

Cycle performance improvement of  
LiMn<sub>2</sub>O<sub>4</sub> cathode material for lithium ion battery  
by formation of “Nano Inclusion”

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## Abstract

LiMn<sub>2</sub>O<sub>4</sub> with a cubic spinel structure is well known as a cathode material for lithium ion battery owing to its advantages of nontoxicity, availability, low cost and safety. However, LiMn<sub>2</sub>O<sub>4</sub> suffers from severe capacity fading during charge and discharge cycles. This dissertation describes that the cycle performance improvement of LiMn<sub>2</sub>O<sub>4</sub> was attained by the introduction of thin-plate shaped ZnMn<sub>2</sub>O<sub>4</sub> crystal (hereafter named as “Nano Inclusion”) with a tetragonal spinel structure within LiMn<sub>2</sub>O<sub>4</sub> single crystal, the crystal chemical investigation of “Nano Inclusion” in LiMn<sub>2</sub>O<sub>4</sub> was studied, and the effect of “Nano Inclusion” on cycle performance of LiMn<sub>2</sub>O<sub>4</sub> “Nano Inclusion” was also investigated.

## Chapter 1

Lithium ion battery is currently used widely not only for consumer electronics, such as mobile phones, laptops and tablets, but also for large-scale devices, such as electric vehicles and large-scale energy storages systems for the grid energy storages because of high-energy density, high-power density, low self-discharge and high efficiency during charge and discharge. Lithium ion battery consists of four main components such as cathode, anode, separator, and electrolyte. The properties of lithium ion battery varies with selected main components.

LiCoO<sub>2</sub> with a layered structure<sup>[1]</sup> has been widely used as a cathode material for lithium ion battery. The cathode materials with the layered structure have a high-energy density. However, the disadvantages of LiCoO<sub>2</sub> are a low thermal stability,<sup>[2]</sup> toxicity, and high cost. The cathode materials with the spinel structure such as LiM<sub>2</sub>O<sub>4</sub> ( $M = \text{Ti, V, Mn}$ ) compounds<sup>[3-5]</sup> show a lower energy density and a higher thermal stability in comparison with the cathode materials with the layered structure. In particular, LiMn<sub>2</sub>O<sub>4</sub> is a promising cathode material due to nontoxicity, availability, low cost, and safety. However, LiMn<sub>2</sub>O<sub>4</sub> suffers from severe capacity fading during the charge / discharge cycles. Many trials have been investigated to solve the factors of capacity fading and improve the cycle performance so far. A substitution of Mn with other elements<sup>[6-17]</sup> has been attempted to restrain the phase transition and to stabilize the crystal structure. A surface modification of LiMn<sub>2</sub>O<sub>4</sub> with other compounds<sup>[18-27]</sup> has been tried to reform the particle surface and to protect Mn from dissolution. Professor Dr. Takeshi Yao has presented an approach to stabilize LiMn<sub>2</sub>O<sub>4</sub> spinel crystal lattice by using another spinel crystal inert to electrochemical reaction through the common oxide ion arrangement for improving the cycle performance of LiMn<sub>2</sub>O<sub>4</sub>.<sup>[28-33]</sup>

Fabrication of the samples by adding Zn<sub>2</sub>SnO<sub>4</sub> to the Li<sub>2</sub>CO<sub>3</sub> and MnO<sub>2</sub> mixtures has been investigated in this study to improve the cycle performance of LiMn<sub>2</sub>O<sub>4</sub>. Through this study, it was first discovered that within the LiMn<sub>2</sub>O<sub>4</sub> single crystals, nano-scale thin plate-shaped ZnMn<sub>2</sub>O<sub>4</sub>

crystals were induced, which were named “Nano Inclusions”<sup>[34,35]</sup> after the similar characteristics of “inclusions” in mineralogy and their nano scale. Moreover, it was revealed that the cycle performance of LiMn<sub>2</sub>O<sub>4</sub> with “Nano Inclusion” is superior to that of LiMn<sub>2</sub>O<sub>4</sub> without it. “Nano Inclusion” is considered to suppress crack propagation caused by volume changes during the charge and discharge process and prevent dead region formation, which causes the capacity decrease.

In this dissertation, the introduction of “Nano Inclusion” in LiMn<sub>2</sub>O<sub>4</sub>,<sup>[34,35]</sup> the crystal chemical investigation of “Nano Inclusion” in LiMn<sub>2</sub>O<sub>4</sub>,<sup>[36]</sup> and the effect of “Nano Inclusion” on cycle performance of LiMn<sub>2</sub>O<sub>4</sub> with “Nano Inclusion”<sup>[37]</sup> were studied and summarized.

