



Synthesis of $\text{Li}_2\text{Mn}_3\text{O}_7$ and Application to Hybrid Capacitor

Hunuk Kim^{a,b}, Kyoung Hee Shin^b, Bum-Suk Lee^b, Myung Seok Jeon^b, Kyu-Nam Jung^b, Yang-Kook Sun^a and Chang Soo Jin^{b,†}

^aDepartment of Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

^bKorea Institute of Energy research, 71-2 Jang-Dong, Yuseong-gu, Daejeon 305-343, Korea

ABSTRACT :

In order to apply hybrid capacitor, $\text{Li}_2\text{Mn}_3\text{O}_7$ was synthesized by combustion method using LiNO_3 , $\text{Li}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. Spinel pattern was identified the samples calcined over 400°C in XRD. Intensity of Mn_2O_3 peak increased as the calcination temperature increased. To decide n/p ratio and to investigate electrochemical properties, charge-discharge tests of $\text{Li}/\text{Li}_2\text{Mn}_3\text{O}_7$ and Li/AC half-cell were carried out. Applying to $\text{AC}/\text{Li}_2\text{Mn}_3\text{O}_7$ hybrid capacitor, it had high discharge capacitance of 32.8 F/cc at 100 mA/g.

Keywords : $\text{Li}_2\text{Mn}_3\text{O}_7$, Hybrid capacitor, Decomposition, Discharge capacitance

Received December 13, 2010 : Accepted December 28, 2010

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 $\text{Li}_4\text{Mn}_5\text{O}_{12}$ which reported high specific discharge capacitance, good electrochemical properties.¹⁻⁵⁾ $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}_2\text{Mn}_3\text{O}_7$ which are lithia-stabilized system have the same as spinel structure.⁶⁾ Also, manganese oxidation number of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{Li}_4\text{Mn}_5\text{O}_{12}$ showed low capacity in 4 V region since manganese in $\text{Li}_4\text{Mn}_5\text{O}_{12}$ was not fully oxidized to +4. Moreover, our previous study reported that $\text{Li}_4\text{Mn}_5\text{O}_{12}$ was able to charge-discharge in 4 V region and $\text{AC}/\text{Li}_4\text{Mn}_5\text{O}_{12}$ capacitor showed good energy density.^{4,5)} It had been also known that $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}_2\text{Mn}_3\text{O}_7$ were synthesized about 400°C for 1~

3days.⁶⁾ But, it was reported that $\text{Li}_4\text{Mn}_5\text{O}_{12}$ synthesized at 400°C for a few hours.¹⁾ Therefore, we expect that it is possible to synthesize at low temperature for short time as well as $\text{Li}_2\text{Mn}_3\text{O}_7$ is also possible to use cathode material in hybrid capacitor. Hence, hybrid capacitor using $\text{Li}_2\text{Mn}_3\text{O}_7$ has been studied, yet.

In this work, $\text{Li}_2\text{Mn}_3\text{O}_7$ 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

$\text{Li}_2\text{Mn}_3\text{O}_7$ was synthesized by combustion method using LiNO_3 , $\text{Li}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. 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.

[†]Corresponding author. Tel.: +82-42-860-3271

E-mail address: csjin@kier.re.kr

Synthesized $\text{Li}_2\text{Mn}_3\text{O}_7$ samples were identified by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation. In order to observe the morphology of the samples, scanning electron microscopy (SEM) was used.

Electrodes of $\text{Li}_2\text{Mn}_3\text{O}_7$ and AC were made by the slurry casting method. Slurry mixture of the $\text{Li}_2\text{Mn}_3\text{O}_7$ electrode consisted of the synthesized $\text{Li}_2\text{Mn}_3\text{O}_7$ (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.

$\text{Li}/\text{Li}_2\text{Mn}_3\text{O}_7$ and Li/AC half-cell tests were accomplished by 2032 coin cell. $\text{Li}_2\text{Mn}_3\text{O}_7$ 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.

