The control and performance of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and Li_2MnO_3 phase ratios in the lithium-rich cathode materials

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Abstract: Lithium-rich (Li-rich) cathode materials with different layered-spinel phase ratios are successfully synthesized by solvothermal and gradient calcination processes. The structure and electrochemical performances of the lithium-rich cathode materials with different layered-spinel phase ratios are investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), high rate transmission electron microscopy (HRTEM), fast Fourier transformation (FFT) and electrochemical charge-discharge measurements. The results show that the calcination time and calcination temperature in gradient calcination processes jointly influence the phase ratios of the layered Li_2MnO_3 and spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ in the hybrid structure. Moreover, the spinel phase can lead to an excellent coulombic efficiency and cycle stability, while the layered phase will provide a high capacity. The materials with different layered-spinel phase ratios prepared in different gradient calcination processes show apparently different electrochemical performances, e.g., the maximum discharge capacity of the sample

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reaches 297 mAh/g at 0.1 C, it even exhibits high capacity retention of 90.6 % after 200 cycles at 0.5 C. Furthermore, the temperatures at 750 and 800 °C are considered to be the suitable selection for the gradient calcination process. The spinel phase can profitably grow at 750 °C, and the layered phase is produced at 800 °C.

Keywords: Lithium-ion batteries; Cathode material; Mechanism analysis; Layered-spinel hybrid structure; Electrochemical performance

1. Introduction:

In recent years, the fast-growing energy demand in electric vehicles has stimulated great interest in developing high energy and high power lithium-ion batteries (LIBs) ^[1-3]. Therefore, it is of great significance to develop the high-performance electrode materials, especially cathode materials, which play a key role in the determination of energy density, safety and life cycle of LIBs. Among the reported cathode materials so far, the Li-rich cathode materials have been considered as one of the most promising cathode materials for future LIBs generations because of their advantages of high specific capacity, low cost and high safety ^[4,5]. However, they also have several inherent disadvantages: firstly, these materials have large irreversible charge capacity loss at the first cycle; secondly, since the charge-discharge voltage could get as high as 4.8 V, the electrolyte may resolve when cycling. The interface between the electrolyte and the cathode material may be damaged leading to the loss of capacity; thirdly, the Li-rich cathode materials own poor rate performance, which limit their future applications in many fields ^[6,7].

In order to overcome these problems, cathode materials' modification and structural design were carried out, and a series of progresses have been made successively by many researchers including our group ^[8,9]. Wu reported the layer-structured $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$ powders with a thin uniform layer of conducting polypyrrole on the surface via Pechini method, after coating, the discharge capacity increases from 262 mAh/g to 280 mAh/g in the 2nd cycle ^[10]. In our previous work, we also rationally designed and successfully prepared the $\text{Li}_{1.5}\text{Mn}_{0.75}\text{Ni}_{0.15}\text{Co}_{0.10}\text{O}_{2+x}$ microspheres with hierarchical multilayer shells through a layer-by-layer self-assembly deposit with a co-precipitation process, the as-prepared spherical cathode material with multilayer shells exhibits an improved rate capability with a capacity of 102.7 mAh/g even at a high discharge rate of 10 C ^[11]. Based on the current results of the researches about Li-rich cathode materials, most of the attentions have been paid to design a facile and reliable structure for cathode materials to achieve Li-rich cathode materials with satisfactory rate performance and high discharge capacity. It has to be admitted that the structure component plays an important role in the improvements of cathode materials, due to the properties of materials strongly depend on the structure, which has a significant impact on the morphology, composition and homogeneity of the materials. Consequently, there is an urgent need to design a more effective and reliable structure for the improvements of Li-rich cathode materials.

Among the reported results so far, the cathode materials with layered-spinel

hybrid structure have attracted more and more attentions because they can not only achieve the over 280 mAh/g high specific capacity, but also combine the advantages of the two phases, such as the excellent cyclic stability and high coulombic efficiency of the spinel phase, and the high discharge capacity and the outstanding structural stability of the layer phase ^[12-14]. For metal oxides with layered- and spinel-type structures, Mn-based compounds are preferred to Ni- and Co-based compounds because of their greater stability (retention of oxygen) in the charged state ^[15,16]. Among the various Mn-based compounds, the layered Li_2MnO_3 and the spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ are considered to be the most appropriate phases in the hybrid structure, the layered Li_2MnO_3 component of the layered-spinel hybrid structure can stabilize the electrode structure and enhance the discharge capacity of the electrode ^[17-19]. And the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ component of the layered-spinel hybrid structure offers theoretical capacities of 163 mAh/g, and has Mn oxidation state (+4), which can suppress Jahn Teller distortion, and also enhances cycling stability of the materials ^[20,21].

