and 117.6 mAh g⁻¹ at 0.7 C, respectively. The cycle performance at 0.7 C was displayed in Fig. 3 (b). It can be found that there is only small capacity decay after 50 cycles. The theoretical capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is about 148 mAh g⁻¹. There is a capacity of about 26 mAh g⁻¹ that is not delivered by the sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1).

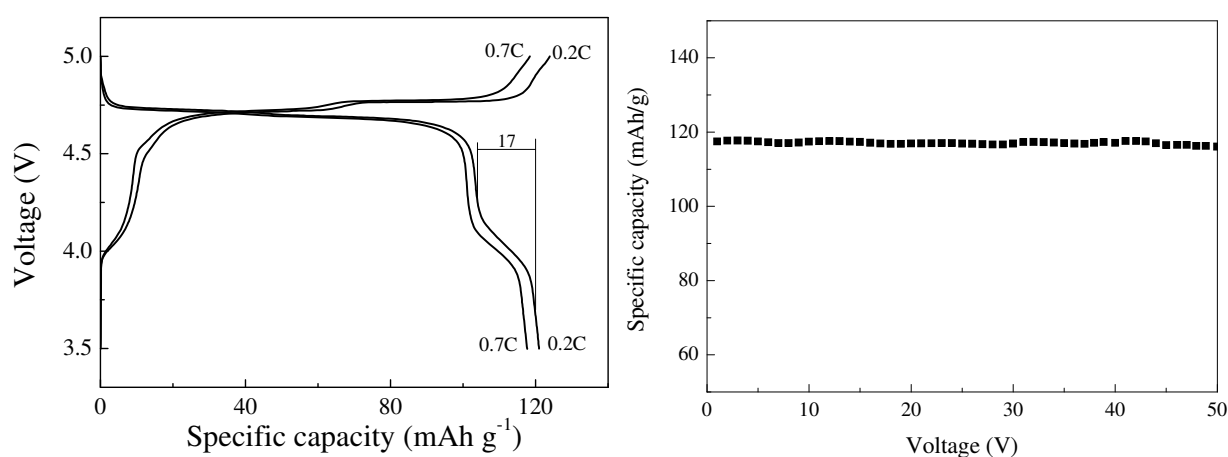


Fig. 3. a) Charge/discharge curves for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1)
b) Cycle performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1)

Figure 4 (a) illustrates the charge-discharge curves of the sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2). This test was conducted at 0.5 C charge current and different discharge current rates. The discharge capacities were 119.5 mAh g^{-1} at 0.5 C and 116.3 mAh g^{-1} at 1 C, respectively. The specific capacity around 4 V was about 13.6 mAh g^{-1} . It is less than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1). The specific capacity of sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1) around 4 V was about 17.0 mAh g^{-1} . This proves that there was less amount of Mn^{3+} in sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2) than sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (1). The reason is that there is less oxygen deficiency due to the annealing process.

The cycle performances of sample $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2) are shown in Fig. 4 (b). Its discharge capacities at 2 C and 4 C were 107.5 and 98.5 mAh g^{-1} , respectively. The capacity retention was good for every current rate.

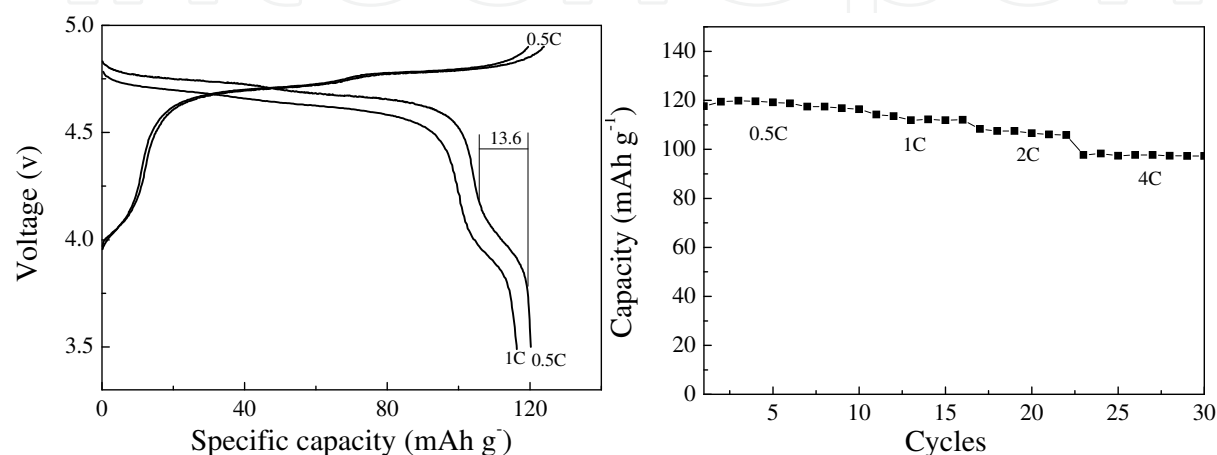


Fig. 4. a) Charge/discharge curves for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2)
b) Cycle performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (2)