$\text{AC}/\text{Li}_2\text{Mn}_3\text{O}_7$ full-cell hybrid capacitor test was accomplished by pouch type cell. Electrode area was $3 \times 3 \text{ cm}^2$. $\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{Li}/\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{Li}/\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{AC}/\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 350, 400, 500, and 600°C for 2, 5, and 10 h. The samples calcined over 400°C showed spinel pattern. But the sample calcined at 350°C showed the

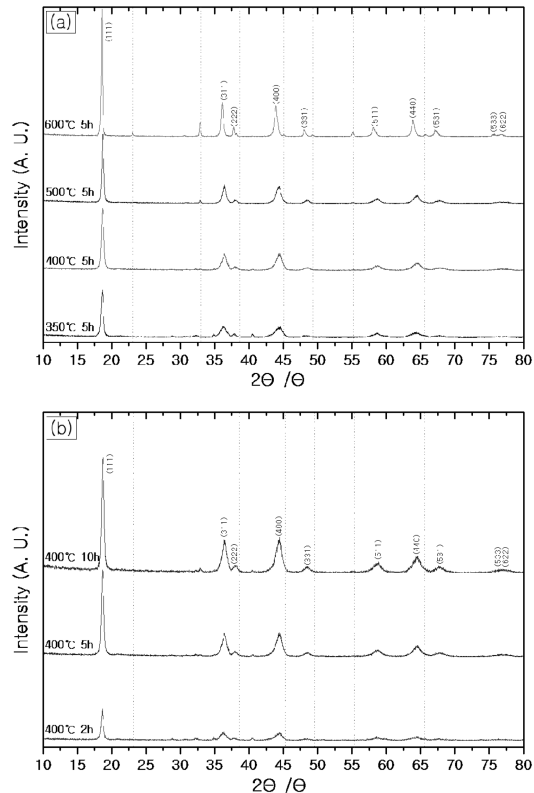


Fig. 1. X-ray diffraction patterns of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at (a) 350, 400, 500, and 600°C for 5 h and (b) calcined at 400°C for 2, 5, and 10 h. (dash lines : Mn_2O_3)

mixture pattern of $\text{Fd}3m$ and unknown. All peaks were broad which was considered to the low crystallinity resulted in the low calcined temperature and time. As the calcined temperature and time increased, peak intensity increased. Intensity of Mn_2O_3 peak also increased as the calcined temperature increased. Some researchers¹⁰⁻¹²⁾ reported that, due to the manganese reduction from tetravalent to trivalent, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ suffered decomposition as the calcined temperature increased. Ideal oxidation number of $\text{Li}_2\text{Mn}_3\text{O}_7$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ was +4. Moreover, Li and Mn ion array of $\text{Li}_2\text{Mn}_3\text{O}_7$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ were similar. Therefore, we suggest that $\text{Li}_2\text{Mn}_3\text{O}_7$ suffered decomposition in which manganese reduced from tetravalent to trivalent. Especially, in the case of the sample calcined at 600°C for 5 h, it was clearly observed that peaks shifted to low angle. In order to investigate the structural change, lattice constant was calculated and summarized in Fig. 2. In Fig. 2, the sample calcined at 600°C for

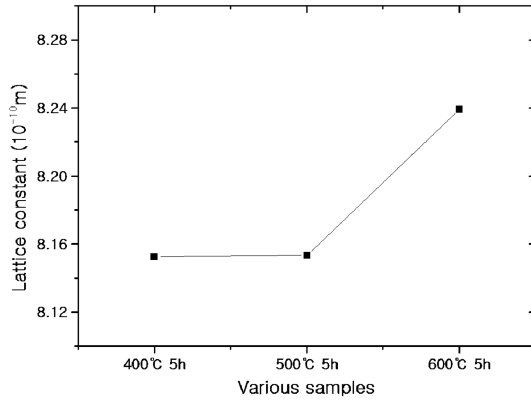


Fig. 2. Lattice constant change of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 400, 500, and 600°C for 5 h.

