

Comparison and improvement of the high rate performance of different types of LiMn_2O_4 spinels

Bohua Deng^{a,b}, Hiroyoshi Nakamura^b, Masaki Yoshio^{b,*}

^a *Venture Business Laboratory of Saga University, 1Honjyo, Saga 840-8502, Japan*

^b *Department of Applied Chemistry, Saga University, 1Honjyo, Saga 840-8502, Japan*

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Abstract

The rate capacity especially the high rate discharge performance is another important aspect for the application of Mn-based spinel cathodes for EV/HEV power sources besides the cycling performance that is now intensively investigated. In this paper, spinel materials differing in chemical composition and thermal processing history were investigated by discharging at constant current rates from C/10 to 4 C at ambient temperature. It was found that the high-rate discharge capability of Mn-based spinels is very excellent if prepared at temperatures below 850 °C, no matter cation doping or not. In contrast, spinels synthesized over 950 °C showed much poorer high rate performance, and some kinds of impurities were proposed to be responsible for the deteriorated behavior. Annealing at lower temperatures was found to be useful for the significant improvement of the high rate discharge capability of Mn spinels.

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1. Introduction

Due to the intensive research effort in the past decade, LiMn_2O_4 type spinel materials are very attractive to be applied as alternative for LiCoO_2 because of low cost, low toxicity, and safer performance [1–6]. However, some problems are still standing in the wider application of Mn spinels in practical Li-ion batteries. The main problem is the capacity fading upon cycling especially at elevated temperatures above 50 °C, and recently we have solved this problem by metal cation doping such as Mg and the control of oxygen stoichiometry for the original spinels [7,8]. In fact, Mn-based spinel cathodes have now been used in the practical Li-ion batteries and are being developed for the large-size batteries for EV/HEV power system [5,6]. Another problem is the capacity fading of graphite anodes together used with Mn spinel cathodes in Li-ion batteries, and this was ascribed to the large

Mn dissolution from the spinel material into the electrolyte [9]. In order to control Mn dissolution, surface encapsulation, reducing specific surface area, etc. have been suggested and investigated. We have succeeded to reduce the Mn dissolution after 2-week storage at 60 °C from ca. 100 ppm for traditional spinels to ca. 3 ppm for our new materials by crystallizing spinels at higher temperatures up to 1000 °C. With respect to the higher calcination temperature and larger particle size, another concern for our new materials needing to be addressed is the high rate discharge capability, which is very important for the power output of the large-scale Li-ion batteries for EV/HEV application. Recently [10], the poor high rate capability of a nominal LiMn_2O_4 spinel (no doping) with about 50% of the reversible capacity at C/10 being retained when discharged at 4 C rate was reported by some researchers, and this seems contrary to the excellent high rate capacity generally expected of for LiMn_2O_4 -type spinels. Moreover, they reported that the high rate capability was improved after doping with Li and Ni cations. Their results enlightened us to consider the rate capacity of our new

* Corresponding author. Fax: +81 952 288 591.

E-mail address: yoshio@ccs.ce.saga-u.ac.jp (M. Yoshio).

spinel. And we synthesized different types of spinel samples with or without doping by different thermal processing and then compared their performances. It was found that the high rate discharge capability of the nominal spinel is as excellent as that of the spinel doped with Ni or Mg if properly prepared. Additionally, calcination at temperatures over 950 °C yields spinels with poor high rate discharge capability, and it could be improved after annealing at lower temperatures especially with LiOH additive.

2. Experimental

Except for the sample Mg010-N600 described elsewhere [8], all the spinel materials in the present paper were synthesized by conventional melt-impregnation method [3]. As for the nominal spinel designated Mn800, the mixture of LiOH and MnO₂ with mole ratio of 1:2 was first preheated at 470 °C for 5 h to get a precursor, and then calcinated at 800 °C for 20 h to get the final product. And about 0.1/2.0 of MnO₂ of the starting mixtures was substituted by NiO or MgO for the samples designated Ni010-800 or Mg010-T, respectively. The composition of the as-prepared materials was determined by chemical analysis unless otherwise specified (the third decimal of the results is reliable) [7,8]. All the spinel materials in this paper are examined by powder XRD to be single cubic phase and belonging to (*Fd* $\bar{3}m$) space group. The calculation of lattice constants was refined by 20 times and the accuracy can reach the fifth decimal.

