

Preparation and Electrochemical Properties of Cathode Materials for Lithium Ion Battery by Aerosol Process

メタデータ	言語: English 出版者: 公開日: 2009-12-21 キーワード (Ja): キーワード (En): 作成者: OGIHARA, Takashi, KODERA, Takayuki, MYOUJIN, Kenichi, MOTOHIRA, Shigeru メールアドレス: 所属:
URL	http://hdl.handle.net/10098/2321

Preparation and Electrochemical Properties of Cathode Materials for Lithium Ion Battery by Aerosol

Process

Takashi Ogihara, Takayuki Koderu, Kenichi Myoujin and Shigeru Motohira

Department of Fiber Amenity Engineering, University of Fukui

3-9-1 Bunkyo, Fukui-shi, Fukui, 910-8507 JAPAN

ogihara@matse.fukui-u.ac.jp

Abstract

Lithium transition metal oxide powders such as LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiFePO_4 were prepared by spray pyrolysis. The particle characteristics of them were determined by SEM, XRD, BET and AAS. Lithium transition metal oxide powders had spherical morphology of 1- 2 μm with narrow size distribution and homogeneous chemical composition. The electrochemical properties of cathode were also estimated by rechargeable capacity, cycle performance, thermal stability and high rate charging. The cathodes obtained by spray pyrolysis exhibited higher rechargeable capacity and good cycle stability. Mass production of lithium transition metal oxide powders was carried out by using internal combustion type of spray pyrolysis. The electrochemical properties of cathode obtained by internal combustion type spray pyrolysis were comparable with these obtained by spray pyrolysis.

Keywords: Lithium ion battery, Oxide, Aerosol, Spray pyrolysis

Introduction

Lithium ion batteries have been extensively used as energy storage devices for portable electronics. Recently, these are well noted as the power sources for the vehicles such as EV and HEV [1]. Both layered type LiCoO_2 and spinel type LiMn_2O_4 is the most important cathode materials because of their high operating voltage at 4 V [2,3]. LiCoO_2 have been mostly used as cathode material of commercial lithium ion batteries. However, LiCoO_2 has a problem related to capacity fading due to the instability in rechargeable cycles. Cobalt is also expensive and its resource is not sufficient. Therefore, LiCoO_2 cathode material is not suitable as a lithium ion battery for EV and HEV. LiMn_2O_4 is regarded as a promising cathode material for large lithium ion batteries due to their

advantages such as low cost, abundance, non-toxicity and thermally stable [4]. It was also known that Ni-substitute lithium manganese oxide spinel ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) was exhibited rechargeable behavior at about 5V [5,6]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been considerably noticed as a cathode material with high power density. Park et.al., reported [7] that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode obtained by spray pyrolysis exhibited excellent rechargeable capacity and stable cycle performance. The layered type $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was found to exhibit superior high potential cathode properties. This shows rechargeable capacity with more 150 mAh/g at higher charge rate and milder thermal stability [8]. Park et.al., also reported [9] that $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ obtained by spray pyrolysis exhibited excellent rechargeable properties as well as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. Recently, olivine-type LiFePO_4 is noted as cathode material for lithium ion batteries because of low-cost, environmentally friendly, high thermally stability and electrochemical performance. LiFePO_4 shows a very flat voltage curve with a plateau around 3.5 V and rechargeable capacity of 170 mAh/g [10-12]. In order to use as cathode, C/ LiFePO_4 composites powders were often prepared by coating conducting materials such as carbon because they had poor electric conductivity [13]. The advantage of spray pyrolysis is that it is possible to directly contain the carbon during the powder preparation using organic compound [14].

For above cathode materials, the spray pyrolysis is an effective process for the rapid synthesis of homogeneous cathode materials. We have been tried to synthesize various type oxide materials such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 for lithium ion battery by spray pyrolysis [15-17]. It was reported that the rechargeable capacity and cycle performance of lithium ion battery were improved by using the cathode materials for lithium ion battery derived from spray pyrolysis. In this paper, the particle characterization and electrochemical properties of lithium transition metal oxide powders produced by spray pyrolysis were described. Furthermore, the mass production apparatus in which the aerosols were efficiently pyrolyzed in flame generated by gas burner (internal combustion type spray pyrolysis) was developed in order to solve the problem of large-scale production of cathode materials. The electrochemical properties of them were also described.

