

# Research Article

# Improved Performance of Hydrothermally Synthesized LiMnPO<sub>4</sub> by Ball Milling as a Positive Electrode for Li Ion Battery

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LiMnPO<sub>4</sub> is anticipated to be a promising cathode material for next generation lithium battery. A reduction of particle size is recognized as a good strategy to improve its performance and it can be achieved by ball milling. However, the ball milling including carbon addition forms small LiMnPO<sub>4</sub> particles with large carbon content, which leads to low volumetric energy density of electrode. In this study, carbon-coated LiMnPO<sub>4</sub> prepared by hydrothermal route was applied to the ball milling without carbon addition. The reduction of particle size of carbon-coated LiMnPO<sub>4</sub> was achieved by the ball milling without destroying the surface carbon layer. The ball-milled LiMnPO<sub>4</sub> particle revealed better cathodic performance than non-milled sample. This was attributed to shortening Li ion diffusion path, improvement of structural flexibility, and large surface area of electrode due to reduction of particle size. The ball milling is attested to be a promising method to improve cathodic performance of carbon-coated LiMnPO<sub>4</sub>.

#### 1. Introduction

LiMPO<sub>4</sub> compounds (M = Fe, Mn, Co, and Ni) with olivine structure have been attracted as alternative cathode materials for lithium ion batteries owing to their low cost, low toxicity, chemical and thermal stabilities compared with currently used LiCoO<sub>2</sub> [1]. Among these compounds, LiMnPO<sub>4</sub> has been recognized the most attractive compound due to its high operation voltage determined by  $Mn^{3+/4+}$  redox couple at 4.1 V versus Li/Li<sup>+</sup> and is compatible with the system presently used in lithium ion battery [2].

However, the most serious problem of this cathode material is low intrinsic electronic and Li ion conductivities [3, 4]. Various experimental reports have indicated that carbon-coating can provide high electronic conductivity [5–7]. In fact, a large charge-discharge capacity of carbon-coated LiFePO<sub>4</sub> synthesized by a hydrothermal synthesis method has been reported [8].

As for improvement of Li ion conductivity, much effort has been paid for particle size reduction to shorten Li ion conduction path [9]. Drezen et al. reported reversible capacities for 140 and 270 nm diameter  $\text{LiMnPO}_4$  particles prepared by sol-gel method were 81 and 7 mA h g<sup>-1</sup>, respectively [10]. Some groups reported a good performance of ball-milled small LiMnPO<sub>4</sub> [11] and LiCoPO<sub>4</sub> particles [12]. However, their processes included conductive carbon addition ( $\leq 20 \text{ wt.\%}$ ) before the ball milling to obtain a carbon composite. This large amount of carbon causes surely improvement of the electronic conductivity, however, such heavy carbon coating decreases volumetric capacity. Additionally, commercial battery foils typically only contain 2.5 weight percent (or lower) carbon blacks with close to 95 weight percent active materiel. Therefore, it may not appeal for practical application.

The carbon coated olivine type cathode materials prepared by hydrothermal route have been reported [13, 14]. The method allows us to prepare carbon-coated particles readily by only addition of a carbon source to start materials under appropriate condition. Consequently, it is guessed that if carbon-coated LiMnPO<sub>4</sub> (LiMnPO<sub>4</sub>/C) prepared by hydrothermal condition was supplied to the ball milling, carbon amount could be suppressed by omission of further carbon addition. On the other hand, harmful influence by the ball-milling of  $LiMnPO_4/C$  is also surmised, such as destroying the carbon coating layer. Hence, research on effect of the ball-milling to  $LiMnPO_4/C$  on electrochemical properties is a worthwhile work.

Herein, we applied to the ball-milling technique to hydrothermally synthesized  $\text{LiMnPO}_4/\text{C}$  and its electrochemical property was compared with non-milled  $\text{LiMnPO}_4/\text{C}$  to clarify influence of the ball-milling technique on electrochemical property of  $\text{LiMnPO}_4/\text{C}$ .