The cathodes were prepared by mixing 70 wt.% spinel samples with 30 wt.% TAB (e.g., teflonized acetylene black) and then pressing the mixture into pellets. After vacuum drying at 150 °C for 5 h, the pellets were assembled with a metal lithium anode to make CR2032-type coin cells. The discharge capability was tested in the voltage region of 3.0–4.3 V at a constant current rate by charging at C/10 and discharging at C/10, C/2, 1 C, 2 C and 4 C, respectively. The cycling performance was evaluated in the voltage region of 3.5–4.3 V at 0.4 mA/cm² at 60 °C. The 1 C discharge rate is set by discharging the reversible capacity (multiply the specific capacity at 0.1 mA/cm² by the weight of active material) in 1 h, or discharging to 3.0 V in 1 h after charging to 4.3 V in 0.1 mA/cm². And it is about C/3 for 0.4 mA/cm² in the present paper. The electrolyte was 1 M LiPF₆ in EC/DMC (1:2 in volume) supplied by Ube Industries Ltd.

3. Results and discussion

3.1. Comparison of the rate capacity of Mn spinels differing in chemical composition and thermal processing

The discharge behaviors of the nominal spinel Mn800 and Ni-doped spinel Ni010-800 at different current rates were investigated. In contrast to the results in reference [10], the high

rate discharge capability of our spinel Mn800 is very excellent, and ca. 92.7% of the reversible capacity at C/10 (ca. 137 mAh/g) was obtained at 4 C rate. The material Ni010-800, with composition of LiNi_{0.10}Mn_{1.90}O₄ (calculated from the mole ratio of LiOH, NiO and MnO₂ in the starting mixture), was synthesized by the same method as Mn800. The reversible capacity at C/10 is reduced to ca. 110 mAh/g for Ni010-800 because of Ni-doping, and about 93.1% was retained when discharged at 4 C. Therefore, we can conclude that the high rate discharge capability of spinel materials is very excellent if synthesized by proper method, and doping with Ni did not affect the rate capacity. It is well understood that the fabrication method and thickness of electrodes play a very important role in the high rate performance of the cathodes. In the present paper, our cathodes are prepared by a pellet method with about 30 wt.% TAB was added to guarantee the good electric contact between the material powders and current collector. The thickness of our cathode pellets is about 200 μm, which is much thicker than the commercially used thin-film type electrodes by slurry coating (about 60–100 μm). Considering that only about 10% carbon black is added as conductive agent in the thin-film type electrodes, the high rate capacity problem may become more pronounced than that of the pellet-type. Therefore, it is emphasized here that the pellet-type electrode in the present paper is used only for comparison and the results herein do not represent the real performance in commercial application.

The poor high rate performance of nominal LiMn₂O₄ was also observed by other researchers of reference [11], and it is noted here that it is not strange to see different charge/discharge behavior or rate capability for Mn spinel materials investigated by different research groups. Because the examined samples may be different in their thermal processing history and chemical composition especially the oxygen content. It has been well recognized that the calcination temperature is of great importance to the physical and chemical characteristics of spinel materials. Recently, we have reported that the particle size of Mg-doped spinels could be enlarged by nearly eight-fold if increasing the crystallization temperature from 800 to 1000 °C, however the oxygen defect became much severe [8]. A series of materials designated Mg010-T are prepared by the same method as Ni010-800 and Mn 800 but at different temperatures, *T*, 800, 850, 900, 950, and 1000 °C corresponding to the calcination temperature. Fig. 1 shows the discharge behaviors of materials Mg010-T at different rates at ambient temperature. Increasing the calcination temperature from 800 to 1000 °C, the high rate discharge capability become worse and worse especially for 1000 °C. As for material Mg010-800, ca. 94% of the available capacity at C/10 can be released when discharged at 4 C, and it is only ca. 77% for Mg010-1000. The physiochemical properties of Mg010-T such as the particle size, crystallization and the chemical composition from chemical analysis are summarized in Table 1. Judging only from the information in Table 1, one may think that the enlarged particle size, improved crystallization and the oxygen deficiencies obtained