The above results demonstrate that the impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$ can reduce the specific capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. However, there is no obvious evidence that the impurity $\text{Li}_x\text{Ni}_{1-x}\text{O}$ impairs the cycle performances of products. According to previous reports, the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ phase can be used as an anode material for lithium ion batteries, exhibiting good electrochemical properties. At 100 mA g^{-1} , its discharge capacity of the first cycle was up to 1480 mAh g^{-1} below 1.5 V [96].

5. Nano-sized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels

Nanostructure materials have both advantages and disadvantages for lithium batteries. The advantages include short path lengths for Li^+ transport, short path lengths for electronic transport, higher electrode/electrolyte contact area leading to higher charge/discharge rates, while the disadvantage include an increase in undesirable electrode/electrolyte reactions due to high surface area, leading to self-discharge, poor cycling and calendar life [97, 98].

Usually, nano-sized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be obtained via wet chemical methods. In this process, the precursor compounds including Li, Ni and Mn salts are mixed homogeneously at atomic scale. After further calcination, nano-sized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles can be obtained at a low temperature. When sintering temperature continues to go up, the particle size of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ increases, and finally they will turn into micro-sized products.

The methods to synthesize nano-sized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ include polymer-pyrolysis method [99], hydrothermal synthesis [100], thermal decomposition of acetate [101], composite carbonate process [102] and so on.

Based on the research results that have been reported, the formation temperature of spinel phase is as low as 450 °C, whereas the growth of integrated LiNi_{0.5}Mn_{1.5}O₄ crystals takes place at relatively higher calcination temperature. The calcination temperature has significant effects on the structure and morphology of the materials so as to affect their electrochemical performance. The higher calcination temperature leads to higher crystallinity that helps to increase the electrode capacity while it may produce particles with relatively large size and long diffusion distances for lithium ions, which makes lithium ions insertion–extraction difficult. Therefore, with the combination of these two factors, the powders calcined at proper temperature will deliver the highest discharge capacity.

Some researches relative to nano-sized LiNi_{0.5}Mn_{1.5}O₄ spinels have been reported. In general, the nanometer particles exhibit a good performance at high rates due to the shortened diffusion paths, whereas at low rates the reactivity towards the electrolyte increases and the cell performance is lowered. Micrometric particles, which are less reactive towards the electrolyte, are a better choice for making electrodes under these latter conditions.

Recently, some improvements have been achieved. Nanometer LiNi_{0.5}Mn_{1.5}O₄ with good electrochemical performance over a wide range of rate capabilities by modifying the experimental synthetic conditions has also been reported. For example, Lafont [103] synthesized a nano material LiMg_{0.05}Ni_{0.45}Mn_{1.5}O₄ of about 50 nm in size with an ordered cubic spinel phase (P4₃32) by auto-ignition method. It displayed good capacity retention of 131 mAh g⁻¹ at C/10 and 90 mAh g⁻¹ at 5C. By using a template method, Arrebola [104] synthesized LiNi_{0.5}Mn_{1.5}O₄ nanorods and nanoparticles using PEG 800 (PEG: polyethyleneglycol) as the template. Highly crystalline nanometric LiNi_{0.5}Mn_{1.5}O₄ of 70–80 nm was prepared at 800°C. Its electrochemical properties were measured at different charge/discharge rates of C/4, 2C, 4C, 8C and 15C, the capacity values were 121 mAh g⁻¹ at 2C to 98 mAh g⁻¹ at 15C, and faded slowly on cycling.

Hydrothermal synthesis includes various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition. Now it is often used to synthesize nano scale materials including electrode materials for lithium ion batteries. Recently, it is reported that nano LiNi_{0.5}Mn_{1.5}O₄ was fabricated by this approach, and the products exhibited good performances. For example, LiOH·H₂O, MnSO₄·H₂O, NiSO₄·6H₂O, (NH₄)₂S₂O₈ were used as reactants, and they were dissolved in deionized water in a Teflon-lined stainless steel autoclave. Then, the autoclave was sealed and heated at 180°C for some time. The nano scale products were finally obtained. It delivered 100, 91, 74, and 73 mAh g⁻¹ at current densities of 28, 140, 1400, and 2800 mA g⁻¹, respectively. The rate capability of such a nanosized 5 V spinel is better than those of a submicron LiNi_{0.5}Mn_{1.5}O₄ [105]. Fig. 5 (a) and (b) show the SEM photographs and charge-discharge curves, respectively.

