Oxidation State of Manganese in $LiMn_2O_4$ Powders and its Effect on Electrochemcal Properties

Seon Hye Kim[1, a], Kook Jae Lee[1,b], Kwang Bo Shim[1,c] and Chang Sam Kim[2,d]

[1]Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Korea
[2]Battery Research Center, KIST, Seoul 130-650, Korea
[a]hye@kist.re.kr, [b]lkj6420@hanmail.net, [c]kbshim@hanyang.ac.kr, [d]cskim@kist.re.kr

Abstract

$LiMn_2O_4$ powders for lithium ion batteries were synthesized from two separate raw material pairs of LiOH/MnO and LiOH/MnO_2. The powders prepared at 780 and 850 ℃ and their difference of electrochemical properties were investigated. Both powders calcined at 780 and 850 ℃ were composed of a single-phase spinel structure but those treated at 850 ℃ showed a lower intensity ratio of I_{311} to I_{400}, a slightly larger lattice parameter, and an increased discharge capacity by 10% under 3.0~4.3V voltage range. The XPS study on the oxidation states of manganese repealed that powders made from LiOH/MnO had less Mn^{3+} ion and gave better battery performances than those from LiOH/MnO_2.

Keywords : Lithium ion battery, Cathode, Manganese spinel, Oxidation state, capacity

1. Introduction

Spinel lithium manganese oxide, $LiMn_2O_4$, is one of the candidate cathode materials for large-scale lithium-ion batteries due to its high thermal stability, low cost and less toxicity compared to $LiCoO_2$ [1]. However, $LiMn_2O_4$ has poor rate capability and shows faster capacity fading at elevated temperature, which is closely related with powder morphology, crystal stability and oxidation state of manganese [2].

Jahn-Teller distortion has been known as a cause of capacity fading of the spinel. It occurs when the average oxidation state of Mn in the spinel becomes less than 3.5. Therefore, it is desirable and important to make the oxidation state of Mn higher than 3.5 during powder preparation processes. In this study, we synthesized $LiMn_2O_4$ powders through solid state reaction using two different manganese sources, MnO and MnO_2, and analyzed the relation between powder properties and electrochemical properties. SEM and XRD were used to analyze the powder morphology and crystal structure. The discharge capacity and cycle stability were measured to estimate the electrochemical properties.

2. Experimental and Results

The composition of prepared powders is $Li_{1.1}Al_{0.095}Mn_{1.805}O_4$. $LiOH{\cdot}H_2O$ (98%, Aldrich, USA), Θ-Al_2O_3(99%), MnO (99%, Aldrich, USA), and MnO_2(≥90%, Aldrich, USA) were used as starting materials. MnO and MnO_2 were used as Mn source, whose experimental ratios are given in Table 1. Li and Mn sources were wet ball-milled for 24 hours and then dried using a rotary evaporator followed by heat treatments at 780 and 850℃ for 20 hours. The powders were characterized using XRD, SEM and XPS. Galvanostatic charge/discharge cycling was performed using 2032-type coin cells (Hohsen Co. Ltd., Japan). The charge–discharge characteristics of the cells were galvanostatically tested by means of a battery cycler (Won A Tech., WBC 3000) in a voltage ranges of 3.0–4.3 V at C/2.

Table 1. Mixing ratio of MnO to MnO_2

Sample	Ratio MnO	MnO_2
A	0	1
B	0.25	0.75
C	0.5	0.5
D	0.75	0.25
E	1	0

Fig. 1 shows XRD patterns of prepared spinel powders. All the samples have a single-phase spinel structure. Powder prepared at 850℃ shows sharper peaks with narrow full width at half maximum (FWHM) comparing to powders prepared at 780℃, which means the powder calcined at 850℃ has better crystalinity than that calcined at 780℃. It was suggested that the intensity ratio of I_{311} to I_{400} is an important factor to predict the electrochemical performance of this cathode materials. Poor electrochemical properties had been reported in samples with the ratio larger than unit[3]. The ratio of 850℃ sample is 0.90, while that of A780, C780 and E780 are 0.96, 1.01 and 1.10, respectively. Therefore a good electrochemical preoperties were expected in 850℃ sample.

