Synthesis of Li$_2$Mn$_3$O$_7$ and Application to Hybrid Capacitor

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ABSTRACT:
In order to apply hybrid capacitor, Li$_2$Mn$_3$O$_7$ was synthesized by combustion method using LiNO$_3$, Li(CH$_3$COO)·2H$_2$O and Mn(CH$_3$COO)$_2$·4H$_2$O. Spinel pattern was identified the samples calcined over 400°C in XRD. Intensity of Mn$_2$O$_3$ peak increased as the calcination temperature increased. To decide n/p ratio and to investigate electrochemical properties, charge-discharge tests of Li/Li$_2$Mn$_3$O$_7$ and Li/AC half-cell were carried out. Applying to AC/Li$_2$Mn$_3$O$_7$ hybrid capacitor, it had high discharge capacitance of 32.8 F/cc at 100 mA/g.

Keywords: Li$_2$Mn$_3$O$_7$, Hybrid capacitor, Decomposition, Discharge capacitance

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1. Introduction
For the purpose of higher energy density, easier synthesis of electrode material, less toxic of starting material and lower price, many researchers has been studied hybrid capacitor using Li$_4$Mn$_5$O$_{12}$ which reported high specific discharge capacitance, good electrochemical properties,$^{1-5}$ Li$_4$Mn$_5$O$_{12}$ and Li$_2$Mn$_3$O$_7$ which are lithia-stabilized system have the same as spinel structure.$^6$ Also, manganese oxidation number of Li$_4$Mn$_5$O$_{12}$ and Li$_2$Mn$_3$O$_7$ is the same as +4. So, they had been known as no capacity in 4 V region since manganese is not able to oxidize from +4 to +5. However, some researchers$^{7,8}$ reported that Li$_4$Mn$_5$O$_{12}$ showed low capacity in 4 V region since manganese in Li$_4$Mn$_5$O$_{12}$ was not fully oxidized to +4. Moreover, our previous study reported that Li$_4$Mn$_5$O$_{12}$ showed low capacity in 4 V region and AC/Li$_4$Mn$_5$O$_{12}$ capacitor showed good energy density.$^9$ It had been also known that Li$_4$Mn$_5$O$_{12}$ and Li$_2$Mn$_3$O$_7$ were synthesized about 400°C for 1~3 days.$^9$ But, it was reported that Li$_4$Mn$_5$O$_{12}$ synthesized at 400°C for a few hours.$^3$ Therefore, we expect that it is possible to synthesize at low temperature for short time as well as Li$_2$Mn$_3$O$_7$ is also possible to use cathode material in hybrid capacitor. Hence, hybrid capacitor using Li$_2$Mn$_3$O$_7$ has been studied, yet.

In this work, Li$_2$Mn$_3$O$_7$ was synthesized by combustion method at the various temperature and time. Deformation of structure was identified by XRD. Morphology of the samples was observed by SEM. Cell performance and cycle ability were investigated in non-aqueous electrolyte system.

2. Experimental
Li$_2$Mn$_3$O$_7$ was synthesized by combustion method using LiNO$_3$, Li(CH$_3$COO)·2H$_2$O and Mn(CH$_3$COO)$_2$·4H$_2$O. The molar ratios of Li/Mn and nitrate/acetates were 2 : 3 and 1 : 4, respectively. All materials were dissolved and stirred in deionized water, and then dried at about 80°C overnight. The dried mixture was combusted at 300°C for 30 min. Combusted material was calcined at various temperature (350, 400, 500, and 600°C) for various time (2, 5, and 10 h) in air.
Synthesized Li$_2$Mn$_3$O$_7$ samples were identified by X-ray diffraction (XRD) using CuKα radiation. In order to observe the morphology of the samples, scanning electron microscopy (SEM) was used.

Electrodes of Li$_2$Mn$_3$O$_7$ and AC were made by the slurry casting method. Slurry mixture of the Li$_2$Mn$_3$O$_7$ electrode consisted of the synthesized Li$_2$Mn$_3$O$_7$ (85 wt.%) as active material, super-p (10 wt.%) as conducting material and poly-vinylidene fluoride (PVDF, 5 wt.%) as binder. Slurry mixture of the carbon electrode consisted of A. C. (activated carbon : MSP 20, 85 wt.%) as active material, super-p (10 wt.%) as conducting material and carboxymethyl cellulose (CMC, 3 wt.%), styrene-butadiene rubber (SBR, 1 wt.%) and polytetrafluoroethylene (PTFE, 1 wt.%) as binder. The slurries were coated on etched Al-foil using Dr. blade and then dried at 80°C overnight.