Besides particle sizes, particle morphology and crystallinity also play a role in properties of materials. Kunduraci [106] synthesized a three dimensional mesoporous network structure with nanosize particles and high crystallinity. This morphology allows easy electrolyte penetration into pores and continuous interconnectivity of particles, yielding high power densities at fast discharges.

At present the electrode materials have reached their intrinsic limit, nano materials provide a new chance to improve their properties. It is no doubt that nano-sized electrode materials

including nano $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ will gradually be applied in future high-energy lithium ion batteries. To realize the commercial application of nano materials, some technical obstacles such as undesirable electrode/electrolyte reactions due to high surface area, self-discharge and poor calendar life, etc have to be solved.

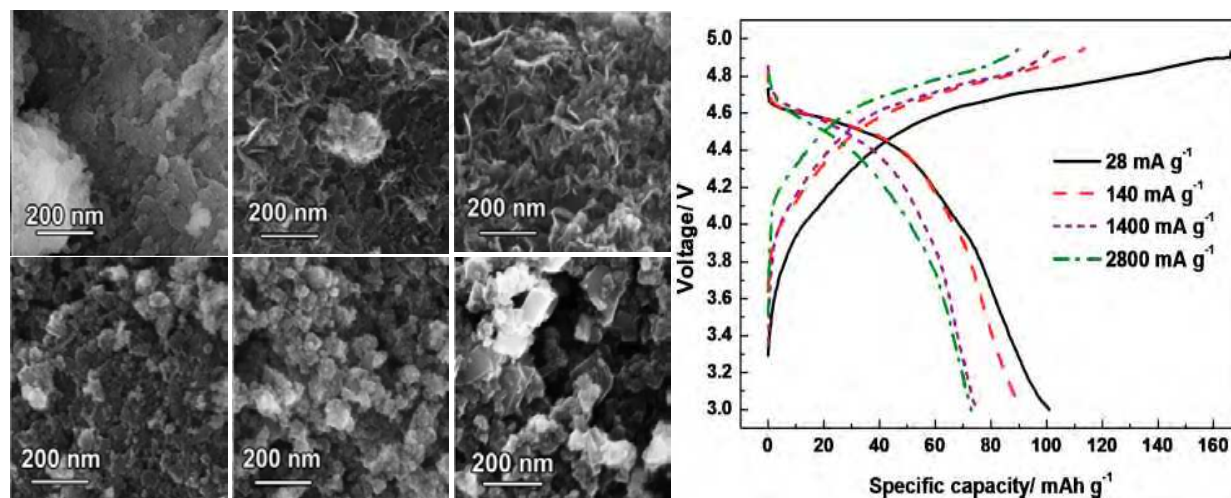


Fig. 5. a) SEM images of the samples synthesized in 1.1 M LiOH at 180°C
b) Charge-discharge curves of products [105], for various hydrothermal reaction times: (a) 0, (b) 2, (c) 6, (d) 12, (e) 24, (f) 336 h

6. Doping elements in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels

The structural and electrochemical properties of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ could also be affected by the substitution of other metal ions. Cation doping is considered to be an effective way to modify the intrinsic properties of electrode materials. Taking doping Cu as an example [107], the amount of Cu will affect the lattice parameters, the cation disorder in the spinel lattice, the particle morphology, as well as the electrochemical properties. In situ XAS experiment, the Cu K-edge XANES spectra of $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ shows that the Cu valence only changes between 4.2 and 4.7 V. Therefore Cu can participate in the charge process in this range may be due to the oxidation of Cu^{2+} to Cu^{3+} . Although the reversible discharge capacity decreases with increasing Cu amount, optimized composition such as $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ exhibits high capacities at high rates. In addition, the doping with appropriate amount in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can improve electrical conductivity, and help to improve electrochemical performances. For example, the electronic conductivity conductivities of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{1.1}\text{Ni}_{0.35}\text{Ru}_{0.05}\text{Mn}_{1.5}\text{O}_4$, and $\text{LiNi}_{0.4}\text{Ru}_{0.05}\text{Mn}_{1.5}\text{O}_4$ measured from EIS at room temperature are 1.18×10^{-4} , 5.32×10^{-4} , and $4.73 \times 10^{-4} \text{ S cm}^{-1}$, respectively. Although substitution of Ni^{2+} ions with heavier Ru^{4+} ions may reduce the theoretical capacity, the results show that a small doping content does not affect the accessible capacity at low current rates; on the contrary, larger accessible capacity can be obtained due to enhanced conductivity.

