Int. J. Electrochem. Sci., 6 **(2011)** 5462 - 5469

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communications

A Study on Improving Drying Performance of Spinel Type $LiMn_2O_4$ as a Cathode Material for Lithium Ion Battery

*Sung Yeon Kim and Sehun Rhee**

Department of Mechanical Engineering, Hanyang University, 17 Haengdang-Dong, Seoul, 133-791, Korea
*E-mail: srhee@hanyang.ac.kr

Received: 15 September 2011 / *Accepted:* 17 October 2011 / *Published:* 1 November 2011

Lithium ion battery is one of the popular power sources for electronic devices. Although various cathode materials have been studied for lithium ion battery, spinel type $LiMn_2O_4$ is more attractive than any other materials due to its low cost, low toxic and high rate. Recently, researches and developments on spinel type $LiMn_2O_4$ have been carried out to improve its electrochemical performance. In this work, especially drying process with respect to spinel type $LiMn_2O_4$ thin film electrode by using NIR drying process was investigated. NIR technology is expected to be used in roll-to-roll process for manufacturing lithium ion battery. NIR drying process, contrary to conventional drying process, furnace, was verified to be necessary less time and provide longer life cycle. It is estimated that the spinel type $LiMn_2O_4$ thin film electrode using NIR drying process can provide more path for lithium ions.

Keywords: Roll-to-Roll Process, Drying Process, NIR Technology, Spinel Type, Lithium Ion Battery

1. INTRODUCTION

1.1 Spinel Type $LiMn_2O_4$

Recently, lithium ion battery has been regarded as electrical energy storage, due to its high energy density and long life cycle [1,2]. Lithium ion battery uses lithium transition metal oxide as cathode material, such as $LiCoO_2$ [3,4], $LiNiO_2$ [5,6], a layered structure, and $LiMn_2O_4$ [7-9], a spinel structure. Among these cathode materials, spinel type $LiMn_2O_4$ is more attractive than any other materials due to its low cost, low toxic and high rate. In spite of many advantages, spinel type $LiMn_2O_4$ is not commercialized, because of its rapid loss of electrode capacity on cycling

1.2 Thin Film Electrode by Slot Die Roll-to-Roll Process

Due to high energy density, cathode materials of lithium ion battery can be used in thin film. Thin films of cathode materials are usually prepared by chemical vapor deposition [10,11], sputtering [12-14], e-beam evaporation [15-16], pulse laser deposition [17] and sol-gel method [18]. However these processes require high cost equipment. In order to commercialize the thin film electrode, the process preparing thin film must be simple and require low cost. Printing process using slot die roll-to-roll coating system [19] is expected to be fast and stable. Figure 1 shows a schematic of roll-to-roll process. The process is conducted while the substrate moves toward the winding roll from the unwinding roll. The first step is pumping the slurry of cathode material into the slot die. Then cathode material can be coated on the substrate (aluminum collector). The next step is drying the slurry coated electrode by drying system.