## Chapter 2

The sample was prepared by mixing Li<sub>2</sub>CO<sub>3</sub>, MnO<sub>2</sub>, and Zn<sub>2</sub>SnO<sub>4</sub> with a molar ratio of Li : Mn : Zn<sub>2</sub>SnO<sub>4</sub> = 1 - x : 2(1 - x) : x (x = 0, 0.02, 0.05, 0.1), calcining and firing. Observation of the cross section for the samples was carried out. The cycle performance of thus obtained samples was investigated in a two-electrode cell.

For  $x > 0$ , high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images revealed that nano-scale thin plate-shaped ZnMn<sub>2</sub>O<sub>4</sub> crystals were induced within the LiMn<sub>2</sub>O<sub>4</sub> single crystals. The nano-scale thin plate-shaped crystals were named “Nano Inclusions” after the nano-scale size of the crystal and the similar character of the inclusion in mineralogy. The discharge capacity decreased as  $x$  increased. However, the discharge capacity retention rate at 100 cycles for  $x = 0, 0.02, 0.05, \text{ and } 0.1$ , are 0.862, 0.867, 0.992, and 1.002, respectively and increased with an increase of  $x$ . The cycle performance of LiMn<sub>2</sub>O<sub>4</sub> with “Nano Inclusion” was superior to that of LiMn<sub>2</sub>O<sub>4</sub> without “Nano Inclusion”. It is considered that “Nano Inclusion” suppressed crack propagation caused by volume changes during the charge and discharge process and prevented dead region formation, which causes the capacity decrease.

## Chapter 3

The crystal structure of LiMn<sub>2</sub>O<sub>4</sub> with “Nano Inclusions” was studied in detail by conventional HAADF-STEM observation, HAADF-STEM observation with the electron beam tilted to the TEM specimen, electron diffraction pattern analysis, High-resolution transmission electron microscopy (HRTEM) observation and the fast Fourier transform (FFT) pattern analysis. Observation with the electron beam tilted to the specimen revealed that the “Nano Inclusion” was shaped into a thin plane plate. The electron diffraction pattern analysis indicated that both the atomic arrangement and the orientation of the “Nano Inclusion” is similar to those of the surrounding LiMn<sub>2</sub>O<sub>4</sub>. It was revealed that the “Nano Inclusion” was placed within a single LiMn<sub>2</sub>O<sub>4</sub> crystal with connected to the LiMn<sub>2</sub>O<sub>4</sub>

matrix without forming grain boundaries. It was revealed that the [100]-[010] plane of  $\text{LiMn}_2\text{O}_4$  and the [110]-[110] plane of  $\text{ZnMn}_2\text{O}_4$  connected closely without grain boundaries by HRTEM observation and the corresponding FFT pattern analysis.

## Chapter 4

$\text{ZnMn}_2\text{O}_4$  “Nano Inclusion”-induced  $\text{LiMn}_2\text{O}_4$  was prepared by employing various heat treatment time and its effects to “Nano Inclusion” formation were investigated. XRD pattern analysis and scanning electron microscopy (SEM) observation indicated that  $\text{LiMn}_2\text{O}_4$  formed at low temperature sintering collapsed at the initial stage of heat treatment and  $\text{LiMn}_2\text{O}_4$  particles grew in the subsequent heat treatment. HAADF-STEM observation, EDX elements analysis, and electron energy-loss spectroscopy (EELS) spectra analysis revealed that “Nano Inclusions” were formed within a  $\text{LiMn}_2\text{O}_4$  single crystal and that both the particle size of  $\text{LiMn}_2\text{O}_4$  and that of “Nano Inclusions” increased with the heat treatment time. HRTEM observation and the FFT pattern analysis proved that “Nano Inclusions” connect closely without grain boundaries, that the “Nano Inclusion” was placed within a single  $\text{LiMn}_2\text{O}_4$  crystal for “Nano Inclusion”-induced  $\text{LiMn}_2\text{O}_4$ .