Figure 6 (a) and (b) show the scanning electron microscopy and charge-discharge curves. A remarkable cyclic performance at 1470 mA g^{-1} (10 C) charge/discharge rate is achieved for the $\text{LiNi}_{0.4}\text{Ru}_{0.05}\text{Mn}_{1.5}\text{O}_4$ synthesized by the polymer-assisted method, which can initially deliver 121 mAh g^{-1} and maintain about 82.6% of the initial capacity at the 500th cycle [108].

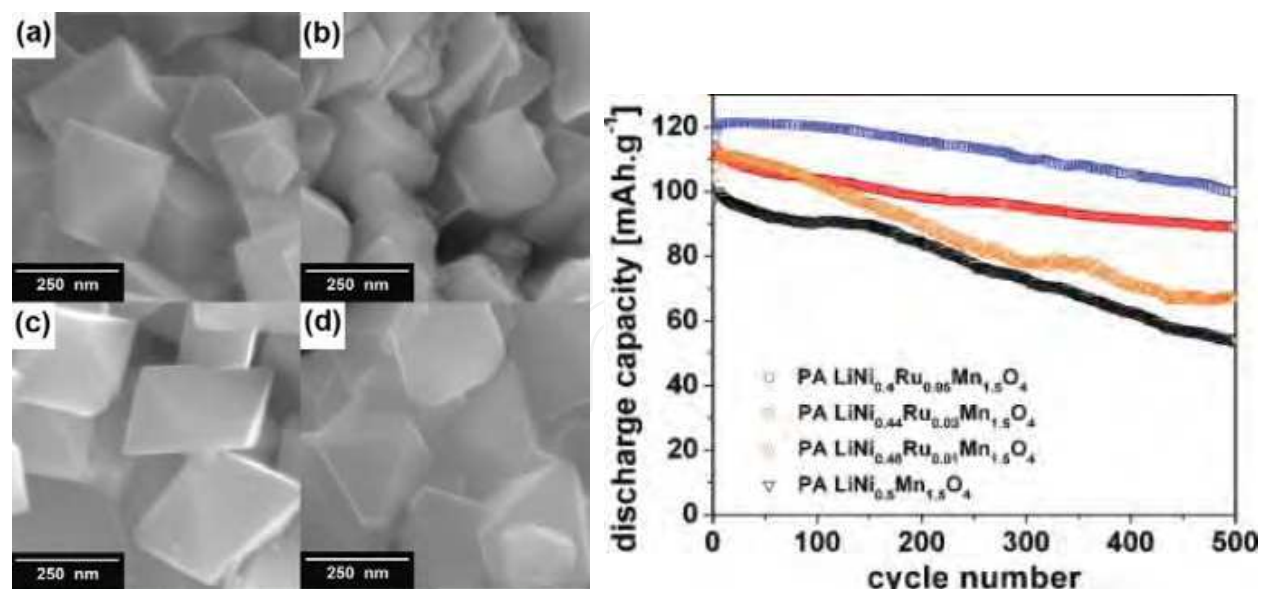


Fig. 6. a) Scanning electron microscopy of the
 b) Capacity retention of PAS-LiNi_{0.5-2x}Ru_xMn_{1.5}O₄
 PA-LiNi_{0.5-2x}Ru_xMn_{1.5-x}O₄: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$ [126]

Generally speaking, doping elements can substitute for Ni or Mn in LiNi_{0.5}Mn_{1.5}O₄. For instance, element Cr will substitute for Ni in LiNi_{0.5}Mn_{1.5}O₄ because the ionic radius of Cr³⁺ is 0.615 Å which is close to that of Ni²⁺ (0.69 Å). Partial replacement of Ni in LiNi_{0.5}Mn_{1.5}O₄ with Cr is an effective approach to improve the electrochemical properties of LiNi_{0.5}Mn_{1.5}O₄ because the bonding energy of Cr-O is stronger than that of Mn-O and Ni-O. The stronger Cr-O bond is in favor of maintaining the spinel structure during cycling. This prevents the structural disintegration of the material. Besides replacing Ni, Mn in LiNi_{0.5}Mn_{1.5}O₄ can also be substituted for. In the case of Al doping, the ionic radius of Al³⁺ is 0.62 Å, which is nearly the same as that of Mn⁴⁺ (0.54 Å), so Al can substitute for Mn in LiNi_{0.5}Mn_{1.5}O₄. The strong Al-O bond is also beneficial to improving the electrochemical properties of LiNi_{0.5}Mn_{1.5}O₄. Doping with Fe has also achieved good experimental results. The LiMn_{1.5}Ni_{0.42}Fe_{0.08}O₄ delivered a capacity of 136 mAhg⁻¹ at C/6 rate with capacity retention of 100% in 100 cycles and a remarkably high capacity of 106 mAhg⁻¹ at 10 C rate. The material could deliver capacities of 143, 118 and 111 mAh g⁻¹ at current densities of 1.0, 4.0 and 5.0 mA cm⁻² with excellent capacity retention, respectively.