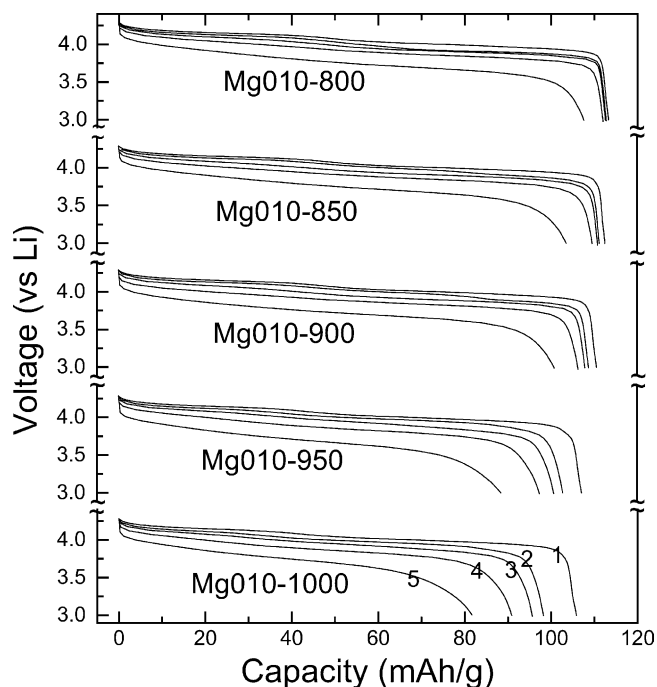


Fig. 1. The discharge behaviors for Mg010-T at different rates: the five curves from the right to left correspond to C/10, C/2, 1C, 2C, and 4C, respectively.

at much higher temperatures, seem to be the reasons for the deteriorated high-rate performance. Later in the present paper this topic will be discussed in more details.

3.2. Improved high rate capability of spinel materials after annealing at lower temperatures especially with the addition of LiOH

The high rate discharge performance for the spinel materials synthesized at much higher temperatures such as 1000 °C is very poor although their Mn dissolution in the organic electrolyte is satisfactory and necessary for Li-ion batteries based on Mn spinel cathodes [8,9]. And it should be improved to meet the requirements for high power output. Recently, we have reported a new kind of spinel materials prepared by

a two-step method: first calcinating the starting mixtures at high temperatures over 950 °C to get an intermediate, then annealing the intermediate at 600 °C with the addition of extra LiOH [7,8]. The new materials, for example Mg010-N600 with composition of $\text{Li}_{1.036}\text{Mg}_{0.010}\text{Mn}_{1.864}\text{O}_{4.021}$ exhibited greatly improved cycling performance at elevated temperatures as shown in Fig. 2 (ca. 1.5% capacity loss after 50 cycles at 60 °C). For comparison, two control materials designated Mg010-C800 and Mg010-C1000 were prepared by the same method as Mg010-T at 800 °C for 20 h and 1000 °C for 10 h, respectively. They have almost the same composition as Mg010-N600 by adding all the necessary LiOH, MgO and MnO₂ in the starting mixture. The determined chemical characteristics are summarized in Table 1. As seen from Fig. 2, the cycling performance of Mg010-N600 at 60 °C is much better than that of Mg010-C800 and Mg010-C1000, and we have ascribed this to the achievement of oxygen stoichiometry and the improved crystallization [8]. It is noted here that the two materials Mg010-C800 and Mg010-800 (see Table 1) are different in their composition although the same synthesis procedure was used.

The discharge behaviors of Mg010-N600, Mg010-C800 and Mg010-C1000 were measured and shown in Fig. 3. The high rate discharge capability of Mg010-C800 is as excellent as Mn800 or Mg010-800, and it becomes very poor for Mg010-C1000. As for Mg010-N600, ca. 94% of the available capacity at C/10 can be retained when discharged at 4C, and it is ca. 94% and 87% for Mg010-C800 and for Mg010-C1000, respectively. This indicates that the deteriorated high rate performance because of crystallization at 1000 °C can be improved to very excellent after annealing with LiOH at lower temperatures such as 600 °C. From Table 1, we know that the particle size of Mg010-C1000 and Mg010-N600 is almost the same (ca. 4.0 μm), so the poorer high-rate performance of Mg010-C1000 cannot be ascribed to enlarged particle size as supposed in the above paragraphs. Attempting to understand the effect of anneal treatment at 600 °C, we prepared another sample designated Mg010-C600 by annealing Mg010-C1000 at 600 °C for 5 h without the addition of LiOH. The discharge behavior of Mg010-C600 was examined and