Although lots of studies have also been carried out about the cathode materials with layered-spinel structure, and some results have been reported, their studies mostly focused on the simplex preparations and electrochemical characteristics of the cathode materials with hybrid structure in the pristine state, such as the spinel-layered Li-rich Li-Mn-Co-O microspheres with maximum discharge capacity of 185.1 mAh/g at a very high current density of 1200 mA/g between 2.0 and 4.6 V ^[21], and the layered-spinel hybrid cathodes prepared by mechanically mixing process ^[22]. These

researches lack of detailed and in-depth exploration for the relationships between the electrochemical performances and the ratios of two phases in the hybrid structure as well as the preparation conditions of the cathode materials.

Herein, we propose a new point of view to make a further study about the cathode materials with layered-spinel hybrid structure. Since the existences of the two phases have positive effects on the improvement of the electrochemical performance, it brings us to find out how to control the ratio of the two phases in the layer-spinel hybrid structure cathode materials. In addition, it is worth investigating whether the distinctions between the ratios of the two phases will lead to a difference in the electrochemical performances. Therefore, the exploration of the various ratios in layer-spinel hybrid structure is important for two main reasons: firstly, to obtain the crucial factors for preparing the Li-rich cathode materials with different ratios of spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and layered Li_2MnO_3 phases; and secondly, to enhance the fundamental understanding about the influences of electrochemical performance on the different phase components in the Li-rich cathode material. Thus, the calcinations temperature and time in gradient calcination processes are reasonably designed and controlled to ascertain the ratio of the two phases in the hybrid structure, and the effects of different phase ratios on the electrochemical performances of Li-rich cathode materials were also discussed.

2. Experimental

2.1. Synthesis of layered-spinel Li-rich cathode material

In a typical experiment, the layered-spinel microspheres samples were synthesized by a hydrothermal method and subsequent gradient calcination process. Firstly, 2.0 m mol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 50 ml ethanediol. Then, 0.498 m mol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.498 m mol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the above solution which was stirred vigorously for 0.5 h in the Teflon wares. At the same time, the prepared NH_4HCO_3 solution was dropwise added into the mixed solution. Next, the sealed Teflon ware was put into a stainless steel autoclave, which was hold at 200 °C for 20 h, followed by cooling at the room temperature to obtain purple precipitates. The precipitate was centrifugalized and washed by ethanol for several times, the residue was dried at 60 °C. Finally, the as-produced carbonate precursor was preheated at 500 °C for 6 h, and mixed with Li_2CO_3 , then calcined in a gradient calcination process, 750 °C for 6 h and then 800 °C for 14 h in air, to form the spherical Li-rich cathode materials. The sample prepared was named as LS-6-14.

For comparison, the carbonate precursor was also synthesized by a hydrothermal method similar to that described previously. The as-prepared carbonate precursor was then ground with Li_2CO_3 . After suitable grinding, the mixtures were respectively annealed at the gradient calcination processes as showed in Table 1. Eventually, five compositions of Li-rich cathode materials with a layered-spinel hybrid structure were successfully synthesized.

2.2. Characterizations of morphology and structure

The morphologies of the as-synthesized samples were examined by emission scanning electron microscopy (SEM). Transmission electron microscope (TEM, JEOL JEM-2100F) with accelerating voltage of 200 kV were used in order to obtain TEM and HRTEM. The powder X-Ray diffraction (XRD) patterns were obtained by a X-ray diffractometer (D/Max-3C, Rigaku, Japan) using Cu K α radiation (λ = 0.154178 nm) and a graphite monochromator at 36 kV, 20 mA, the scanning rate was 2 °min⁻¹ and the scanning range of diffraction angle (2θ) was between 10° and 80°. The surface solid-state chemistry of particles was characterized by X-ray photoelectron spectroscopy (XPS, KAlpha 1063, Thermo Fisher Scientific, England).