2 Experimental procedures

2.1 Powder preparation of spray pyrolysis

Metal nitrates were used as starting materials. H_3PO_4 was also used as raw materials for LiFePO_4 . They were dissolved in an appropriate atomic molar ratio to prepare the starting solution. Furthermore, various types of organic acid were added to aqueous solutions up to 60 wt% in the preparation of starting solution of LiFePO_4 . The starting solution prepared was atomized to generate the aerosol by using an ultrasonic vibrator with 2.4 MHz. The spray pyrolysis apparatus is shown in elsewhere [18]. The aerosol of starting solution was introduced into quartz tube ($38 \text{ mm}\phi \times 2000 \text{ mm}$) in the electrical furnace with air carrier gas ($6 \text{ dm}^3/\text{min}$). The aerosol was drying at 400°C and then pyrolyzed at 900°C . As-prepared particles were continuously collected using the cyclone.

2.2 Mass production by internal combustion types spray pyrolysis

Figure 1 shows the picture and schematic diagram of internal combustion types spray pyrolysis apparatus [19]. This apparatus ($0.4 \text{ m}\phi \times 6 \text{ m} \times 8 \text{ m}$) consisted of two-fluid nozzle atomizer (a), combustion furnace with gas burner using city gas (b) and powder collection box using bag filter (c). The aerosol of aqueous nitrate solutions was generated by two-fluid nozzle atomizer with flow rate of $10 \text{ dm}^3/\text{h}$. The aerosol was continuously sprayed from the upper part of combustion furnace to the downward and then pyrolyzed when the aerosol passed through the flame set at 500°C . This apparatus have the powder production potential of 1 kg/hr . It is possible to produce lithium transition metal oxide powders of 2000 kg/month by this apparatus.

2.3 Powder characterization and electrochemical properties

Crystal phase of lithium transition metal oxide powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using $\text{CuK}\alpha$ radiation. The average particle size and morphology of them were determined by scanning electron microscope (SEM, Hitachi, S-2300). The average particle size was determined by randomly sampling 200 particles from SEM photographs. Specific surface area of lithium transition metal oxide powders was measured by BET method using N_2 adsorption (SSA, Shimadzu, Tristar-3000). The chemical composition of them was determined by atomic adsorption spectrum analysis (AAS, Shimadzu, AAS-6800).

The heat treatment was carried out at 750°C for 2 hr under the air condition to obtain the cathode materials with well crystallization. LiFePO_4 was also heated at 600°C for 2 hr under the argon/hydrogen (5 %) atmosphere

to prevent the volatile of carbon. Cathode was prepared using 80 wt% of cathode material powders, 10 wt% of acetylene black and 10 wt% of fluorine resin. They were mixed to obtain slurry and then coated on aluminum sheet using doctor blade. Li sheet was used as an anode. The polypropylene sheet was used as a separator. 1 mol·dm⁻³ LiPF₆ in ethylene carbonate / 1,2-dimethoxyethane (EC : DME = 1 : 1) was used as the electrolyte. 2032 coin type of lithium ion cell was built up in globe box under an argon atmosphere. The change of voltage during charge/discharge was measured with a battery tester (Hosen, BTS2004) at between 3.0 V and 4.3 V. The current density ranged from 0.3 (1 C) to 6 (20 C) mA/cm². 1 C means that the rechargeable process is done for 1 hr.

3 Results and discussion

3.1 Powder characterization of lithium transition metal oxide

Figure 2 shows typical SEM photographs of lithium transition metal oxide powders prepared by spray pyrolysis. SEM photograph revealed that these powders had the spherical morphology with non-aggregation regardless of the types of starting materials. The average particle size of them determined by SEM photograph was about 1 - 2 μm. The geometrical standard deviation of average particle size ranged from 1.2 to 1.5. These powders had relatively narrow size distribution. Table 1 shows SSA of them measured by BET method. SSA of them ranged from 1 to 4 m²/g.

XRD patterns of lithium transition metal oxide powders are shown in Fig.3. The diffraction peaks of LiAl_{0.05}Mn_{1.95}O₄ and LiNi_{0.5}Mn_{1.5}O₄ were good agreement with spinel structure (space group $\bar{F}d3m$). The diffraction lines of impurities (e.g. Al₂O₃, Mn₂O₃, Li₂CO₃) were not identified. Aluminum was uniformly doped and nickel was substituted in Mn site. The diffraction peaks of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ were also identified to layered structure (space group $\bar{R}3m$). Furthermore the diffraction peaks of LiFePO₄ were identified to olivine structure (space group Pnma). Table 2 shows the chemical composition of lithium transition metal oxide powders determined by AAS. The chemical composition of them was good agreement with starting solution composition. This suggested that the content of each metal was uniformly maintained in each aerosol.