#### 2. Experimental

LiMnPO<sub>4</sub> was synthesized by a modification of hydrothermal process in previous reports for LiFePO<sub>4</sub> [15-17].  $MnSO_4 \cdot 5H_2O$  (43.84 g) and  $Li_3PO_4$  (20.84 g) were dissolved into purified water (44 mL) under N2 atmosphere. A molar ratio of Li: Mn: P in a precursor solution was 3:1:1. In order to prepare carbon-coated LiMnPO<sub>4</sub>, 6.00 g of carboxy methyl cellulose (CMC) was added into the precursor solution [1]. The precursor solution was put into a glass-lined Parr reactor with N<sub>2</sub> gas sealed in a stainless steel autoclave, and then heated at 200°C for 3h with stirring at 680 rpm. A precipitation was produced in the reactor under hydrothermal conditions. The precipitation was separated centrifugally at first, and then by a mean of freeze-drying at  $-50^{\circ}$ C for 12 h. Yield was always higher than 95%. The obtained sample was dispersed into ethanol and ball milled at 400 rpm for 12 h with ZrO<sub>2</sub> ball using a planetary ball mill equipment (Pulverissette P-6, Fritsch GmbH). The milled and non-milled samples were treated at 700°C under 3% H<sub>2</sub>/Ar flow for 1 h to obtain electroconductive graphite carbon [1, 14].

The crystalline phases of the synthesized sample were identified with X-ray diffraction (XRD, RINT-Ultima, Rigaku) with Cu K $\alpha$  radiation. Raman measurement (NRS-1000, JASCO) was carried out at room temperature by a laser radiation of 532 nm. The morphology of the synthesized particle was observed by scanning electron microscope (SEM, JEOL). Coated carbon amount of the samples was estimated by Thermogravimetry (TG) analysis (DTG-60, Shimazu) and BET surface areas of milled and non-milled particles were measured using BELSORP-mini (BEL JAPAN Inc.).

Performances of milled and non-milled LiMnPO4/C as a positive electrode were tested by a galvanostatic charge/discharge test. A composite LiMnPO<sub>4</sub>/C electrode was prepared by mixing LiMnPO4/C, Ketjen black, and Polyvinylidene difluoride (PVdF) in a weight ratio of 90:5:5 in 1.2 mL of NMP (N-methyl pyrrolidone). The LiMnPO<sub>4</sub>/C electrode was painted onto a thin Al sheet and dried overnight at 85°C under reduced pressure for 12 h. The LiMnPO<sub>4</sub> electrode (14 mm diameter) was set in a coin cell 2032 with a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (volume ratio = 1:1) containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> as an electrolyte and with lithium metal as a negative and a reference electrodes. The galvanostatic charge/discharge tests of coin cell with LiMnPO<sub>4</sub> positive electrode were performed by using HJ1001SM8A (HOKU-TODENKO). In the test, charging process was done under

CC-CV (constant current-constant voltage) mode, that is, charge in a constant current condition of 0.1 C until 4.5 V and then constant voltage charging was performed at 4.5 V until current dropped to 0.01 C. The discharge process was carried out at constant current condition of 0.1 C. Cutoff voltages were 2.0 V and 4.5 V for discharge and charge processes, respectively.

#### 3. Results

Figure 1 displays SEM images of non-milled and milled samples. In both cases, particles aggregated each other and formed secondary particles. The sizes of primary particles of non-milled and milled samples were estimated to be about 500 and 50 nm, respectively. The particle shapes of both samples were irregular. It is concluded that much smaller particles can be obtained by ball milling. BET surface area of non-milled and milled samples were 8.9 and 49.0 m<sup>2</sup> g<sup>-1</sup>, respectively. This result is well consistent with SEM observation.

XRD patterns of non-milled and milled samples are depicted in Figure 2. In non-milled sample, all diffraction peaks were attributed to  $\text{LiMnPO}_4$  with olivine structure and no impurity phase was observed. In milled sample, the diffraction peaks were much broader due to small particle and low crystallinity given by the ball milling. An appearance of new phase was not confirmed. Therefore, it is inferred that the ball milling can crash the LiMnPO<sub>4</sub> particles, but did not produce any impurity phase.

The Raman spectroscopy is sensitive to surface of the materials comparing with XRD. Dokko et al. have succeeded in detection of even small amount of impurity on the LiFePO<sub>4</sub> synthesized by the hydrothermal process [17] and carbon coating layer on the surface of the LiFePO<sub>4</sub>/C [8], LiMnPO<sub>4</sub>/C [1], and LiCoPO<sub>4</sub>/C [14]. Thus, the Raman measurement was carried out to detect carbon layer on the samples that could not be detected by the XRD measurement. Figure 3 reveals the Raman spectra of non-milled and milled  $LiMnPO_4/C$ . In non-milled sample, clear peaks appeared at 948, 1361, and 1610 cm<sup>-1</sup>. The peak at 948 cm<sup>-1</sup> is assigned to the symmetric vibration of the PO<sub>4</sub> group [18]. As mentioned above, clear diffraction peaks of the  ${\rm LiMnPO}_4$  were observed in the XRD patterns. The peak at 948 cm<sup>-1</sup> was consistent with the result of XRD and it was clear that the LiMnPO<sub>4</sub> has been synthesized successfully. Peaks at 1610 cm<sup>-1</sup> and 1361 cm<sup>-1</sup> were attributed to graphite and disorder carbon (G and D bands), respectively [19], indicating that conductive carbon layer was formed on the surface. In milled sample, the peak at 948 cm<sup>-1</sup> was not observed because of small particles and low crystallinity of the milled-sample. A high noise level of the spectrum is also possible reason. As for the G and D bands, they clearly appeared in the spectrum although their intensities became weaker, indicating that surface carbon layer still existed even after crashing the particles by the ball milling. The ratio of G band to D band, that is, quality of the carbon layer, was 1.4 and 1.3 for non-milled and milled samples, respectively. Therefore, the qualities of surface carbon layer of both samples are