Table 1
Physiochemical properties of the spinel samples in the present paper

Sample name	Chemical composition	Lattice parameter (Å)	Particle size (ca.) (μm)	I_{\max}/FWHM^a for (1 1 1) peak
Mn-800	$\text{Li}_{1.010}\text{Mn}_{1.990}\text{O}_{3.988}$	8.226	0.5	2280/0.21
Mg010-800	$\text{Li}_{0.995}\text{Mg}_{0.096}\text{Mn}_{1.909}\text{O}_{3.999}$	8.215	0.5	2453/0.22
Mg010-850	$\text{Li}_{1.010}\text{Mg}_{0.094}\text{Mn}_{1.896}\text{O}_{3.999}$	8.219	1.0	2760/0.21
Mg010-900	$\text{Li}_{1.010}\text{Mg}_{0.099}\text{Mn}_{1.900}\text{O}_{3.998}$	8.221	1.5	2667/0.22
Mg010-950	$\text{Li}_{1.009}\text{Mg}_{0.093}\text{Mn}_{1.898}\text{O}_{3.996}$	8.230	2.0	2520/0.20
Mg010-1000	$\text{Li}_{1.005}\text{Mg}_{0.097}\text{Mn}_{1.898}\text{O}_{3.995}$	8.230	4.0	2847/0.18
Mg010-N600	$\text{Li}_{1.036}\text{Mg}_{0.010}\text{Mn}_{1.864}\text{O}_{4.021}$	8.210	4.0	2441/0.18
Mg010-C800	$\text{Li}_{1.035}\text{Mg}_{0.093}\text{Mn}_{1.873}\text{O}_{3.999}$	8.213	0.5	2146/0.22
Mg010-C1000	$\text{Li}_{1.033}\text{Mg}_{0.090}\text{Mn}_{1.877}\text{O}_{3.997}$	8.225	4.0	2441/0.18
Mg010-C600	$\text{Li}_{1.033}\text{Mg}_{0.090}\text{Mn}_{1.877}\text{O}_{4.000}$	8.221	4.0	2460/0.18

^a I_{\max}/FWHM of diffraction peak (1 1 1) is a useful index for the XRD peak sharpness or crystallinity, in which FWHM represents full width at half maximum of I_p [12].

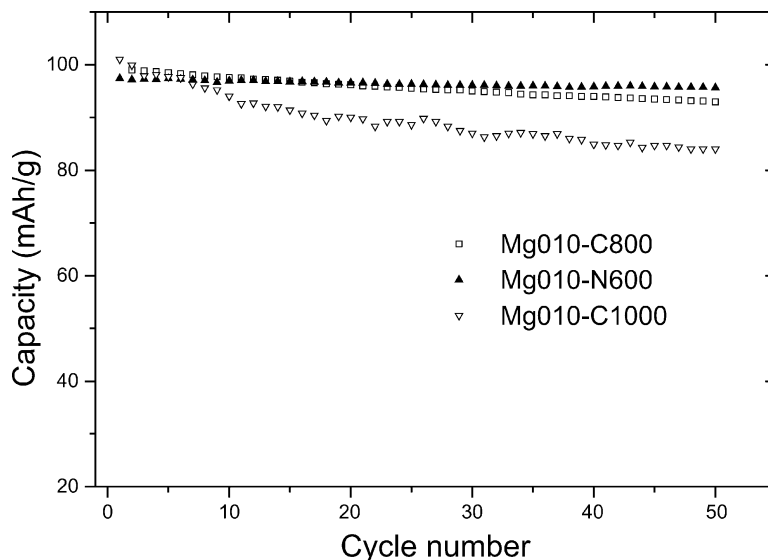


Fig. 2. The variation of discharge capacity as a function of cycle number for Mg010-C800, Mg010-C1000, and Mg010-N600 cathodes at 60 °C (0.4 mA/cm²).

also shown in Fig. 3 for comparison. It could be seen that the high rate capability was improved significantly by annealing at 600 °C only, and ca. 91% of the available capacity at C/10 can be retained when discharged at 4 C. Therefore, the high rate discharge capability of the spinels prepared above 950 °C can be improved by lower temperature annealing, and it will become comparable with that of Mg010-800 or Mn800 if extra LiOH is added during annealing. And the advantages of low Mn dissolution and excellent high rate performance can be obtained at the same time.