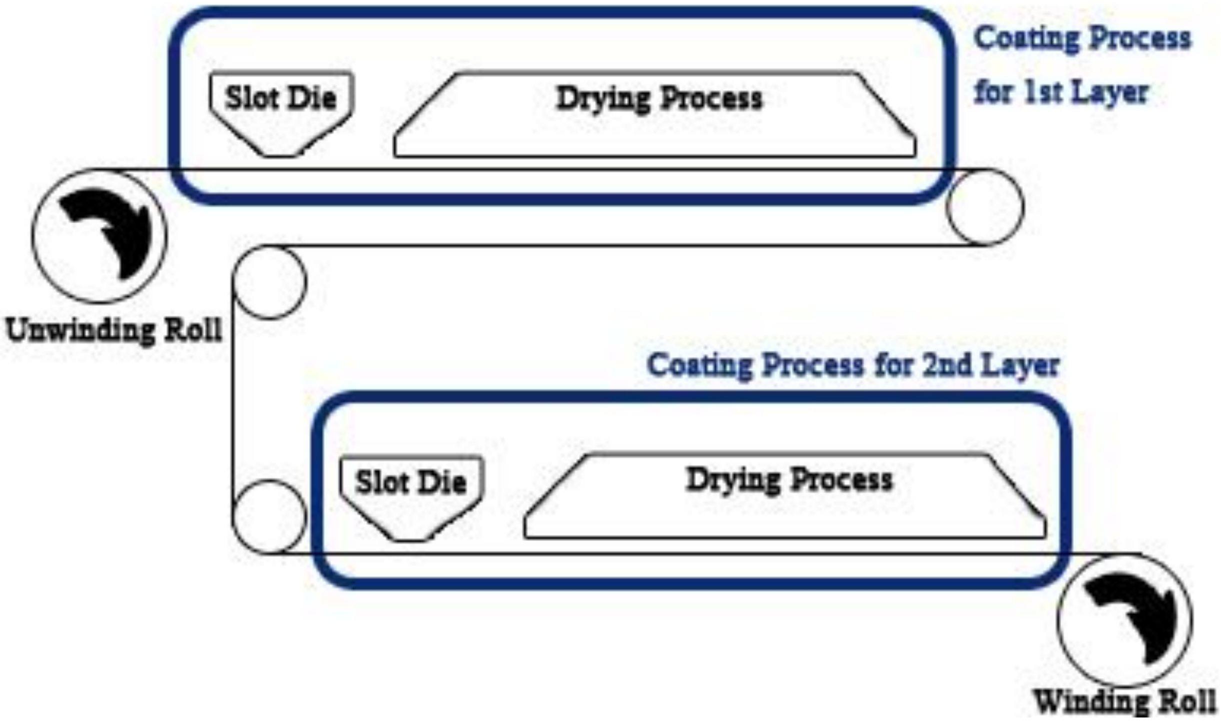
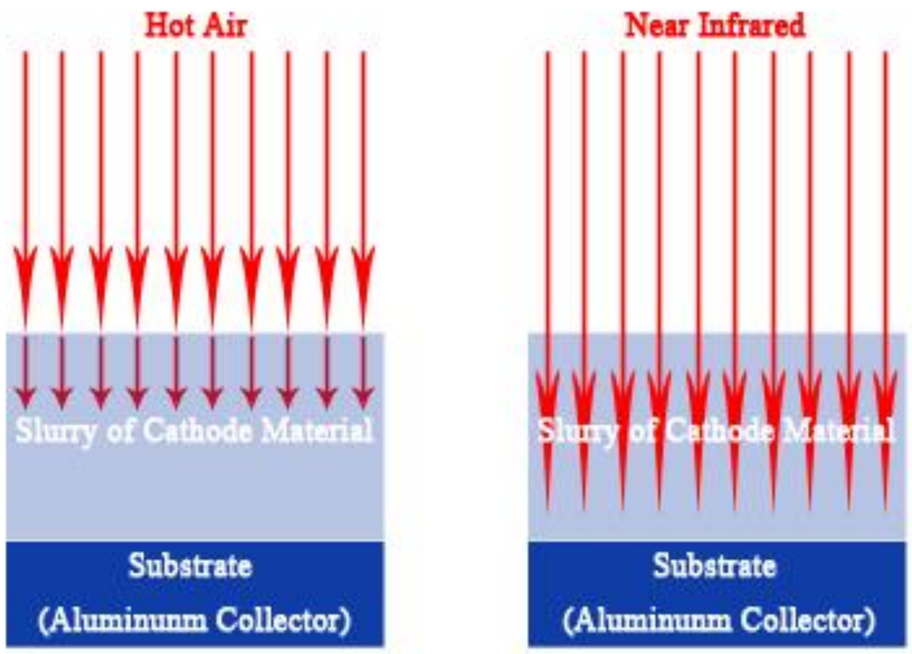


Figure 1. Schematic of Roll-to-Roll System with Drying Process

1.3 Near Infrared Drying Process

Drying process time is to be reduced because of its time consumption. Conventional and proposed drying systems are shown in Figure 2. Furnace, a conventional type of drying process, uses a hot air based on convection. Solvent is evaporated from the surface of substrate in furnace, and hence long drying time is necessary. It is not suitable for drying of roll-to-roll process. Contrary to conventional drying process, near infrared (NIR) drying process uses radiation by heating source with the wavelength of infrared region. The energy transfer by radiation is faster than convection, and NIR wave permeates into the slurry of cathode material and evaporates the entire area of solvent simultaneously. Therefore, drying is to be fast. And so, NIR drying process is expected to be an appropriate drying process for roll-to-roll process. In this work, drying performance of using NIR drying process has been conducted and analyzed the electrochemical performance of spinel type $LiMn_2O_4$.