## Chapter 5

The cycle performance for  $0.95\text{LiMn}_2\text{O}_4\text{-}0.05\text{Zn}_2\text{SnO}_4$  prepared by employing various heat treatment time was estimated. The cycle performance of the prepared samples was dependent on the heat treatment time. The capacity fading during the charge / discharge cycles is clearly improved in all the samples with “Nano Inclusion”. The heat-treated for 4 hours sample surpass  $\text{LiMn}_2\text{O}_4$  without “Nano Inclusion” in discharge capacity at over the 31st cycle at 25 °C and 24st cycle at 60 °C, respectively. It is indicated that the cycle performance of  $\text{LiMn}_2\text{O}_4$  with “Nano Inclusion” is superior to that of  $\text{LiMn}_2\text{O}_4$  without “Nano Inclusion” both at 25 °C and at 60 °C, and that the cycle performance of  $\text{LiMn}_2\text{O}_4$  with “Nano Inclusion” is more improved by changing heat treatment time. Also, it is revealed even for a full cell battery that the cycle performance of  $\text{LiMn}_2\text{O}_4$  was improved by inducing “Nano Inclusion” with an appropriate heat treatment time. It is considered that appropriate size of “Nano Inclusion” was formed by the 4 hours heat treatment. Moreover, observation of SEM images for electrodes treated with charge/ discharge cycles revealed that “Nano Inclusion” suppressed crack formation and propagation caused by volume changes during the charge and discharge process.

## Chapter 6

$\text{ZnMn}_2\text{O}_4$  “Nano Inclusion”-induced  $\text{LiMn}_2\text{O}_4$ , which is expressed as  $(1 - x)\text{LiMn}_2\text{O}_4\text{-}x\text{Zn}_2\text{SnO}_4$ ,

was fabricated and investigated for the cycle performance at 3 V range. The discharge capacity decreased with the increase of  $x$ . However, the discharge capacity retention rate at 100 cycles for  $x = 0, 0.05, 0.075, 0.1,$  and  $0.125$  are 0.405, 0.433, 0.835, 0.781, and 0.827, respectively, and increased with an increase of  $x$ . The cycle performance of  $\text{LiMn}_2\text{O}_4$  with “Nano Inclusion” is superior to that of  $\text{LiMn}_2\text{O}_4$  without it. It is considered that “Nano Inclusion” suppressed crack propagation caused by volume changes during the charge and discharge process and prevented dead region formation, which causes the capacity decrease at 3 V range as well as at 4 V range.

Moreover, the sample of  $(1 - x)\text{LiMn}_2\text{O}_4\text{-}x\text{Zn}_2\text{SnO}_4$  ( $x = 0.075$ ) which has the best cycle performance, were prepared by employing various heat treatment time,  $z$ . The effect of heat treatment time on cycle performance was investigated and discussed. The cycle performance changes according to the value of heat treatment time,  $z$ . For the discharge capacity at 1st cycle, all the samples with “Nano Inclusion” were smaller than  $\text{LiMn}_2\text{O}_4$  without it. However, for the discharge capacity retention rate, all the samples with “Nano Inclusion” were larger than  $\text{LiMn}_2\text{O}_4$  without it. The samples of  $z = 4, 8, 10,$  and  $12$  showed the higher discharge capacity than that of  $\text{LiMn}_2\text{O}_4$  without “Nano Inclusion” at over 22nd, 9th, 14th, and 13th cycles, respectively. In particular, discharge capacity of the sample heat-treated for 8 hours has the highest capacity and the better cycle performance. It is considered that appropriate size of “Nano Inclusion” was formed by the 8 hours heat treatment for the cycle performance of  $\text{LiMn}_2\text{O}_4$  at 3 V range.

## Chapter 7

Chapter 7 summarizes the results on improvement of the cycle performance for  $\text{LiMn}_2\text{O}_4$  with “Nano Inclusion”. It is thought that more various experiments are needed to elucidate the formation mechanism of “Nano Inclusion”, which can be expanded in the field of material science and to apply “Nano Inclusion” to any other commercialized cathode material such as  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ , which might contribute to the battery technology field due to the improved cycle performance. It can be expected that “Nano Inclusion” is a useful method to improve cycle performance for not only  $\text{LiMn}_2\text{O}_4$  but also other electrode materials, such as cathode materials for lithium ion batteries mentioned above, and post-lithium ion batteries’ active electrode material.

## References

- [1] T. Ohzuku, A. Ueda, M. Nagayama, Y. Yasunou, and H. Komori, *Electrochim. Acta*, 1993, **38**, 1159-1167.
- [2] Y. Baba, S. Okada, and J. Yamaki, *Solid State Ionics*, 2002, **148**, 311-316.
- [3] J. C. Hunter, *J. Solid State Chem.*, 1981, **39**, 142-147.