So far, many researches related to doping elements have been reported. These researches include doping Al [109], Fe [110-112], Cu [113], Co [114,115], Ti [116-118], Cr [119-123], Mg [124], Zn [125] and Ru [126].

Cation doping like doping Ru and Fe has achieved some encouraging results, improving the rate capability to a certain extent. Cation doping can improve conductivity, enlarge lattice constants and form stronger M-O bond, etc., which are favorable for the migration of lithium ions and maintaining stable crystal structure. When choosing appropriate element and amount better electrochemical properties can be expected. Perhaps electronic structure of the crystal can provide another theoretical explanation to the role of cation doping.

Besides cation doping, there are some researches relative to the substitution of small amount of F⁻ for O²⁻ anion [127-129]. In this case it is assumed that O²⁻ and F⁻ ions are located at the

32e sites. The doped compounds like $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-x}\text{F}_x$ have smaller lattice parameter than $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because fluorine substitution changes the oxidation state of transition metal components and more Mn^{3+} ions with larger ionic radius ($r = 0.645 \text{ \AA}$) will replace Mn^{4+} ions ($r = 0.53 \text{ \AA}$) for electro-neutrality. The content of fluorine has influence on electrochemical properties of the doped compounds. On one hand, strong Li-F bonding may hinder Li^+ extraction, leading to a lower reversible capacity. On the other hand, fluorine doping makes spinel structure more stable due to the strong M-F bonding, which is favorable for the cyclic stability. According to the previous research report [129], the compound $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.9}\text{F}_{0.1}$ displayed good electrochemical properties of an initial capacity of 122 mAh g^{-1} and a capacity retention of 91% after 100 cycles. In addition, Oh [127] studied the effect of fluorine substitution on thermal stability. He reported that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode had an abrupt exothermic peak at around $238.3 \text{ }^\circ\text{C}$ (1958 J g^{-1}) when charged to 5.0V, while $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{3.9}\text{F}_{0.1}$ electrodes exhibited smaller exothermic peaks at higher temperatures, i.e., $246.3 \text{ }^\circ\text{C}$ (464.2 J g^{-1}). So fluorine substitution is advantageous for the thermal stability of $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-x}\text{F}_x$ spinel.

7. Surface modification

Although surface modifications applied to high voltage material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are much less than those applied to cathode materials with layer structure like LiCoO_2 , they are also effective ways to improve the properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. It is believed that the high surface reactivity of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte at high operating voltage results in the formation of SEI film, which significantly hinders the insertion/extraction of Li^+ ion, the charge transfer and hence the kinetics of the electrochemical processes. In order to improve its electrochemical behavior, coating the electrode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with chemically stable compounds has been applied. The coating layer can hinder the formation of SEI film, and protect cathode materials from being attacked by HF. So far, surface modification of 5 V spinels has been limited mainly to Bi_2O_3 [130], Al_2O_3 [131, 132], ZnO [133-135], Li_3PO_4 [136], SiO_2 [137], Zn [138], Au [139], AlPO_4 [140], ZrP_2O_7 [141], BiOF [142] which lead to better cycle performance and rate capability retention. However, the effect of coating the nanometric spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Ag on its rate capability was negative [143]. According to Liu [131], Al_2O_3 -modified sample exhibited the best cyclability (99% capacity retention in 50 cycles) with a capacity of 120 mAh g^{-1} , while Bi_2O_3 -coated sample exhibited the best rate capability. At a rate of 10C, the Bi_2O_3 -coated sample could deliver a capacity of about 90 mAh g^{-1} after 50 cycles. Liu [132] thought that Al_2O_3 reacted with the surface of $\text{LiMn}_{1.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_4$ during the annealing process and formed LiAlO_2 that exhibited good lithium-ion conductivity. Therefore, " Al_2O_3 " modification layer acts as both a protection shell and as a fast lithium-ion diffusion channel, rendering both excellent cycling performance and good rate capability for the Al_2O_3 -coated $\text{LiMn}_{1.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_4$. Similarly, Bi_2O_3 is reduced on the cathode surface during electrochemical cycling to metallic Bi, which is an electronic conductor, rendering both excellent rate capability and good cycling performance for the Bi_2O_3 -coated $\text{LiMn}_{1.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_4$. In addition, the microstructure of the surface modification layer plays an important role in determining the electrochemical performances of the active material. Some experimental results indicate that the surface modifications neither change the bulk structure nor cause any change in the cation disorder of the spinel sample. In addition, electrolyte is easy to decompose on the surface of the 5 V spinel cathodes because of the higher operating voltage, resulting in the formation of thick

SEI layers. The Al₂O₃ coating is the most effective in suppressing of the development of the SEI layer. Thin SEI layer allow lithium-ion conduction. Fig. 7 shows the TEM images and rate capabilities of 2 wt % Al₂O₃-coated LiMn_{1.42}Ni_{0.42}Co_{0.16}O₄.