(a) Furnace (b) Near Infrared

Figure 2. Heat Transfer Mechanisms

2. EXPERIMENTAL

The material used for anode was graphite coated thin film and the electrolyte used was 1.2 M $LiPF_6$ dissolved in a solution containing ethylene carbonate (EC) and ethyl-methyl carbonate (EMC) in a ratio of 3 to 7 by Techno Semichem, a company developing liquid electrolyte. The material used for cathode was aluminum doped spinel type $LiMn_2O_4$ by Phoenix PDE, a company developing cathode materials. Slurry of cathode material contains 85 wt. % of aluminum doped spinel type $LiMn_2O_4$, 3.75 wt. % of graphite, 3.75 wt. % of carbon and 7.5 wt. % of binder (PVDF) dissolved in NMP (N-Methly-2-Pyrrolide) solution.

$LiMn_2O_4$ slurry was coated on the aluminum collector by 150 μm with doctor blading. And the slurry coated electrode was dried in furnace and NIR drying systems. After drying process, thickness of the thin film electrode reduces to 100 μm, including thickness of aluminum collector, 20 μm. And then, by using roll press, the thin film electrodes are condensed. After pressing process, thickness of the thin film electrode reduces to 50 ㎛. Thin film electrodes were dried by 110℃ for 30 minutes with furnace. And also those were dried by heat flux 299.65 W/m^2, 674.22 W/m^2, 1030.05 W/m^2 and 1310.97 W/m^2 for 3 minutes for each, with NIR drying system. And the values of heat flux were determined by a specification of the equipment. Heat fluxes were measured with each level (Lv. 3, 4, 5 and 6) [20].

Charging and discharging was conducted for 100 cycles, with 0.1 C-rate for the first 2 cycles and 1 C-rate for the 100 cycles. Analysis of the phases of the thin film electrode was performed by XRD. And morphologies of the thin film were observed by SEM. And sheet resistances were also measured.