5 h had higher lattice constant than other calcined samples. Lattice constants of LiMn_2O_4 and $\text{Li}_2\text{Mn}_3\text{O}_7$ were $a = 8.247 \text{ \AA}$ (JCPDS card no. : 35-0782) and $a = 8.160 \text{ \AA}$ (JCPDS card no. : 83-0321), respectively. Compared to the lattice constant of LiMn_2O_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_2O_4 . Therefore, it is considered that molecular formula of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 600°C for 5 h would be changed. In the XRD pattern of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 600°C for 5 h, the intergrated intensity ratio between $I_{(111)}$ of the highest spinel peak and $I_{(222)}$ of highest Mn_2O_3 (about $2\theta = 32.8$) peak was about 9 : 1. So, decomposition process of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 600°C for 5 h was

considered as below,

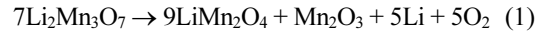


Fig. 3 is SEM picture of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 350, 400, and 500°C for 2, 5, and 10 h. In the case of the sample calcined at 400°C for 5 h, particle size was about $1 \mu\text{m}$. It was larger particle size compared to $\text{Li}_4\text{Mn}_5\text{O}_{12}$.^{7,8)} All samples 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 $\text{Li}_2\text{Mn}_3\text{O}_7$ 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 $\text{Li}_2\text{Mn}_3\text{O}_7$ determined 400°C and 5 h, respectively.

Charge-discharge curves at different current density of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 400°C for 5 h were showed in Fig. 5. Compared to $\text{Li}_4\text{Mn}_5\text{O}_{12}$, the shape of charge-discharge curves was similar. However, these curves were more distinctly observed to two plateau than $\text{Li}_4\text{Mn}_5\text{O}_{12}$. Discharge capacity of $\text{Li}_2\text{Mn}_3\text{O}_7$ at low current density was higher than $\text{Li}_4\text{Mn}_5\text{O}_{12}$.^{4,5)}

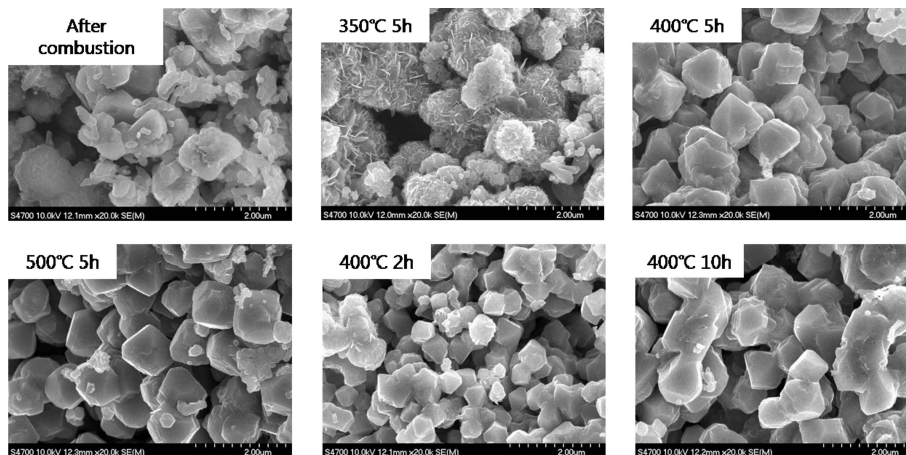


Fig. 3. SEM picture of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at various temperature for various time.

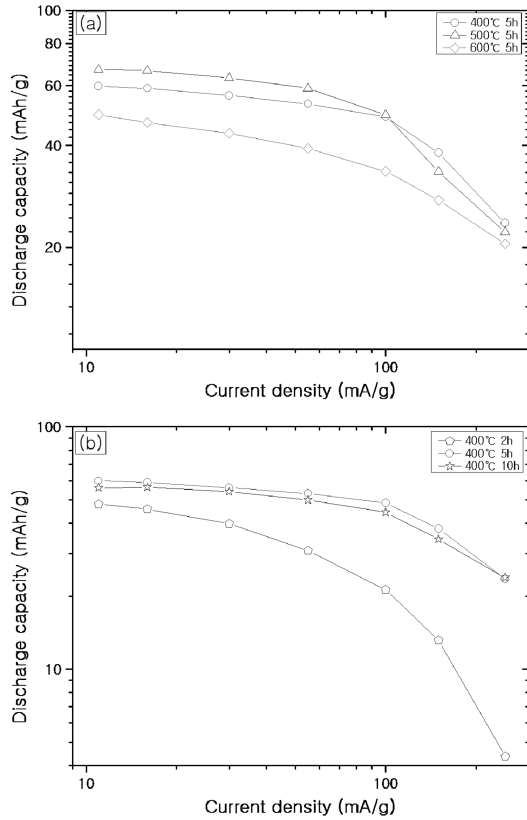


Fig. 4. Rate capability of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at (a) 400, 500, and 600°C for 5 h and (b) calcined at 400°C for 2, 5, and 10 h.