3.3. Discussion on the reasons for the poor high rate performance

From the preliminary results and discussions above, we know that ascribing the poorer high-rate performance of

Mg010-C1000 or Mg010-1000 to the enlarged particle size is not right. Furthermore, it can be seen that Mg010-N600 shows almost the same performance as that of Mg010-C800 (in Fig. 3) although its crystallization degree is as high as that of Mg010-C1000 (see Table 1). And the oxygen defect of Mn800 is much severer than that of Mg010-C1000, but its high rate performance is very excellent. This indicates that the higher crystallization degree and oxygen deficiency cannot be responsible for the deteriorated high rate performance either. Therefore, the three reasons: enlarged particle size, improved crystallinity and oxygen defect once supposed to be responsible in the above paragraphs cannot explain the poor high rate performance of Mg010-1000 or Mg010-C1000. Then, what should be the real reason?

It is proposed here that some kinds of non-cubic impurities existing in the bulk of Mg010-1000 or Mg010-C1000

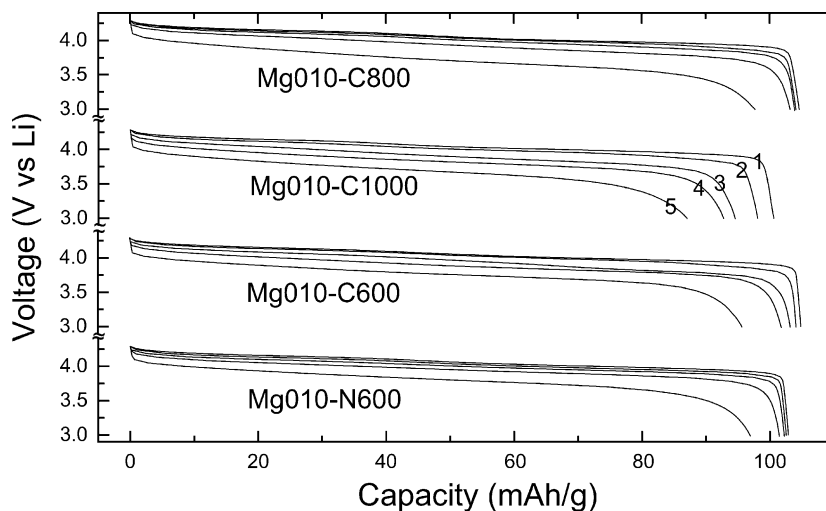


Fig. 3. The discharge behaviors for Mg010-C800, Mg010-C1000, Mg010-N600 and Mg010-C600 at different rates: the five curves from the right to left correspond to C/10, C/2, 1 C, 2 C, and 4 C, respectively.

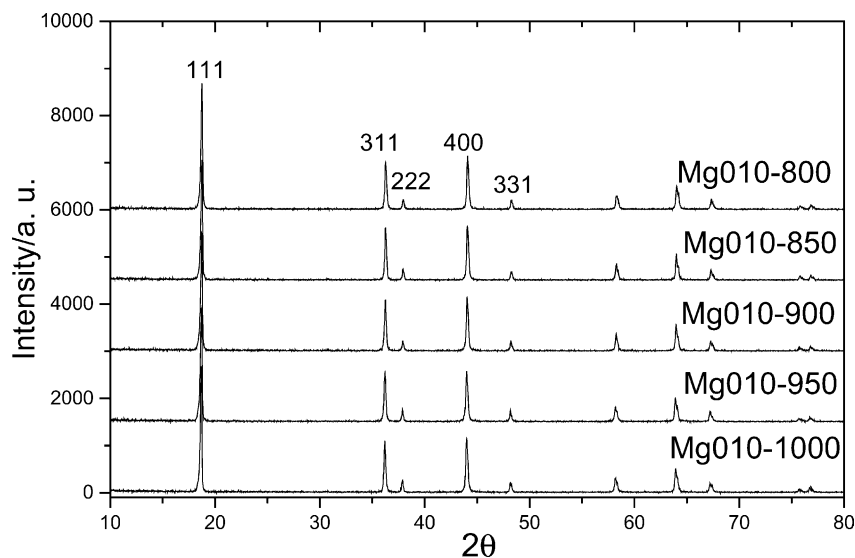


Fig. 4. The powder XRD patterns for materials Mg010-T (T corresponding to the calcination temperature) with diffraction intensity being adjusted for clarity.