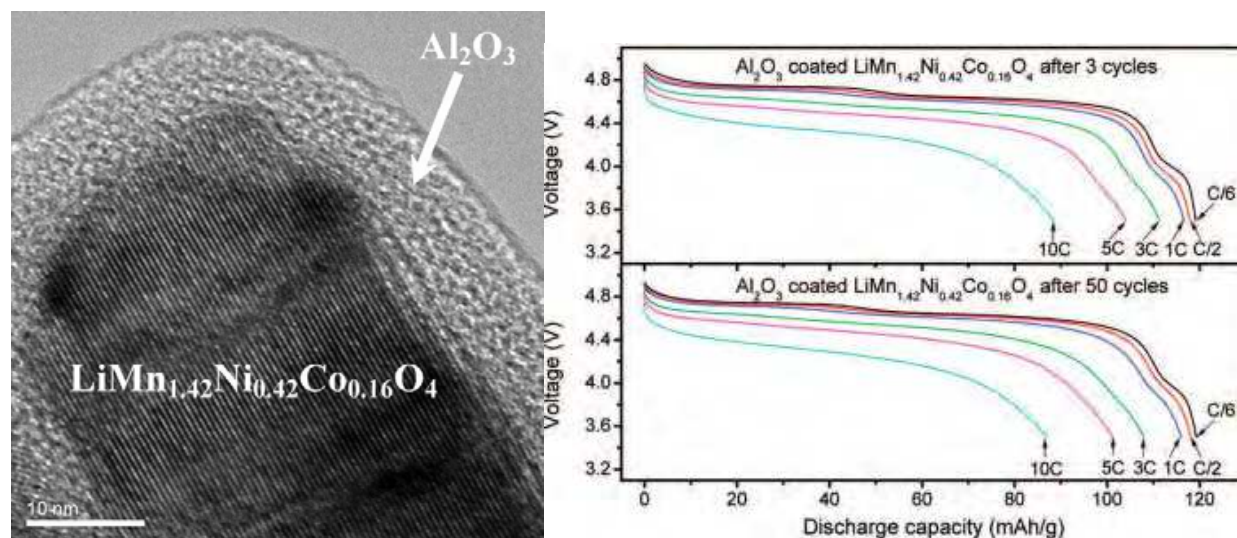


Fig. 7. a) TEM images of Al₂O₃-coated LiMn_{1.42}Ni_{0.42}Co_{0.16}O₄
b) Discharge profiles illustrating rate capabilities [132]

Besides the above mentioned coating layers, coating carbon should also be a good choice because it is a better conductor. Recently, it was reported that the carbon-coated material LiNi_{0.5}Mn_{1.5}O₄ was synthesized by a sol-gel method. The XRD patterns demonstrate that the spinel structure is not affected after coating the LiNi_{0.5}Mn_{1.5}O₄ powder with carbon. The lattice parameter was 0.8178 nm for pristine LiNi_{0.5}Mn_{1.5}O₄, while lattice parameters of LiNi_{0.5}Mn_{1.5}O₄ coated with different amount of carbon varied from 0.8171 to 0.8177 nm. The carbon layer was consecutive, and the thickness range of carbon layer was from approximate 10 to 20 nm. The carbon coating made the powders coarser and more agglomerated. The conductive carbon layer not only avoided the direct contact between the active cathode material and the electrolyte, but also provided pathways for electron transfer. Accordingly, the electrochemical properties of LiNi_{0.5}Mn_{1.5}O₄ were also improved due to carbon layer, for example, when the LiNi_{0.5}Mn_{1.5}O₄ was modified with optimal 1wt.% sucrose, its discharge capacity could reach 130 mAh g⁻¹ at 1 C discharge rate with a high retention of 92% after 100 cycles and a high 114 mAh g⁻¹ at 5 C discharge rate [144].

8. Fabrication advanced LI-ion batteries

The 5V material LiNi_{0.5}Mn_{1.5}O₄ has also been considered in new lithium-ion battery system. The LiNi_{0.5}Mn_{1.5}O₄/Li₄Ti₅O₁₂ (LNMO/LTO) cell is a good example [145-154].