Li/Li$_2$Mn$_3$O$_7$ and Li/AC half-cell tests were accomplished by 2032 coin cell. Li$_2$Mn$_3$O$_7$ and AC were used as positive material. Li-foil was used as negative material. LiPF$_6$ in PC and Celgard 3501 were prepared for electrolyte and separator, respectively.

AC/Li$_2$Mn$_3$O$_7$ full-cell hybrid capacitor test was accomplished by pouch type cell. Electrode area was 3 × 3 cm$^2$. Li$_2$Mn$_3$O$_7$ and AC were used as positive and negative material in full-cell, respectively. LiPF$_6$ in PC and Celgard 3501 were prepared for electrolyte and separator, respectively. All cells were fabricated in argon-filled glove box.

Charge-discharge tests of Li/Li$_2$Mn$_3$O$_7$ and Li/AC half-cell were performed at various current density in 3.7–4.4 V and 2–3 V, respectively. Applied current of Li/Li$_2$Mn$_3$O$_7$ half-cell was 11, 16, 30, 55, 100, 150 and 250 mA/g. Applied current of Li/AC half-cell was 10, 20, 50, 100, 200 and 400 mA/g.

Charge-discharge test of AC/Li$_2$Mn$_3$O$_7$ full-cell hybrid capacitor was carried out constant current (CC) - constant voltage (CV) charge and constant current discharge. Each step of charge-discharge test set rest time for 10 second. Applied current was 100, 300, 600, 900, and 1200 mA/g and operating window was 1–2.5 V.

3. Results and Discussion

Fig. 1 is the X-ray diffraction patterns of Li$_2$Mn$_3$O$_7$ calcined at 350, 400, 500, and 600°C for 5 h and (b) calcined at 400°C for 2, 5, and 10 h. (dash lines : Mn$_2$O$_3$)
5 h had higher lattice constant than other calcined samples. Lattice constants of LiMn$_2$O$_4$ and Li$_2$Mn$_3$O$_7$ were $a = 8.247$ Å (JCPDS card no.: 35-0782) and $a = 8.160$ Å (JCPDS card no.: 83-0321), respectively. Compared to the lattice constant of LiMn$_2$O$_4$, the lattice constant of the sample calcined at 600°C for 5 h was only similar. The others were similar lattice constant compared to the lattice constant of LiMn$_2$O$_4$. Therefore, it is considered that molecular formula of Li$_2$Mn$_3$O$_7$ calcined at 600°C for 5 h would be changed. In the XRD pattern of Li$_2$Mn$_3$O$_7$ calcined at 600°C for 5 h, the integrated intensity ratio between I$_{111}$ of the highest spinel peak and I$_{222}$ of highest Mn$_2$O$_3$ (about $2\theta = 32.8°$) peak was about 9 : 1. So, decomposition process of Li$_2$Mn$_3$O$_7$ calcined at 600°C for 5 h was considered as below,

$$7\text{Li}_2\text{Mn}_3\text{O}_7 \rightarrow 9\text{LiMn}_2\text{O}_4 + \text{Mn}_2\text{O}_3 + 5\text{Li} + 5\text{O}_2 \quad (1)$$

Fig. 3 is SEM picture of Li$_2$Mn$_3$O$_7$ calcined at 400, 500, and 600°C for 2, 5, and 10 h. In the case of the sample calcined at 400°C for 5 h, particle size was about 1 µm. It was larger particle size compared to Li$_4$Mn$_5$O$_{12}$. All samples showing spinel pattern observed a square shape. However, the shape of the sample calcined at 350°C for 5 h looked like sea urchin. It was observed that particles were larger as the calcined temperature and time increased.

Fig. 4 is the rate capability of Li$_2$Mn$_3$O$_7$ calcined at 400, 500, and 600°C for 2, 5, and 10 h. Discharge capacity of the sample calcined at 500°C for 5 h was higher than other calcined samples at 10 mA/g. But, at higher current density, discharge capacity of the sample calcined at 500°C for 5 h was lower than of the sample calcined at 400°C for 5 h. When the calcined temperature fixed at 400°C and the calcined time changed, the sample calcined for 5 h showed better discharge capacity and rate capability than other calcined samples. So, calcined temperature and time of Li$_2$Mn$_3$O$_7$ determined 400°C and 5 h, respectively.