3. RESULTS AND DISCUSSION

3.1 Furnace and Near Infrared Drying Process

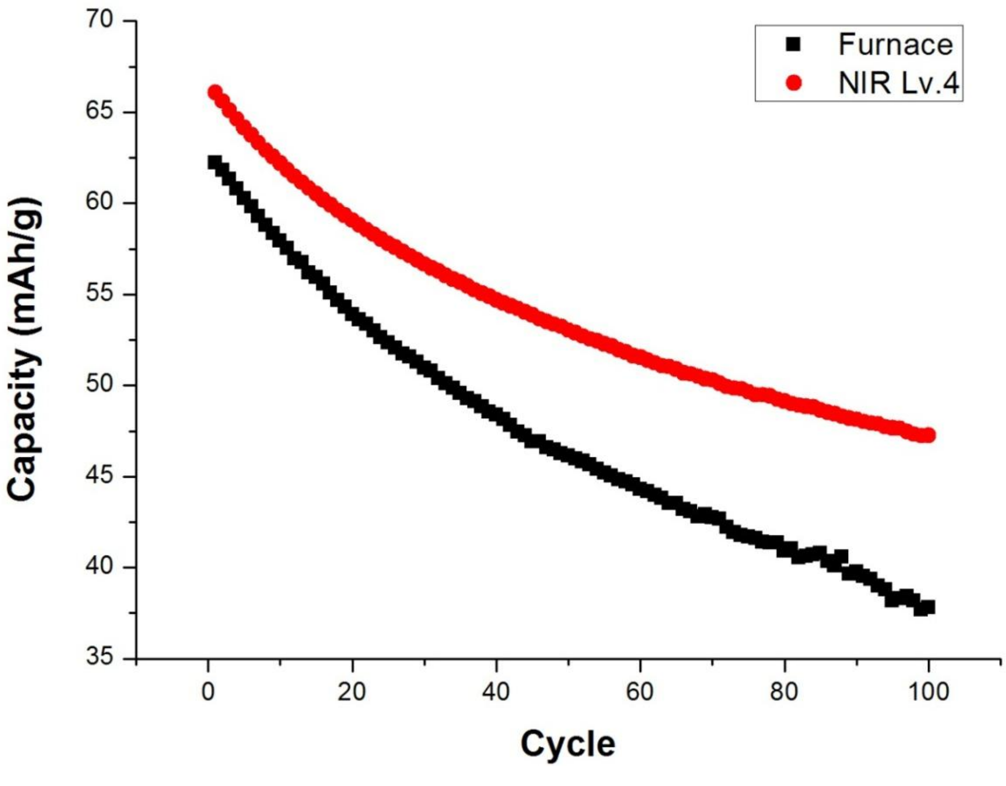


Figure 3. Life Cycles of Lithium Ion battery using Thin Film Electrode dried by Furnace and NIR

Since the drying mechanisms of furnace and NIR are different, as shown in Figure 2, the first experiment was conducted to verify the differences of electrochemical performance between the lithium ion batteries using thin film electrode dried by furnace with 110℃ for 30 minutes and NIR with heat flux 674.22 W/m^2 (LV. 4) for 3 minutes. NIR drying process uses a near infrared, which is the wave between the wavelength ranges of about 740 nm ~ 3000 nm. NIR drying process is based on radiation, which causes the vibration of the molecules by activating the molecules directly. It vibrates the molecules and generates heat and evaporates the solvent from the slurry of cathode material. And so, the rapid drying is possible by using NIR drying process.

Figure 3 indicates the result of the capacity of the lithium ion batteries made by thin film electrode dried by furnace and NIR. And the capacity and the percentage of the capacity loss of two different types are expressed numerically in Table 1. The most interesting result is that the capacity of the lithium ion battery is larger in case of lithium ion battery using thin film electrode dried by NIR. And after the 100 cycles of charging and discharging, 39.27% of the capacity of lithium ion battery using thin film electrode dried by furnace fades out, and 28.50% of the capacity fades out in case of NIR drying process. The fade out ratio of the capacity has been reduced by NIR drying process.

Table 1. Capacities of Lithium Ion Battery using Thin Film Electrode dried by Furnace and NIR

Drying type	Heat Treatment	Drying Tine	Capacity		
			1^{st} Cycle	100^{th} Cycle	% Loss
Furnace	100℃	30 min	62.22 mAh/g	37.79 mAh/g	39.27%
NIR (Lv. 4)	674.22 W/m^2	3 min	66.09 mAh/g	47.25 mAh/g	28.50%