The graphite anode with brittle layer structure can suffer from exfoliation when lithium ion inserts into its structure in electrolyte, which deteriorates the properties of batteries. Also, it is believed that the operating potential plateau of the carbon anode is close to that of metal lithium so that "dendrite" could still be unavoidable. And the solid electrolyte interface (SEI) layer on the carbon electrode, which is usually formed at the potential below 0.8V versus Li⁺/Li and accompanied over time with active lithium loss, an increase in impedance and a decrease in specific capacity, limits the lifetime and rate capability of the lithium-ion

batteries. Furthermore, there are some other drawbacks, such as thermal stability concerns, and the bad compatibility with propylene carbonate-based electrolytes and some functional electrolytes, i.e. the flame-retardant electrolytes containing phosphates or phosphonate. The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been considered as a zero-strain insertion material due to its excellent reversibility and structural stability in the charge-discharge process. So it is a promising alternative anode material. In addition, its structure remains nearly unchanged in PC-containing electrolyte, which makes batteries safer than those with graphite anode [155, 156]. In recent years, there have been some researches about full lithium-ion cells. Many 2V lithium-ion battery systems have been studied, such as $\text{LiCoO}_2/\text{LTO}$, $\text{LiMn}_2\text{O}_4/\text{LTO}$, $\text{LiFePO}_4/\text{LTO}$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{LTO}$, etc. Although these batteries exhibit good cycleability, rate capability and stability associated with safety, the low voltage indicates that the battery has low energy density.

Because the operating voltage of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can reach 4.7V, the full batteries can output a voltage of over 3 V if using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode respectively. Fig. 8 (a) and (b) show the charge-discharge curves and cyclic voltammograms of LNMTO/LTO batteries. LNMTO represents Ti-doped compound $\text{LiNi}_{0.3}\text{Mn}_{1.2}\text{Ti}_{0.3}\text{O}_4$. It can be seen that this battery displays a discharge voltage profile at around 3.2V.

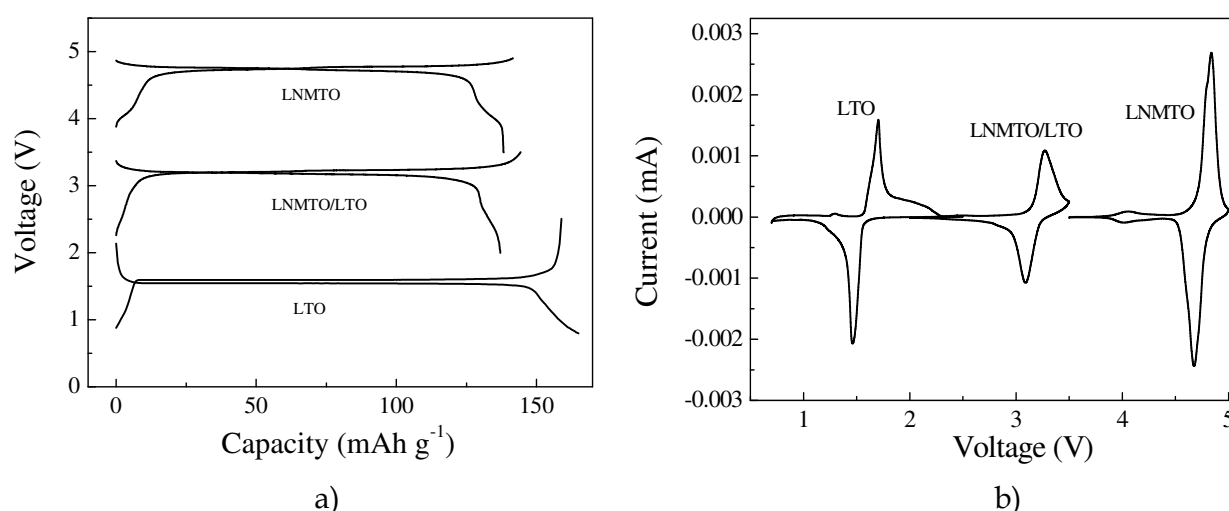


Fig. 8. a) Charge-discharge curves; b) Cyclic voltammograms

The properties of new battery $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ depended on both cathode and anode materials. Nano scale $\text{Li}_4\text{Ti}_5\text{O}_{12}$ displays good electrochemical properties, and will be applied in this battery. Because cathode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and anode $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have different specific capacities, there are two ways to fabricate the full batteries. One is LNMTO-limited cell, another is LTO-limited cell. The experiment results indicate that the LNMTO/LTO cell system with the capacity limited by LTO has the better cycling performance than that limited by LNMTO [145].

Figure 9 show that the 3V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ lithium-ion battery with electrolyte (1M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1)) exhibit perfect cycling performance. A LTO-limited cell showed high capacity retention of 85% after 2900 cycles.