2.3. Electrochemical measurements

To prepared the positive electrodes, a mixture of the as-prepared cathode materials (80 wt%), polyvinylidene fluoride (10 wt%), graphite (5 wt%), and acetylene black (5 wt%), dissolved in N-methylpyrrolidone (NMP) solution, was coated onto Al foils. Generally, the loading mass of the active substances is 4-5 mg cm⁻². Note that the coated Al foils should be dried at 110 °C for 24 h in a vacuum oven before processing. Then the positive electrodes were fabricated by cutting the coated Al foils into circular films with 10 mm diameter. CR2025 coin cells were assembled in glove box using Lithium foil as the anode, 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, V:V) as the electrolyte, and porous polypropylene based membrane (Celgard) as the separator, under argon atmosphere. To determine the electrochemical characteristics of the as-obtained cathode materials,

the cells were charged and discharged at different current densities between 2.0 V and 4.6 V (vs Li^+/Li), using a Neware battery test system (Shenzhen, China).

3. Results and discussion

Fig. 1 shows the morphology of precursor particles obtained after preheated at 500 °C. It can be seen that the shape of the particle is regularly spherical, and the size is homogeneous with the average diameter of about 1 μm . Besides, as shown in Fig. 2, after the carbonate precursors were calcined at high temperatures with Li_2CO_3 , the resultant cathode materials still maintained a good spherical morphology like precursor particles. As revealed by the images in Fig. 2, after calcinations for different times at 750 and 800 °C, there are many significant differences between the morphologies of the samples. The particle sizes of these five samples can all be seen an obvious change in diameter. The result in Fig. 1(a) clearly shows uniform spherical particles with an average size of 1-2 μm in diameter, which is corresponding to the sample of LS-6-14. But the samples of LS-8-12, LS-10-10 and LS-12-8 gradually become larger as being seen from Fig. 1(b), (c) and (d), interestingly, the particles of LS-8-12 in Fig.1(e) even show a deformation on the surface, suggesting that the structures inside the particles for different preparation conduction are different, and the calcination temperature and time in gradient calcination processes may be significant factors. Based on the comparison of the precursor particles and samples after different gradient calcination processes, it can be found that the increase of the

particle size mainly appears in the sample of LS-8-12, which corresponds to an increased time heated at 750 °C (following a decreased time heated at 800 °C). So, the particle size is relative to calcination times at 750 °C and 800 °C, while the pretreatment at 500 °C has no effect on the particle size. In general, the particle sizes should be uniform, but this regular observation is often seen in a pure phase. However, in this work we find that the spinel structure will gradually appear with the increase of the calcinations time at 750 °C, meanwhile the layered structure will be replaced.

To further study the structures of the five samples, the phase compositions of the samples prepared in different gradient calcination processes were identified by X-ray diffraction (XRD) and the corresponding results have been shown in Fig. 3. The main peaks can be indexed as Li_2MnO_3 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, which are the desired phases in the hybrid structure and the PDF standard cards have also been given in Fig. 3(b). It can be seen that the standard peaks of the two phases are similar to each other and the positions of some peaks are very closer, proving an easy transformation of structure between them and this will be given a detailed explanation later. In addition, it can be seen from Fig. 3(a) that all diffraction peaks are quite narrow and sharp, which indicates a high crystallinity of the cathode materials. With the detailed comparison of peaks in Fig. 3(a), the peaks at 20~25° can be assigned to (020) and (110) planes of the monoclinic Li_2MnO_3 ($C2/m$) phase resulting from the ordering of Li and transition metals in the transition metal layer of the layered lattice^[17]. Although all the strong peaks could be indexed to a layered $\alpha\text{-NaFeO}_2$ phase with $R\bar{3}m$ symmetry

which is normally taken as the signature of LiMO_2 phase, several weak peaks located in the range of 30° are consistent with the cubic $\text{Li}_4\text{Mn}_5\text{O}_{12}$ with space group of $Fd3m$ (PDF#46-0810), as distinguished with “tetragonum” in Fig. 3 [20,26]. It can be seen from the results of the XRD that the real differences between the samples are not very clear. Accordingly, to make the discussion be more substantial, the relative amounts of the two phases were semiquantitatively provided by XRD analysis approach and the corresponding results are shown in Table 2. From the view of the table, the quantity of the layered phase decreases gradually from 80 % to 19 %, with the decreasing of the layered phase, the spinel phase exhibits an opposite changing trends from 20 % to 81%. Another interesting thing can be also observed that the increasing of the percentage composition is not homogeneous. When the calcination time at 750°C in gradient calcination processes is less than 10 hours, the formation of spinel phase is quite inactive, but once the calcination time is longer than 10 hours at 750°C , the quantity of spinel phase in the hybrid structure will increase rapidly. The reasons will also be analyzed in more detail below.