Charge-discharge curves at different current density of Li$_2$Mn$_3$O$_7$ calcined at 400°C for 5 h were showed in Fig. 5. Compared to Li$_4$Mn$_5$O$_{12}$, the shape of charge-discharge curves was similar. However, these curves were more distinctly observed to two plateau than Li$_4$Mn$_5$O$_{12}$. Discharge capacity of Li$_2$Mn$_3$O$_7$ at low current density was higher than Li$_4$Mn$_5$O$_{12}$.
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Fig. 6 is $dQ/dV$ vs. $V$ curve of the sample calcined at 400°C for 5 h. The peak voltage was observed around 4 and 4.15 V. The values of peak voltage and the shape of the curve resembled LiMn$_2$O$_4$. Thackeray et al. suggested that Li$_2$Mn$_3$O$_7$ could be rewritten to spinel notation like Li$_{0.83}$[Mn$_{1.74}$Li$_{0.26}$]O$_4$ (or Li$_{1.11}$Mn$_{2.32}$O$_4$). This notation was similar to lithium rich spinel such as Li$_{1+x}$Mn$_{2-x}$O$_4$. So, it is considered when Li$_2$Mn$_3$O$_7$ cycled in 4 V range, values of peak voltage and shape of the curve looked like LiMn$_2$O$_4$.

In order to decide the n/p ratio, half-cell test of AC carried out, and the result showed in Fig. 7. All curves seemed to be linear shape. In Fig. 5, discharge capacity at 100 mA/g was 48.53 mAh/g. And, in Fig. 7, charge capacity at 100 mA/g of AC was 23.28 mAh/g. So, the mass ratio between Li$_2$Mn$_3$O$_7$ calcined at 400°C for 5 h and AC decided to 1 : 2.08. AC/Li$_2$Mn$_3$O$_7$ full cell fabricated by the decided mass ratio, and then charge-discharge test performed.

Fig. 8 is discharge curves of AC/Li$_2$Mn$_3$O$_7$ hybrid capacitor at various current density in 1–2.5 V. Discharge curves showed nearly linear at low current density, although non-linear discharge shape was...
observed at higher current density. By using the data in Fig. 8, volumetric discharge capacitance was calculated, and the result showed in Fig. 9. The equation as below:

\[ C = \frac{\Delta t \times I}{\Delta V \times A} \]  

(2)

where \( C \) is volumetric discharge capacitance, \( \Delta t \) is discharge time, \( I \) is applied current, \( \Delta V \) is voltage difference and \( A \) is sum of total electrode volume.

AC/Li\textsubscript{2}Mn\textsubscript{3}O\textsubscript{7} hybrid capacitor had high discharge capacitance of 32.8 F/cc at 100 mA/g and it had good discharge capacitance of 14.1 F/cc at 1200 mA/g.

4. Conclusion

Li\textsubscript{2}Mn\textsubscript{3}O\textsubscript{7} was synthesized by combustion method using LiNO\textsubscript{2}, Li(CH\textsubscript{3}COO)\textsubscript{2}2H\textsubscript{2}O and Mn(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O. The samples calcined over 400°C showed spinel pattern. However, intensity of Mn\textsubscript{3}O\textsubscript{4} peak increased as the calcined temperature increased. It is considered that Li\textsubscript{2}Mn\textsubscript{3}O\textsubscript{7} suffered decomposition since oxidation number of manganese changed when temperature elevated. Decomposition process of the sample calcined 600°C 5 h described using direct comparison method. Through the SEM pictures, particle size was about 1 µm and it was larger compared to Li\textsubscript{4}Mn\textsubscript{5}O\textsubscript{12}. In half-cell test, discharge capacity of the sample calcined at 400°C for 5 h was not only good at 10 mA/g but also better rate capability than other calcined sample. In dQ/dV vs. V curve, values of peak voltage and shape of the curve were similar between Li\textsubscript{2}Mn\textsubscript{3}O\textsubscript{7} and LiMn\textsubscript{2}O\textsubscript{4}.

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References