In addition, Arrebola [157] have tried to combine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel and Si nanoparticles to fabricate new Li-ion batteries. Because Si composite could deliver capacities as high as 3850

(with super P) and 4300 (with MCMC) mAh g⁻¹, this LiNi_{0.5}Mn_{1.5}O₄/Si cell was expected to have higher capacity. At present, the battery could deliver a capacity of around 1000 mAh g⁻¹ after 30 cycles with good cycling properties. Xia [158] reported that the properties of LiNi_{0.5}Mn_{1.5}O₄/ (Cu-Sn) cell which has an average working voltage at 4.0 V.

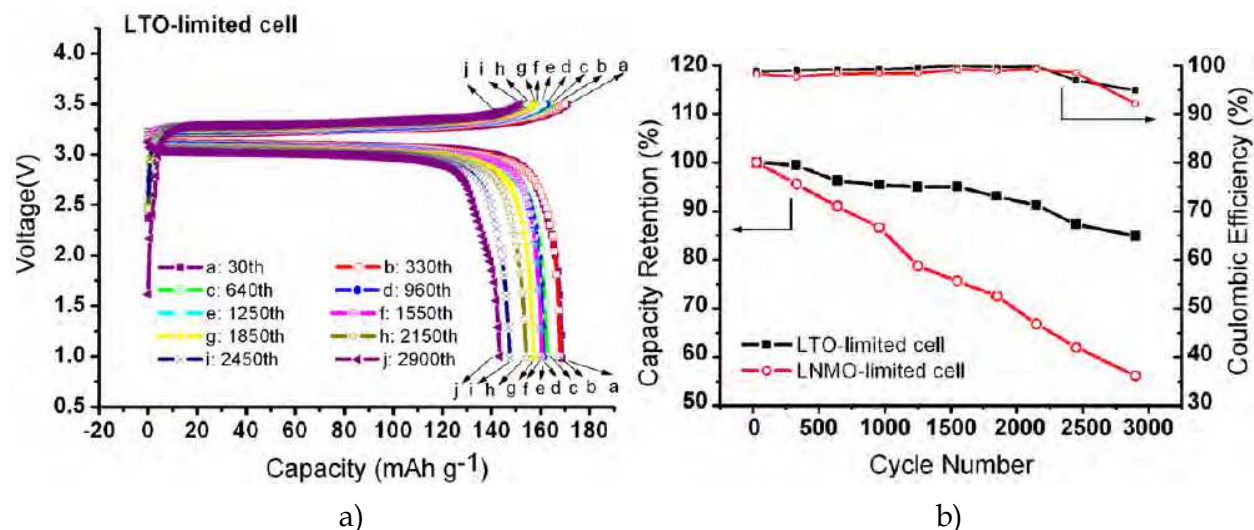


Fig. 9. a) Charge-discharge curves; b) Capacity retention [145]

9. Summary

In recent years, spinel LiNi_{0.5}Mn_{1.5}O₄ has become a research focus, and great advance has been achieved. This material has the merits of LiMn₂O₄ such as inexpensive and environmentally benign, and it has a prominent advantage of 4.7 discharge plateau which is much higher than other cathode materials. The spinel LiNi_{0.5}Mn_{1.5}O₄ has two possible structures, i.e., face-centered spinel (*Fd3m*) and primitive simple cubic crystal (*P4₃32*). According to the previous studies, the spinel with *Fd3m* structure exhibits better cycling performance than spinel with *P4₃32* structure at high rates. However, recent research demonstrates that the activation barrier for Li ion transportation in ordered (*P4₃32*) LiNi_{0.5}Mn_{1.5}O₄ is the lowest one, so the ordered LiNi_{0.5}Mn_{1.5}O₄ can exhibit the best cycle ability at high current rates. Further studies are needed to solve this disagreement. The microstructure and surface are the key factors affecting its electrochemical properties. Doping elements can improve electrochemical properties, such as doping Ru, Fe and so on. It is well known that the doped elements can make crystal structure more stable, which is in favor of Li insertion/deinsertion. However, the transportation of Li ion in structure is also affected by electronic structure of materials. So far there has not been satisfactory and scientific explanation for this aspect. Making surface modification on the surface of LiNi_{0.5}Mn_{1.5}O₄, can not only protect electrode materials from attacking of HF which generates from electrolyte decomposing, but also suppress the development of the SEI layer. This also helps to improve the electrochemical properties of spinel LiNi_{0.5}Mn_{1.5}O₄. The Li insertion/deinsertion is affected by particle morphology and size which depend on synthesis methods as well. Nano materials can lead to higher charge/discharge rates. New lithium-ion battery system can be put into practice when combining LiNi_{0.5}Mn_{1.5}O₄ and other anode materials such as Li₄Ti₅O₁₂. This system has exhibited excellent electrochemical properties.

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