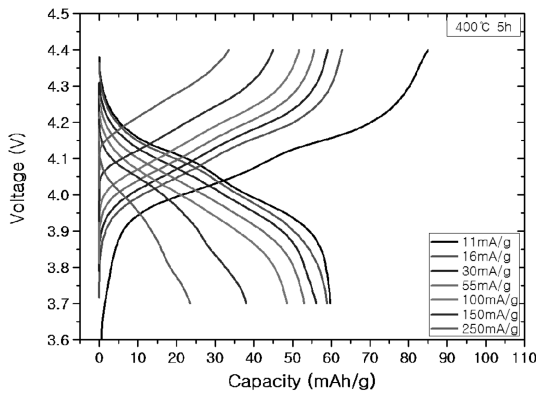


Fig. 5. Charge-discharge curves at different current density of $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 400°C for 5 h.

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_2O_4 . Thackeray et al.¹³⁾ suggested that $\text{Li}_2\text{Mn}_3\text{O}_7$ could be rewrite

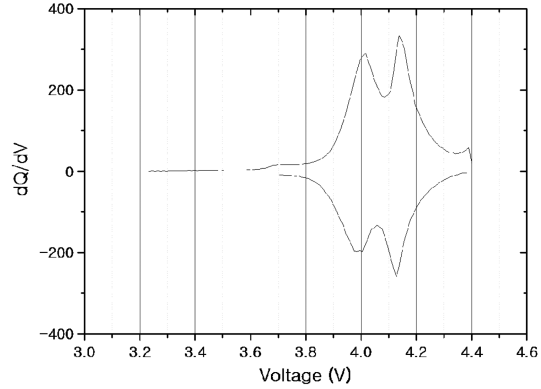


Fig. 6. dQ/dV vs. V curve of the sample calcined at 400°C for 5 h.

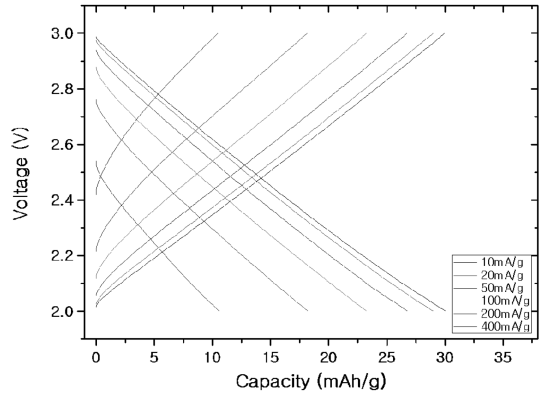


Fig. 7. Charge-discharge curves at different current density of AC.

to spinel notation like $\text{Li}_{0.85}[\text{Mn}_{1.74}\text{Li}_{0.26}]\text{O}_4$ (or $\text{Li}_{1.11}\text{Mn}_{1.74}\text{O}_4$). This notation was similar to lithium rich spinel such as $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$. So, it is considered when $\text{Li}_2\text{Mn}_3\text{O}_7$ cycled in 4 V range, values of peak voltage and shape of the curve looked like LiMn_2O_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 mA/g. So, the mass ratio between $\text{Li}_2\text{Mn}_3\text{O}_7$ calcined at 400°C for 5 h and AC decided to 1 : 2.08. AC/ $\text{Li}_2\text{Mn}_3\text{O}_7$ full cell fabricated by the decided mass ratio, and then charge-discharge test performed.

Fig. 8 is discharge curves of AC/ $\text{Li}_2\text{Mn}_3\text{O}_7$ 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

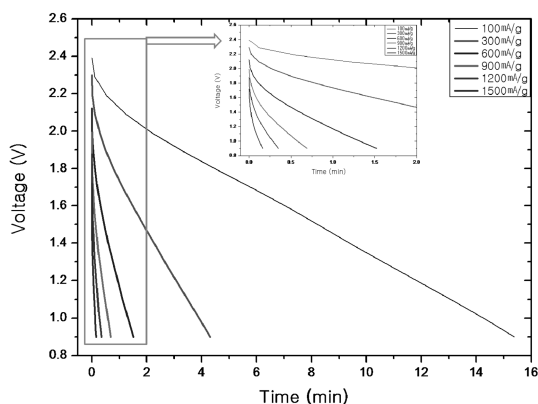


Fig. 8. Discharge curves of AC/Li₂Mn₃O₇ hybrid capacitor at various current density in 1~2.5 V.