The formation of integrated layered-spinel structures was evidenced explicitly by comparative HRTEM and FFT analysis. In addition, the orientation relationships of the single spinel phase, single layered phase and layered-spinel hybrid phases were also showed in Fig.4 to make a comparison. As the different orientation relationships of the three structures are clearly illustrated in Fig.4 (f), and the FFT images with corresponding indexing results for subareas are shown in each HRTEM images of the

five samples. It can easily recognize the distribution of the layered-spinel hybrid structure in the samples, thus it could be concluded that there exist two phases of layered and spinel structures in all of the samples, which are layered monoclinic structure Li_2MnO_3 with the (020) and (111) planes, and the spinel phase corresponding to the plane (400) and (511) of (*Fd3m*) $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ^[21]. In the meanwhile, with a detailed observation of the edges in each HRTEM images, it can be found that the crystal lattices of LS-8-12, LS-10-10 and LS-12-8 samples are more distinct than the LS-6-14 and LS-14-6 samples, indicating a better crystal structure and a more inerratic structural distribution, the corresponding FFT images also proved the orderly and obvious crystal structures existed in the samples of LS-8-12, LS-10-10 and LS-12-8. Whether the calcination time at 750 °C or 800 °C in gradient calcination processes is too less, it will lead to an obvious distinguish between the relative quantity of the two phases, as well as the randomly mixed structures of layered and spinel phases, which can be easily found in samples of LS-6-14 or LS-14-6.

LS-6-14 and LS-14-6 are characterized by X-ray photoelectron spectroscopy (XPS) to confirm the oxidation state of manganese during the phase transition processes and the corresponding spectra are presented in Fig.5. All of the binding energies (BEs) in the XPS analysis were corrected for specimen charging by referencing them to the C 1s peak (set at 284.6 eV). It can be seen from Table 1 that the samples of LS-6-14 and LS-14-6 represent the starting and ending in the gradient calcination processes, corresponding to the different components of layered and spinel

phases. As being seen from Fig.5 and Table 2, when the layered structure appears in LS-6-14, the two major peaks with binding energies of 642.3 and 654.1 eV can be observed. While the layered structure will disappear in LS-14-6, the binding energy for the Mn 2p_{1/2} and Mn 2p_{3/2} can also be seen at 642.4 and 654.1 eV. Fig.5 shows both Mn³⁺ and Mn⁴⁺ coexist in Mn 2p_{3/2} spectrum of LS-6-14 since two major peaks with binding energies of 641.6 and 642.7 eV were observed ^[27], the peaks of Mn³⁺ and Mn⁴⁺ do not shift in the sample of LS-14-6. It seems that the hybrid phase transition process does not affect the oxidation state of Mn. Additionally, these results also make an effect to analyze the formation process of these layered-spinel hybrid structure.

Combined with the investigations shown above, the formation process of the layered-spinel hybrid structure can be depicted as follows, which is also schematically illustrated in Fig.6. The Li₄Mn₅O₁₂ phase is proverbially described as a single phase with a cubic spinel structure, but there is an inhomogeneous distribution of Li in the spinel lattice of Li₄Mn₅O₁₂ as shown in the schematic ^[15,21,28]. As the pure Li₄Mn₅O₁₂ is proved to be comprised of a Li₂MnO₃-like and a Li_{4/3-x}Mn_{5/3+x}O₄ compositions rather than a single spinel phase with Li in tetrahedral and Li_{1/3}Mn_{5/3} in octahedral spinel sites ^[20], this will lead to its decomposition into monoclinic Li₂MnO₃ and Li[Li_xMn_{2-x}]O₄ when it is treated at a temperature above 700 °C ^[21], in the meanwhile, Li₄Mn₅O₁₂ is a lithium-poor phase compared with the lithium-rich layered phase, thus during higher calcination temperature the lithium ions heterogeneously distributed in

$\text{Li}_4\text{Mn}_5\text{O}_{12}$ will transfer into Li_2MnO_3 phase and promote the formation of Li_2MnO_3 layered phase. Based on the possibility of the transformation from spinel phase to layered phase at a temperature of higher than 700 °C, the hybrid structure was successfully prepared by gradient calcination process. Besides, in our previous work^[29], it has been experimentally indicated that when the calcination temperature is equal to 700 °C, the obtained material shows only a spinel structure; while the calcination temperature is above 850 °C, the as-prepared material shows just a lithium-rich layered structure. Furthermore, it has been confirmed that the spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ component can be controllably introduced into the lithium-rich layered material at 700 ~ 850 °C. Therefore, the percentage contents of the two phases mainly depend on these two factors: (i) two disparate calcination temperatures corresponding to two different phases, the spinel phase grows at 750 °C and the layered phase is produced at 800 °C; (ii) the different calcination time remained at 800 °C in the gradient calcination process may lead to a transformation from spinel phase to layered phase in different quantities. Consequently, both of the calcination temperature and time can make impacts on the formation of layered-spinel hybrid structure.