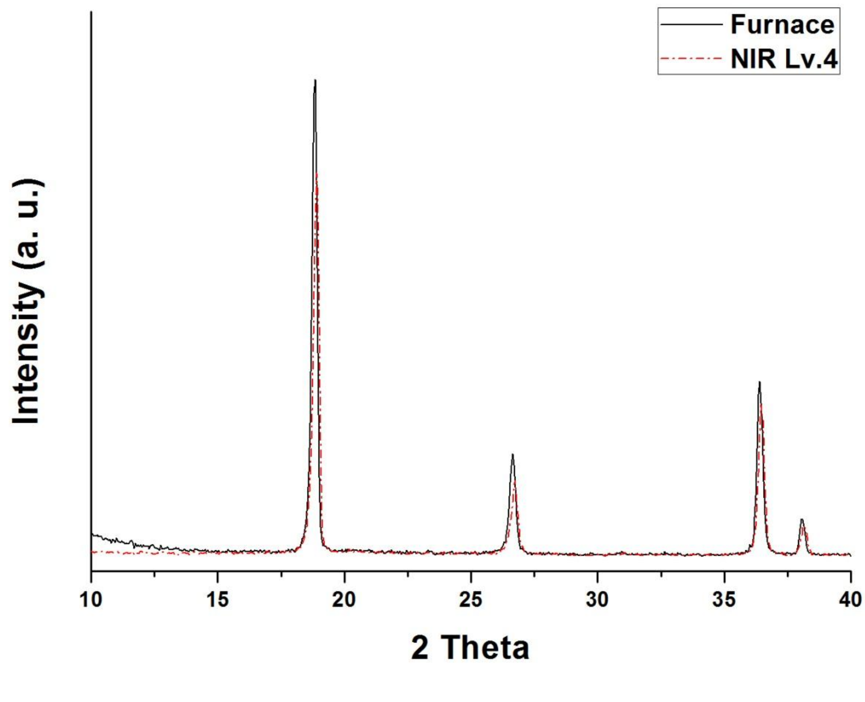
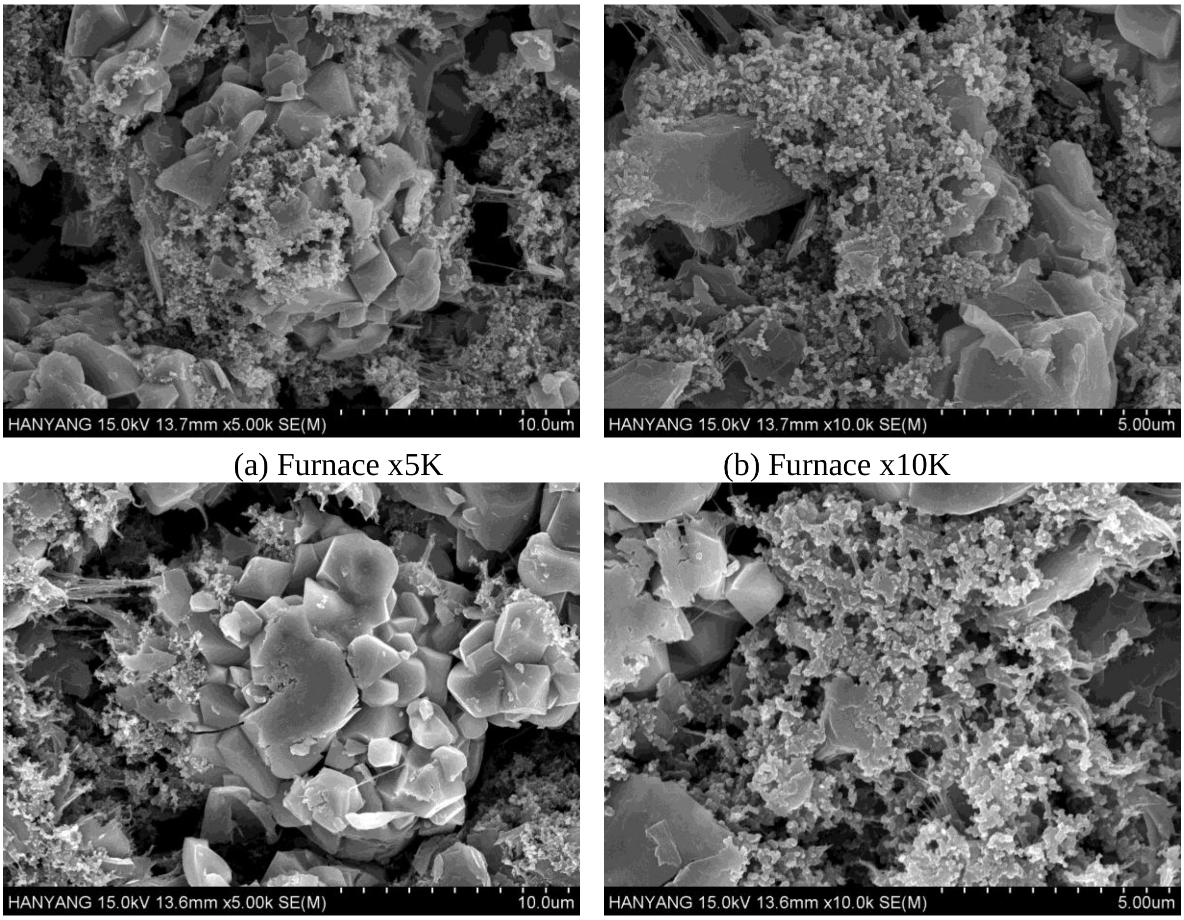