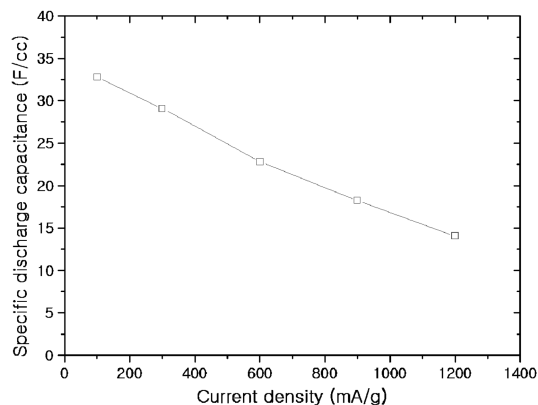


Fig. 9. Rate capability of AC/Li₂Mn₃O₇ hybrid capacitor.

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:

$$C = \frac{\Delta t \times I}{\Delta V \times A} \quad (2)$$

where C is volumetric discharge capacitance, Δt is discharge time, I is applied current, ΔV is voltage difference and A is sum of total electrode volume. AC/Li₂Mn₃O₇ 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

Li₂Mn₃O₇ was synthesized by combustion method

using LiNO₃, Li(CH₃COO)·2H₂O and Mn(CH₃COO)₂·4H₂O. The samples calcined over 400°C showed spinel pattern. However, intensity of Mn₂O₃ peak increased as the calcined temperature increased. It is considered that Li₂Mn₃O₇ 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 Li₄Mn₃O₁₂. 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 Li₂Mn₃O₇ and LiMn₂O₄. Applying to AC/Li₂Mn₃O₇ hybrid capacitor, discharge curves showed nearly linear at low current density. Volumetric discharge capacitance showed 32.8 F/cc at 100 mA/g and 14.1 F/cc at 1200 mA/g.

Acknowledgment

This work was supported by the Ministry of Knowledge Economy, Korea (2010T100100970).

References

1. Y.J. Hao, Y.Y. Wang, Q.Y. Lai, Y. Zhao, L.M. Chen and X.Y. Ji, *J. Solid State Electrochem.*, **13**, 905 (2009).
2. H.Y. Chu, Q.Y. Lai, Y.J. Hao, Y. Zhao and X.Y. Xu, *J. Appl. Electrochem.*, **39**, 2207 (2009).
3. Y. Zhao, X.Y. Xu, Q.Y. Lai, Y.J. Hao, L. Wang and Z. Lin, *J. Solid State Electrochem.*, **14**, 1509 (2010).
4. H.U. Kim, Y.-K. Sun, K.H. Shin and C.S. Jin, *Phys. Scr.*, **T139**, 014053 (2010).
5. H.U. Kim, Y.-K. Sun, B.-S. Lee, C.S. Jin and K.Y. Shin, *J. Kor. Electrochem. Soc.*, **13**, 103 (2010).
6. M.M. Thackeray, *Prog. Solid St. Chem.*, **25**, 1 (1997).
7. Y.J. Shin and A. Manthiram, *Electrochim. Acta*, **48**, 3583 (2003).
8. T. Takada, H. Hayakawa, E. Akiba, F. Izumi and B.C. Chakoumakos, *J. Power Sources*, **68**, 613 (1997).
9. J.P. Zheng, *J. Electrochemical Soc.*, **150**, A48 (2003).
10. T. Takada, H. Hayakawa and E. Akiba, *J. Solid State Chem.*, **115**, 420 (1995).
11. T. Takada, H. Hayakawa, T. Kumagai and E. Akiba, *J. Solid State Chem.*, **121**, 79 (1996).
12. M.M. Thackeray, M.F. Mansuetto and C.S. Johnson, *J. Solid State Chem.*, **125**, 274 (1996).
13. M.M. Thackeray, A de Kock and W.I.F. David, *Mater. Res. Bull.*, **28**, 1041 (1993).