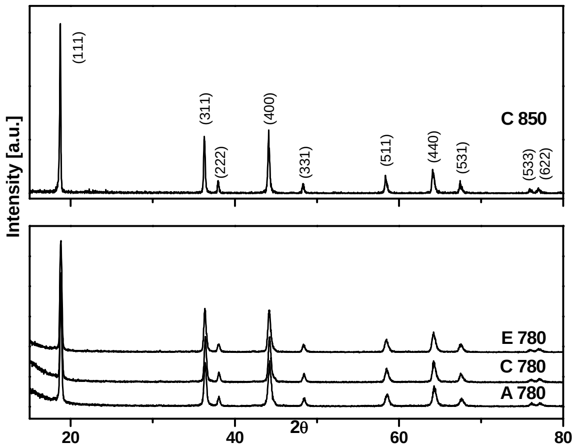
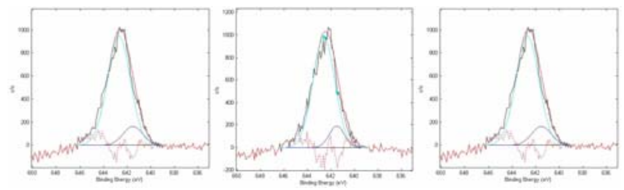


Fig. 1. XRD patterns of samples A, C and E calcined at 780 and 850℃.

Fig. 2 illustrates Mn XPS core spectra for samples A, C and E each calcined at 780℃. The major peak centered at 642.6 eV corresponds to Mn^{4+} and the secondary one at 641.5 eV matches Mn^{3+} in the samples. Considering the average oxidation state of Mn in $LiMn_2O_4$ is 3.5, the peaks of Mn^{4+} in all samples are too high compared to those of Mn^{3+}. There is, however, a significant difference in the peak height among the samples; the sample A shows a relatively high Mn^{3+} peaks comparing to the others. As mentioned previously, Mn^{3+} causes the Jahn-Teller distortion in this compound, which would resulted in inferior electrochemical properties in the sample A.



A C E

Fig. 2. XPS spectra of Mn ($2P_{3/2}$) in samples A, C, and E calcined at 780℃ in air.

Fig. 3 shows the changes of discharge capacity with cycling number in a field voltage range of 3.0~4.3 V at C/2 rate. As expected, the sample A calcined at 780℃ shows the lowest discharge capacity of 84 mAh/g and the sample D made from higher MnO ratio and calcined at 850℃ shows the highest discharge capacity of 97 mAh/g and a good capacity retention of 95% after 130 cycles at room temperature.

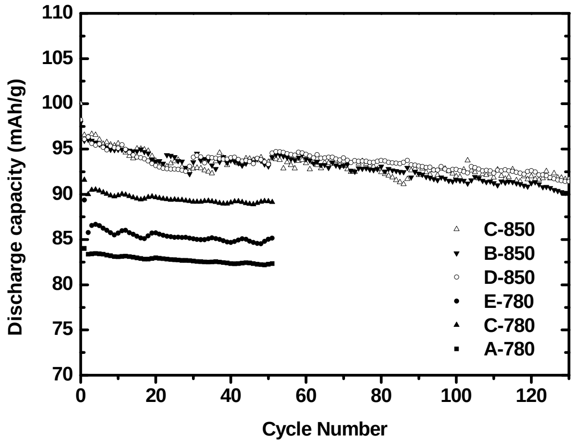


Fig. 3. Discharge capacity as a function of cycle number at C/2 in 3.0~4.3 V.

3. Summary

$LiMn_2O_4$ for lithium ion batteries was synthesized from mixtures of LiOH/MnO and LiOH/MnO_2. All powders calcinated both at 780 and 850℃ consisted of a single spinel structure. But the powders made at 850℃ showed sharper peaks with narrow FWHM, lower intensity ratio of I_{311} to I_{400}, and the increasing discharge capacity of ~10% in a voltage range of 3.0~4.3 V than 780℃. The oxidation states of Mn at the powders were investigated with XPS and Mn^{3+} ions were found to exist less in case of MnO. The samples made from MnO/MnO_2 ratio of 0.75 and calcined at 850℃ gave the highest capacity of 97 mAh/g and good capacity retention of 95% after 130 cycles at room temperature. Therefore, the powders made from LiOH/MnO were thought to be more appropriate for cathode of lithium ion batteries than from LiOH/MnO_2.

4. References

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