FIGURE 1: SEM images of the hydrothermally synthesized LiMnPO<sub>4</sub>/C. (a) Non-milled and (b) milled samples.



FIGURE 2: XRD patterns of the hydrothermally synthesized  $LiMnPO_4/C$ . (a) Non-milled and (b) milled samples.



FIGURE 3: Raman spectra of the hydrothermally synthesized  $LiMnPO_4/C$ . (a) Non-milled and (b) milled samples.

considered to be same. TG analysis was performed to estimate surface carbon amount. Estimated carbon amounts of nonmilled and milled samples were 3.4 and 2.2 wt%, respectively. It seems that some carbon coatings were destroyed and peeled off during the ball milling.

The charge/discharge test of non-milled and milled  $LiMnPO_4/C$  was carried out (Figure 4). In both cases, charge

and discharge plateaus at around 4.1 V versus Li/Li<sup>+</sup>, which are attributed to intrinsic redox of LiMnPO<sub>4</sub>, were observed. In non-milled LiMnPO<sub>4</sub>, the plateau was much shorter than milled sample and the discharge capacity was  $109 \text{ mA h g}^{-1}$ . This was 64% of theoretical one (171 mA h  $g^{-1}$ ) [20]. In milled LiMnPO<sub>4</sub>/C, a potential difference of the plateau between charge and discharge curves was small owing to small internal resistance of the milled LiMnPO<sub>4</sub>/C electrode. The discharge capacity improved, 145 mA h  $g^{-1}$ , 85% of theoretical capacity. A rate capability test also revealed favorable performance of milled sample (Figure 5). In this experiment, the charge process was performed at constant current condition of 0.1 C. The discharge capacities of milled and non-milled samples at 0.1 C were 127 and 98 mA h  $g^{-1}$ , respectively. Then, the capacity of non-milled sample decreased more quickly, only  $6\,\mathrm{mA}\,\mathrm{h}\,\mathrm{g}^{-1}$  at 5.0 C. On the other hand, the milled sample still maintained high capacity,  $64 \text{ mA h g}^{-1}$  at same C rate. This corresponded to 50% of capacity retention.

### 4. Discussion

In this study, we applied the ball milling to hydrothermally synthesized LiMnPO<sub>4</sub>/C and its electrochemical property was compared with non-milled LiMnPO<sub>4</sub>/C. By the ball milling, small particle of LiMnPO<sub>4</sub>/C was obtained, although a little loss of surface carbon layer was confirmed. The ballmilled LiMnPO<sub>4</sub>/C demonstrated larger discharge capacity than non-milled LiMnPO<sub>4</sub>/C. Fey et al. studied on a dependency of discharge capacity on surface carbon amount of LiFePO<sub>4</sub> [21]. They reported the discharge capacities of LiFePO<sub>4</sub>/C with coated carbon from 1.0 to 6.0 wt% were almost identical. In this study, carbon amounts of nonmilled and milled samples were 3.4 and 2.2 wt.%, respectively. Consequently, it can be said that the carbon layer on the LiMnPO<sub>4</sub> particle surface was destroyed a little by the ball milling; however, the deconstruction would hardly influence on electrochemical property. The difference of cathodic performance between non-milled and milled samples seems to be attributed to difference in length of Li ion transport paths by diverse particle size. Also, it is fairly well known that the charged LiMn<sup>II</sup> PO<sub>4</sub> phase undergoes a severe lattice



FIGURE 4: Charge and discharge curves of the hydrothermally synthesized  $LiMnPO_4/C$ . (a) Non-milled and (b) milled samples.