should be responsible for the deteriorated performance, although they cannot be detected for the limitation of the XRD machine as seen from the powder XRD patterns in Fig. 4. We can compare the reversible capacities at C/10 observed in Fig. 1 for the series of materials Mg010-T. It can be seen that the available capacity at C/10 was reduced by nearly 8% from Mg010-800 to Mg010-1000. So some component with cubic structure may lose oxygen and become non-cubic impurities upon sintering at 1000 °C. It had been observed by Tarascon et al. [2] that the cubic spinel may change to tetragonal $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ or orthorhombic LiMnO_2 if the crystallization temperature was increased to above 850 °C. And these non-cubic components can be recovered back to cubic spinels by cooling slowly. However, it is possible that some

impurities although very little may still exist in the powder bulk, and some capacity is lost as observed for Mg00-1000. Furthermore, it is believed that the existence of non-cubic impurities may bring in poor electronic conductivity between spinel microcrystals in the powders, and then result in poor high rate performance. This speculation was confirmed by the significantly increased R_{ct} (charge transfer resistance) for the lithium intercalation/extraction kinetics of Mg010-1000 cathodes as measured by ac impedance (Fig. 5). The R_{ct} was read from the second semicircle in the plot diagram although it is not separated very well for Mg010-800. The discussion on impedance analysis in more details will be described in other papers following reference [13]. After annealing treatment at 600 °C especially with LiOH, the lost oxygen at temperatures over 850 °C can be recombined and the impurities can be reactivated into cubic spinels. As we can see in Fig. 3, the capacity increase of about 5 mAh/g at C/10 was observed for Mg010-C600 prepared by annealing Mg010-C1000 at 600 °C. In the above discussions, we have postulated that all the available capacity for the spinel cathodes could be released at C/10 discharge rate. And this could be reasonable for our pellet electrodes pressed on the steel mesh, and good conductive contact of all spinel powders with the current collector can be guaranteed by the adding of 30 wt.% TAB as conductive additives.

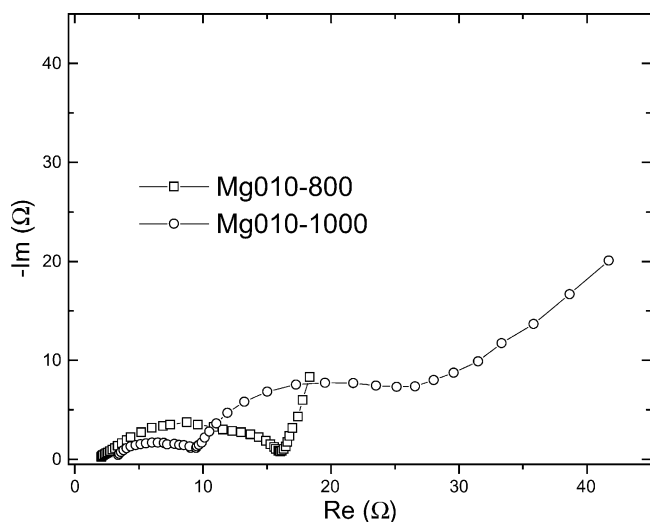


Fig. 5. The ac impedance plots for Mg010-800 and Mg010-1000 cathodes in the charged state of ca. 70 mAh/g (4.12 and 4.13 V vs. Li metal for them respectively). The ac signal of 10 mV is used in the measurements.

4. Conclusions

The discharge behaviors of the LiMn_2O_4 type spinels differing in chemical composition and thermal treating history are investigated in this paper. It was found that the high rate discharge capability of the nominal LiMn_2O_4 spinel is as excellent as that of the spinels doped with Ni or Mg cations if it was prepared below 850 °C. And calcination at tem-

peratures over 950 °C for sample synthesis will yield Mn spinels with poor high-rate discharge performance, and post-annealing at lower temperatures especially with LiOH can improve it significantly. After comparing and discussing the results with more details, the reasons including enlarged particle size, higher crystallization degree and oxygen deficiency are excluded. And impurities with non-cubic structure embedded in the bulk that were originated from crystallization above 950 °C, are proposed to result in poor electronic contact between the spinel microcrystals and then poor high rate discharge performance. Therefore, the thermal treating process should be controlled very carefully in synthesizing Mn spinels with both excellent cycling performance and high rate capacity.

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