Figure 4. Result of XRD of Spinel Type $LiMn_2O_4$ Thin Film Electrode

Experimental results by XRD are shown in Figure 4, and SEM images are shown in Figure 5. And the sheet resistances are also measured and shown in Table 2. By analyzing the result of XRD, the phase of the thin film electrode dried by furnace and NIR are different. The intensity of the thin film electrode dried by NIR is slightly below than the furnace. And the sheet resistance is higher in case of

NIR. The lower intensity is considered to have more cavities. And it is also regarded that because of these cavities, the sheet resistance increases. It is estimated that the lower intensity with more cavities provides more paths for lithium ions and causes the increase of the capacity and reduces the capacity fade out on cycling, simultaneously. Therefore, the reasons for increased capacity and less capacity loss of electrode on cycling are estimated as followed; NIR drying process causes the higher efficiency by providing more paths for lithium ions.



(a) Furnace x5K (b) Furnace x10K

(c) NIR Lv.4 x5K (d) NIR Lv.4 x10K

Figure 5. SEM Images of Spinel Type $LiMn_2O_4$ Thin Film Electrode

Table 2. Sheet Resistance of Thin Film Electrode dried by Furnace and NIR

	Furnace	NIR (Lv.4)
Sheet Resistance (mΩ/□)	2.003 ~ 3.284	2.304 ~ 3.564

3.2 Near Infrared Drying Process in Different Heat Flux

The second experiment was conducted to verify the differences of electrochemical performance between the lithium ion batteries using the thin film electrode dried by different heat fluxes (Lv. 3 to

Lv. 6) of NIR for 3 minutes. In case of Lv. 2 of NIR drying process, after 10 minutes, solvent evaporated completely. And in case of Lv. 7 of NIR drying process, the fire erupted after 27 second. Therefore the electrochemical performances of both cases were not measured. The capacity and the percentage of the capacity loss were measured.

Table 3. Capacities of Lithium Ion Battery using Thin Film Electrode dried by NIR Lv. 3, 4, 5 and 6

NIR Level	Heat Flux	Drying Tine	Capacity		
			1^{st} Cycle	100^{th} Cycle	% Loss
Lv. 3	299.65 W/m^2	3 min	32.55 mAh/g	7.56 mAh/g	76.77%
Lv. 4	674.22 W/m^2	3 min	66.09 mAh/g	47.25 mAh/g	28.50%
Lv. 5	1030.05 W/m^2	3 min	99.27 mAh/g	84.18 mAh/g	15.19%
Lv. 6	1310.97 W/m^2	3 min	50.11 mAh/g	28.49 mAh/g	43.15%

The capacity and the percentage of the capacity loss of four different types are expressed numerically in Table 3. As it is shown, after 100 cycles of charging and discharging, 76.77% of the capacity of lithium ion battery using thin film electrode dried by NIR with heat flux 299.65 W/m^2 (Lv. 3) fades out, 28.50 % fades out in case of NIR with heat flux 674.22 W/m^2 (Lv. 4), only 15.19% fades out in case of NIR with heat flux 1030.05 W/m^2 (Lv. 5), and 43.15% fades out in case of NIR with heat flux 1310.97 W/m^2 (Lv. 6). In case of lithium ion battery using thin film electrode dried by NIR with heat flux 1030.05 W/m^2 (Lv. 5) verified to have best life cycle contrary to other heat fluxes. And also the capacity is larger in the same case than any other heat fluxes. Interesting result in case of lithium ion battery using thin film electrode dried by NIR with heat flux 299.65 W/m^2 (Lv. 3) and 1310.97 W/m^2 (Lv. 6) have been observed. The capacity is even worse than furnace. It is estimated that the heat energy wasn't enough to evaporate the solvent sufficiently, in case of NIR with heat flux 299.65 W/m^2 (Lv. 3). And in case of NIR with heat flux 1310.97 W/m^2 (Lv. 6), it is estimated that the heat energy was oversupplied, so the binder was over heated and act up. It was verified that the cathode material was easily detached with the aluminum collector. Thus the capacities are even worse in both cases. Therefore, the electrochemical performance in case of NIR with heat flux 1030.05 W/m^2 (Lv. 5) was verified to be the best.