The first charge/discharge curves cycled between 2.0 and 4.6 V at 0.1 C (1 C corresponds to 200 mA/g current density) and the corresponding differential capacity versus voltage plots (dQ/dV) are compared in Fig.7. Similar to other Li-rich cathodes, all the cells shown in Fig.5(a) exhibit a voltage plateaus around 4.5 V in the first charge process, which corresponds to the removal of lithium ions and oxygen from

the Li_2MnO_3 component^[30]. Besides, all the samples show a sloping curve below 4.5 V, which is consistent with the lithium ions extraction from the layered LiMO_2 component with the concomitant oxidation of $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ ^[31]. These results again prove that all of the five samples own the layered Li_2MnO_3 phase. With a detailed observation on the plateaus of the samples, it can be obviously found that the 4.5 V plateau of LS-8-12 is much longer than LS-10-10, LS-12-8 and LS-14-6, and a high charge capacity of 375.6 mAh/g is delivered. Combined with the results of XRD, the LS-8-12 has the higher quantity of layered phase than LS-10-10, LS-12-8 and LS-14-6, but it's not like that the higher quantity of layered phase, the larger the charge capacity in first charge capacity. Comparing the charge capacity of the samples with the results of XRD, it can be found that further increasing (LS-6-14 and LS-8-12) of layered phase can shorten the plateau around 4.5 V and decrease the first charge capacity when the content of spinel phase is lower than others, this may be caused by the structure transformation which is initiated by Jahn Teller distortion when reducing the calcinations time at 750 °C or adding the calcinations time at 800 °C, then the lower charge capacity has been linked to a lower discharge capacity, the first discharge capacity of LS-6-14 is just 269.8 mAh/g at 0.1 C, but the first discharge capacity of LS-12-8 can reach 297.8 mAh/g, which is the highest capacity of these five samples. In the meanwhile, the coulombic efficiencies are used to make a comparison to understand the influences of the structure on the electrochemical performance, which can be seen in Table 3. It is a remarkable fact that the coulombic

efficiencies do not show a decrease when the charge capacity reduces, they exhibit a similar trend with the quantity of spinel phase in the hybrid structure. The sample of LS-14-6 shows the highest coulombic effect of 88%, but the sample of LS-8-12 which exhibits the highest charge capacity just shows a low coulombic effect of 78 %. These results indicate that the spinel phase plays an important role in reducing the premature capacity loss for the first time. It simultaneously explains the decrease of charge capacity mentioned previous when the quantity of layered phase increases. Although the increase of the layered phase in hybrid structure can bring a high capacity due to the higher theoretical capacity compared with spinel phase, this improvement in capacity comes at the expense of better coulombic effect, which is not desired ^[32]. As the different effects come from two different phases and present on different electrochemical performances, it can thus be concluded that the layered phase offers a high charge capacity roughly in first cycle, but the spinel phase brings a high coulombic effect with the increase of percent content ^[33]. Therefore, based on the combination of the effects mentioned above, LS-12-8 sample shows a preferable electrochemical performance, the highest discharge capacity of 297.8 mAh/g and a fairish coulombic effect of 85% in first cycle.

In addition, as being seen from the corresponding differential capacity versus voltage plots (dQ/dV), which are employed as a complementary and well-suited technique to understand the behaviors of the electrode materials. Obviously, there is an oxidation peak in first cycle occurred at ~ 4.5 V, which is corresponding to the net

loss of Li_2O , and another peak at ~ 4.0 V is roughly correspond to the expected value for $\text{Ni}^{2+}/\text{Ni}^{4+}$ reaction ^[19]. Besides, the peak at 3.3 V indicates that the lithium ion inserts into the MnO_2 which is derived from Li_2MnO_3 at 3.3 V (Mn^{4+} to Mn^{3+}) ^[20]. With detailed comparison of the peaks mentioned above in these five samples, the peak position in sample of LS-6-14 gradually shifts towards the high voltage area, this is considered to be brought by the spinel structure, which has been mentioned in previous reports ^[34,35]. With these results and the charge/discharge plots above, the existence of the layered and spinel phases in hybrid structures can be confirmed.