FIGURE 5: Rate capabilities of the hydrothermally synthesized  $LiMnPO_4/C$ . (a) Milled and (b) Non-milled samples.

deformation due to the asymmetric electronic configuration of  $Mn^{3+}$  ions  $(3d^4(t_{2g}^{3}e_{g}^{1}))$  [22, 23]. The Jahn-Teller deformation as well as the large lattice misfit between LiMnPO<sub>4</sub> and MnPO<sub>4</sub> phases destroys the integrity of lattice, thus leading to a low electrochemical activity. The small size of LiMnPO<sub>4</sub> enhances structural flexibility against lattice deformation [24]. Thus, improvement of integrity of the lattice by structural flexibility of small particles would be also another reason for superior performance of the milled sample. Moreover, the surface area of electrode increased with reduction of LiMnPO<sub>4</sub> particle size as indicated by BET surface area measurement, leading to large contact area between electrolyte and electrode. This enlargement of electrode area would also help improved performance of milled sample.

The reduction of LiMnPO<sub>4</sub>/C particle size by the ballmilling was achieved and improved performance of ballmilled LiMnPO<sub>4</sub>/C was confirmed. This is attributed to short Li ion diffusion paths, improvement of structure flexibility, and large surface area of electrode by reduction of LiMnPO<sub>4</sub>/C particle size. The ball milling is attested to be a promising method to improve cathodic performance of carbon-coated LiMnPO<sub>4</sub>.

#### **5.** Conclusion

The ball milling was applied to hydrothermally synthesized  $\text{LiMnPO}_4/\text{C}$ . The  $\text{LiMnPO}_4/\text{C}$  particle size was successfully reduced by the ball milling. Although a little loss of surface carbon layer by the ball milling was observed, this loss did not influence on electrochemical properties. The ball-milled  $\text{LiMnPO}_4/\text{C}$  demonstrated higher cathodic performance than non-milled sample. This would be attributed to short Li ion diffusion paths, improvement of structure flexibility, and large surface area provided by reduction of  $\text{LiMnPO}_4/\text{C}$  particle size. The ball milling is proven to be a promising method to improve cathodic performance of carbon-coated  $\text{LiMnPO}_4$ .

#### References

- Y. Mizuno, M. Kotobuki, H. Munakata, and K. Kanamura, "Effect of carbon source on electrochemical performance of carbon coated LiMnPO<sub>4</sub> cathode," *Journal of the Ceramic Society of Japan*, vol. 117, no. 1371, pp. 1225–1228, 2009.
- [2] H. Fang, L. Li, and G. Li, "Hydrothermal synthesis of electrochemically active LiMnPO<sub>4</sub>," *Chemistry Letters*, vol. 36, no. 3, pp. 436–437, 2007.
- [3] C. Delacourt, L. Laffont, R. Bouchet et al., "Toward understanding of electrical limitations (electronic, ionic) in LiMPO<sub>4</sub> (M = Fe, Mn) electrode materials," *Journal of the Electrochemical Society*, vol. 152, no. 5, pp. A913–A921, 2005.
- [4] M. Yonemura, A. Yamada, Y. Takei, N. Sonoyama, and R. Kanno, "Comparative kinetic study of olivine LixMPO<sub>4</sub> (M = Fe, Mn)," *Journal of the Electrochemical Society*, vol. 151, no. 9, pp. A1352–A1356, 2004.
- [5] Z. Chen and J. R. Dahn, "Reducing carbon in LiFePO<sub>4</sub>/C composite electrodes to maximize specific energy, volumetric energy, and tap density," *Journal of the Electrochemical Society*, vol. 149, no. 9, pp. A1184–A1189, 2002.
- [6] R. Dominko, M. Bele, M. Gaberscek et al., "Impact of the carbon coating thickness on the electrochemical performance of LiFePO<sub>4</sub>/C composites," *Journal of the Electrochemical Society*, vol. 152, no. 3, pp. A607–A610, 2005.
- [7] J. Moskon, R. Dominko, R. Cerc-Korosec, M. Gaberscek, and J. Jamnik, "Morphology and electrical properties of conductive carbon coatings for cathode materials," *Journal of Power Sources*, vol. 174, no. 2, pp. 683–688, 2007.
- [8] H. Nakano, K. Dokko, S. Koizumi, H. Tannai, and K. Kanamura, "Hydrothermal synthesis of carbon-coated LiFePO<sub>4</sub> and its application to lithium polymer battery," *Journal of the Electrochemical Society*, vol. 155, no. 12, pp. A909–A914, 2008.
- [9] C. Delacourt, P. Poizot, M. Morcrette, J. M. Tarascon, and C. Masquelier, "One-step low-temperature route for the preparation of electrochemically active LiMnPO<sub>4</sub> powders," *Chemistry* of Materials, vol. 16, no. 1, pp. 93–99, 2004.
- [10] T. Drezen, N. H. Kwon, P. Bowen, I. Teerlinck, M. Isono, and I. Exnar, "Effect of particle size on LiMnPO<sub>4</sub> cathodes," *Journal of Power Sources*, vol. 174, no. 2, pp. 949–953, 2007.
- [11] S. K. Martha, B. Markovsky, J. Grinblat et al., "LiMnPO<sub>4</sub> as an advanced cathode material for rechargeable lithium batteries," *Journal of the Electrochemical Society*, vol. 156, no. 7, pp. A541– A552, 2009.
- [12] M. E. Rabanal, M. C. Gutierrez, F. Garcia-Alvarado, E. C. Gonzalo, and M. E. Arroyo-de Dompablo, "Improved electrode