4. CONCLUSION

NIR drying process was verified to be appropriate drying process in slot die roll-to-roll process. Not only because of the rapid drying, but also improved the electrochemical performance of the lithium ion battery. Especially the loss of thin film electrode capacity of spinel type $LiMn_2O_4$ was reduced to 15.19%. The reduction of capacity loss on cycling is estimated to be caused by the low intensity with cavities. These cavities may cause the increase of sheet resistance of the spinel type $LiMn_2O_4$ thin film electrode, but can provide more paths for lithium ions. However, not all the heat fluxes of NIR drying process reduced the capacity loss. In case of NIR with heat flux 299.65 W/m^2 (Lv. 3), the solvent didn't evaporate sufficiently, and in case of NIR heat flux 13310.97 W/m^2 (Lv. 6), the binder acted up. And so, the electrochemical performance of lithium ion battery was even worse than furnace. The best NIR drying condition for spinel type $LiMn_2O_4$ thin film electrode was verified to be heat flux 1030.05 W/m^2 (Lv. 5).

References

1. K. Ozawa, *Lithium Ion Rechargeable Batteries*, Wiley-VCH (2009)
2. K. E. Aifantis, Stephen A. Hachney and R. Vasant Kumar, *High Energy Density Lithium Batteries: Materials, Engineering, Applications*, Wiley-VCH (2010)
3. J. N. Remers and J. R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2019.
4. K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mat. Res. Bull.* 15 (1980) 783.
5. J. B. Goodenough, G. Wichham and W. J. Croft, *J. Phys. Chem. Solids* 5 (1958) 382.
6. E. Plichta, S. Slane and H. W. Lin, *J. Electrochem. Soc.* 136 (1989) 1865.
7. J. M. Tarascon, W. R. Mckinnon, F. Coowar, T. N. Bownmer, G. A. Matucci and D. Guyomard, *J. E lectrochem. Soc.* 141 (1994) 1421.
8. J. M. Tarascon and D. Guyomard, *J. Electrochem. Soc.* 138 (1991) 2864.
9. D. Guyomard and J. M. Tarascon, *J. Electrochem. Soc.* 139 (1992) 937.
10. P. Fragnaud, R. Nagarajan, K. M. Schleich and D. Vujic, *J. Power Sources* 54 (1995) 362.
11. P. Fragnaud and D. M. Schleich, *Sensors and Actuators* A 51 (1995) 21.
12. K. H. Hwang, S. H. Lee and S. K. Joo, *J. Power Sources* 54 (1995) 224.
13. K. H. Hwand, S. H. Lee and S. K. Joo, *J. Electrochem. Soc.* 141 (12) (1994) 3296.
14. J. B. Bates, G. R. Gruzalski, N. J. Dudney, C. F. Luck and X. Yu, *Solid State Ionics* 70/71 (1994) 61 9.
15. J. B. Bates, N. J. Dudney, D. C. Lubben, G. R. Gruzalski, B. S. Kwak, X. Yu and R. A. Zuhr, *J. Po wer Sources* 54 (1005) 58.
16. S. J. Lee, J. K. Lee, D. W. Kim and H. K. Baik, *J. Electrochem. Soc.* 143 (11) (1996) L368.
17. K. A. Striebel, C. Z. Deng, S. J. Wen and E. J. Cairns, *J. Electrochem. Soc.* 143 (6) (1996) 1821.
18. Y. J. Park, J. G. Kim, M. K. Kim, H. T. Chung, W. S. Um, M. H. Kim and H.G. Kim, *J. Power Sour ces* 76 (1998) 41.
19. C. Lee, H. Kang, H. Kim, Ho Anh Duc Nguyen and K. Shin, *J. Mech. Sci. and Tech.* 24 (2010) 315.
20. J. Park and S. Rhee, *Jap. J. Appl. Phys.* 49 (2010) 05EC10.