Fig. 8 shows the cycling properties of the samples. As the different effects on the discharge capacity and coulombic effect, the structures have an obvious influence on the cycle stability of the materials. The discharge capacity of LS-12-8 diminished from 259.4 mAh/g to 233.4 mAh/g over 200 cycles with the capacity retention of 89.6 %, which is the highest capacity retention among the samples. However, the sample of LS-6-14 just exhibits a discharge capacity of 152.4 mAh/g after 200 cycles at the same rate of 0.5 C, corresponding to poor capacity retention of 79.1 %. It can be found from Tab. 3 that the trend of the capacity retention is similar to the change of coulombic efficiency among the samples. This proves once again that the enhanced cycle stability of LS-12-8 is attributed to the appropriate introduction of spinel phase to layered phase, which is a desired result as we mentioned previously.

4. Conclusions

In conclusion, the Li-rich layered-spinel hybrid cathode materials with different compositions have been successfully synthesized by solvothermal and gradient calcination process. Each of the particles shows a uniform spherical morphology with an average size of 1-2 μm in diameter. Firstly, the influential factors of structural composition have been discussed, the relative amounts of each phase depend on the calcination temperature and calcination time in gradient calcination process: (i) when the temperature stays at 750 $^{\circ}\text{C}$, the spinel phase will be formed mainly, and it will lead to a formation of layered phase when the temperature stays at 800 $^{\circ}\text{C}$; (ii) when the calcination time at 750 $^{\circ}\text{C}$ is less than 10 hours, the formation of spinel phase is quite inactive, and the major components is layered phase, but once the calcination time at 750 $^{\circ}\text{C}$ is longer than 10 hours, the quantity of spinel phase in the hybrid structure will increase rapidly; besides, the different time stayed at 800 $^{\circ}\text{C}$ will lead to a transformation from spinel phase to layered phase in different quantities. In addition, different compositions of structures will make different effects on the electrochemical performances: spinel phase brings an excellent coulombic efficiency and cycle stability, the layered phase leads to high capacity, one of the samples exhibits a high discharge capacity of 297 mAh/g at 0.1 C, and it even shows the high capacity retention of 90.6 % after 200 cycles at 0.5 C.

Acknowledges

This work is supported financially by the National Natural Science Foundation of

China under project No. 51472211, Scientific and Technical Achievement Transformation Fund of Hunan Province under project No. 2012CK1006, Key Project of Strategic New Industry of Hunan Province under project No. 2013GK4068 and the Natural Science Foundation of Hunan Province under project No 2015JJ6103. National Science Foundation for Post-doctoral Scientists of China under project No. 2015M570682. Scientific Research Foundation of the Higher Education institutions of Hunan Province under project No. 15C1313.

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Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Table 1. The different gradient calcination processes for the as-prepared precursor.

Sample	LS-6-14	LS-8-12	LS-10-10	LS-12-8	LS-14-6
Time for 750 °C	6 h	8 h	10 h	12 h	14 h
Time for 800 °C	14 h	12 h	10 h	8 h	6 h

Table 2. The relative percentage compositions of spinel and layered phases in hybrid structure

Sample		LS-6-14	LS-8-12	LS-10-10	LS-12-8	LS-14-6
Percentage compositions	Layered	80.3%	78.6%	50.4%	29.7%	18.8%
	Spinel	19.7%	21.4%	49.6%	70.3%	81.2%

Table 3. Comparison of electrochemical performances of different samples prepared at different gradient calcination process.

Sample	LS-6-14	LS-8-12	LS-10-10	LS-12-8	LS-14-6
Charge capacity: 1 st cycle (0.1C) (mAh/g)	354.1	375.6	358.5	347.5	332.6
First coulombic effect (%)	76.2	77.8	80.5	85.7	88.1
Discharge capacity: 1 st cycle (0.1C) (mAh/g)	269.8	292.4	288.6	297.8	293.1
Discharge capacity: 200 th cycle (0.5C) (mAh/g)	152.4	172.8	165.8	233.4	200.5
Capacity retention after 200 cycle (%)	79.1	80.5	82.5	90.6	84.3