characteristics of olivine-LiCoPO<sub>4</sub> processed by high energy milling," *Journal of Power Sources*, vol. 160, no. 1, pp. 523–528, 2006.

- [13] H. Nakano, K. Dokko, S. Koizumi, H. Tannai, and K. Kanamura, "Hydrothermal synthesis of carbon-coated LiFePO<sub>4</sub> and its application to lithium polymer battery," *Journal of the Electrochemical Society*, vol. 155, no. 12, pp. A909–A914, 2008.
- [14] M. Kotobuki, Y. Mizuno, H. Munakata, and K. Kanamura, "Electrochemical properies of hydrothermally synthesized LiCopO<sub>4</sub> as a high voltage cathode material for lithium secondary battery," *Phosphorus Research Bulletin*, vol. 24, pp. 12–15, 2010.
- [15] K. Dokko, K. Shiraishi, and K. Kanamura, "Identification of surface impurities on LiFePO<sub>4</sub> particles prepared by a hydrothermal process," *Journal of the Electrochemical Society*, vol. 152, no. 11, pp. A2199–A2202, 2005.
- [16] K. Dokko, S. Koizumi, and K. Kanamura, "Electrochemical reactivity of LiFePO<sub>4</sub> prepared by hydrothermal method," *Chemistry Letters*, vol. 35, no. 3, pp. 338–339, 2006.
- [17] K. Dokko, S. Koizumi, K. Sharaishi, and K. Kanamura, "Electrochemical properties of LiFePO<sub>4</sub> prepared via hydrothermal route," *Journal of Power Sources*, vol. 165, no. 2, pp. 656–659, 2007.
- [18] A. Ait Salah, A. Mauger, K. Zaghib et al., "Reduction Fe<sup>3+</sup> of impurities in LiFePO<sub>4</sub> from pyrolysis of organic precursor used for carbon deposition," *Journal of the Electrochemical Society*, vol. 153, no. 9, pp. A1692–A1701, 2006.
- [19] R. L. McCreery, "Carbon electrodes: structural effects on electron transfer kinetics," in *Electroanalytical Chemistry*, A. J. Bard, Ed., vol. 17, Marcel Dekker, New York, NY, USA, 1991.
- [20] W. F. Howard and R. M. Spotnitz, "Theoretical evaluation of high-energy lithium metal phosphate cathode materials in Liion batteries," *Journal of Power Sources*, vol. 165, no. 2, pp. 887– 891, 2007.
- [21] G. T. K. Fey, Y. G. Chen, and H. M. Kao, "Electrochemical properties of LiFePO<sub>4</sub> prepared via ball-milling," *Journal of Power Sources*, vol. 189, no. 1, pp. 169–178, 2009.
- [22] Y. G. Xia, Q. Zhang, H. Y. Wang, H. Nakamura, H. Noguchi, and M. Yoshio, "Improved cycling performance of oxygenstoichiometric spinel Li<sub>1+x</sub>Al<sub>y</sub>Mn<sub>2-x-y</sub>O<sub>4+δ</sub> at elevated temperature," *Electrochimica Acta*, vol. 52, no. 14, pp. 4708–4714, 2007.
- [23] G. Amatuci and J. M. Tarascon, "Optimization of insertion compounds such as LiMn<sub>2</sub>O<sub>4</sub> for Li-Ion batteries," *Journal of The Electrochemical Society*, vol. 149, no. 12, pp. K31–K46, 2002.
- [24] Y. G. Guo, J. S. Hu, and L. J. Wan, "Nanostructured materials for electrochemical energy conversion and storage devices nanostructured materials for electrochemical energy conversion and storage devices," *Advanced Materials*, vol. 20, no. 15, pp. 2878– 2887, 2008.



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