- [4] M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, 1983, **18**, 461-472.
- [5] M. M. Thackeray, P. J. Johnson, L. A. de Picciotto, P. G. Bruce, and J. B. Goodenough, *Mat. Res. Bull.*, 1984, **19**, 179-187.
- [6] Y. Xia and M. Yoshio, *J. Electrochem. Soc.*, 1996, **143**, 825-833.
- [7] L. Guohua, H. Ikuta, T. Uchida, and M. Wakihara, *J. Electrochem. Soc.*, 1996, **143**, 178-182.
- [8] H. J. Choi, K. M. Lee, and J. G. Lee, *J. Power Sources*, 2001, **103**, 154-159.
- [9] C. H. Shen, R. S. Liu, R. Gundakaram, J. M. Chen, S. M. Huang, J. S. Chen, and C. M. Wang, *J. Power Sources*, 2001, **102**, 21-28.
- [10] C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard, and M. Tournoux, *Solid State Ionics*, 1995, **81**, 167-170.
- [11] A. D. Robertson, S. H. Lu, and W. F. Howard Jr, *J. Electrochem. Soc.*, 1997, **144**, 3505-3512.
- [12] A. D. Robertson, S. H. Lu, W. F. Averill, and W. F. Howard Jr, *J. Electrochem. Soc.*, 1997, **144**, 3500-3505.
- [13] Y. Gao and J. R. Dahn, *J. Electrochem. Soc.*, 1996, **143**, 100-114.
- [14] J. M. Tarascon, E. Wang, F. K. Shokoohi, W. R. McKinnon, and S. Colson, *J. Electrochem. Soc.*, 1991, **138**, 2859-2864.
- [15] A. de Kock, E. Ferg, and R. J. Gummow, *J. Power Sources*, 1998, **70**, 247-252.
- [16] F. Le Cras, D. Bloch, M. Anne, and P. Strobel, *Solid State Ionics*, 1996, **89**, 203-213.
- [17] R. J. Gummow, A. de Kock, and M. M. Thackeray, *Solid State Ionics*, 1994, **69**, 59-67.
- [18] A. M. Kannan and A. Manthiram, *Electrochem. Solid-State Lett.*, 2002, **5**, A167-A169.
- [19] S. Guo, X. He, W. Pu, Q. Zeng, C. Jiang, and C. Wan, *Int. J. Electrochem. Sci.*, 2006, **1**, 189-193.
- [20] Y.-K. Sun, K.-J. Hong, and J. Prakash, *J. Electrochem. Soc.*, 2003, **150**, A970-A972.
- [21] S.-W. Lee, K.-S. Kima, H.-S. Moon, H.-J. Kim, B.-W. Cho, W.-I. Cho, J.-B. Ju, and J.-W. Park, *J. Power Sources*, 2004, **126**, 150-155.
- [22] A. Eftekhari, *Solid State Ionics*, 2004, **167**, 237-242.
- [23] M. M. Thackeray, C. S Johnson, J.-S. Kim, K. C. Lauzze, J. T. Vaughey, N. Dietz, D. Abraham, S. A. Hackney, W. Zeltner, and M. A. Anderson, *Electrochem. Commun.*, 2003, **5**, 752-758.
- [24] G. G. Amatucci, A. Blyr, C. Sigala, P. Alfonse, and J. M. Tarascon, *Solid State Ionics*, 1997, **104**, 13-25.
- [25] R. Vidu and P. Stroeve, *Ind. Eng. Chem. Res.*, 2004, **43**, 3314-3324.
- [26] C. Arbizzani, A. Balducci, M. Mastragostino, M. Rossi, and F. Soavi, *J. Electroanal. Chem.*, 2003, **553**, 125-133.
- [27] M. Nishizawa, K. Mukai, S. Kuwabata, C. R. Martin, and H. Yoneyama, *J. Electrochem. Soc.*, 1997, **144**, 1923-1927.
- [28] N. Ozawa, K. Donoue, and T. Yao, *Electrochem. Solid-State Lett.*, 2003, **6**, A106-A108.

- [29] T. Yao. JP Patent 1999-0089158, 1999-03-30.
- [30] T. Yao, JP Patent 4330758, 2009-06-26.
- [31] T. Yao and N. Ozawa, JP Patent 4056271, 2008-03-05.
- [32] T. Yao, U. S. Patent 6582853, 2003-06-24.
- [33] M. Hibino, M. Nakamura, Y. Kamitaka, N. Ozawa, and T. Yao, *Solid State Ionics*, 2006, **177**, 2653-2656.
- [34] T. Yao, S. Esaki, M. Nishijima, M. Hibino, and A. Fujita, JP Patent 5115891, 2012-10-26.
- [35] S. Esaki, M. Nishijima, and T. Yao, *ECS Electrochem. Lett.*, 2013, **2**, A93-A97.
- [36] S. Esaki, M. Nishijima, S. Takai and T. Yao, *RCS Adv.*, 2014, **4**, 59858-59861.
- [37] S. Esaki, M. Nishijima, S. Takai and T. Yao, *RCS Adv.*, 2015, **5**, 42455-42460.