3.2 Electrochemical properties of cathode material

The electrochemical measurement of cathode which was produced by lithium transition metal oxide powders

derived from spray pyrolysis was examined. Figure 4 shows the charge and discharge curves of cathode at rate of 1 C (Current density : 0.3 mA/cm²). The discharge capacity of LiAl_{0.05}Mn_{1.95}O₄ and LiNi_{0.5}Mn_{1.5}O₄ was 125 and 145 mAh/g, respectively. Al doping led to the disappearance of typical voltage jump at 4V and then the S curve with average operating voltage of 3.6 was observed. On the other hand, the average operation voltage increased up to 4.7 V by substituting Ni to LiMn₂O₄. This suggested that the application as high power sources such as electric tool was expected. The discharge capacity of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ and LiFePO₄ was 180 and 150 mAh/g, respectively and had higher capacity than LiMn₂O₄. The discharge capacity of LiFePO₄ without carbon was 40 mAh/g. The rechargeable capacity of LiFePO₄ was considerably improved by the addition of carbon. It was shown that the cathode had the excellent discharge capacity and was expected to apply as high energy sources such as HEV. The long plateau was observed at about 3.5V in the discharge curve of LiFePO₄.

Figure 5 shows the relation between cycle number and discharge capacity of LiAl_{0.05}Mn_{1.95}O₄ cathode at rate from 1C to 15C. The rechargeable test was carried out up to 1000 times. It was clear that the excellent cycle stability was shown. The discharge capacity was reduced to 80% of initial discharge capacity after about 1000 cycle number at rate of 1 C. The discharge capacity of LiAl_{0.05}Mn_{1.95}O₄ cathode decreased with increasing charging rate. The discharge capacity reduced to about 70 mAh/g at a rate of 15 C. The discharge capacity was maintained more 90% of initial discharge capacity at rate of more 5 C. This suggested that the addition of Al led to the increase of Mn valence.

Figure 6 shows the relation between cycle number and discharge capacity of LiNi_{0.5}Mn_{1.5}O₄, LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ and LiFePO₄ cathode at rate from 1C to 15C. LiNi_{0.5}Mn_{1.5}O₄ maintained 92% of initial discharge capacity after about 500 cycle number at rate of 1C. The discharge capacity reduced to about 70 mAh/g at a rate of 15 C, but maintained 89% of initial discharge capacity. LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ maintained 80 % of initial discharge capacity after about 500 cycle number at rate of 1 C. The discharge capacity reduced to about 90 mAh/g at a rate of 15 C. LiFePO₄ maintained 84 % of initial discharge capacity after about 500 cycle number at rate of 1 C. The discharge capacity reduced to about 70 mAh/g at a rate of 15 C, but maintained 94 % of initial discharge capacity.

Figure 7 shows the relation between cycle number and discharge capacity of cathode at 50 °C and 60 °C. The rechargeable test carried out up to 300 cycles at rate of 1 C. The cycle stability of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes at 50 °C and 60 °C was maintained as well as the room temperature. The discharge capacity of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiFePO_4 cathodes gradually decreased with increasing cycle number at 60 °C. The discharge capacity of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiFePO_4 cathodes was 74% and 77% of discharge capacity, respectively.

3.3 Mass production of cathode materials by internal combustion type spray pyrolysis

It is difficult for spray pyrolysis to homogeneously pyrolyze a large quantity of aerosol at short time in the electrical furnace that the scale-up was done. In the spray pyrolysis, the difference of pyrolysis temperature inside and outside of the electrical furnace increases with increasing the dimension of electrical furnace. So far, we have been developed the internal combustion type spray pyrolysis apparatus by using gas burner to produce homogeneous cathode materials at large-scale furnace. As a result, it would be possible to overcome the problem of mass production by spray pyrolysis. Figure 8 shows SEM photograph and particle size distribution of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders produced by this apparatus. They had the spherical morphology and consisted of primary particles. They are seen like the porous particle from SEM photograph. The average particle size of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders was 2.7 μm and had broad size distribution because of use of two-fluid nozzle with 5 μm of diameter. The geometrical standard deviation of average particle size was 1.5. XRD analysis showed that the crystal structure was spinel type structure with space group of $\text{Fd}\bar{3}\text{m}$. SSA of them was 10 m^2/g . The chemical composition analysis showed that the molar ratio of Li : Al: Mn was 0.99 : 0.051 : 1.95.

Figure 9 shows the rechargeable properties and cycle performance of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode at rate from 0.1 C to 10C. The rechargeable capacity of it decreased from 125 mAh/g to 90 mAh/g, when the charging rate increased from 0.1 C to 10 C. The discharge capacity at each rate maintained 90% of initial discharge capacity after 300 cycles. $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode obtained by internal combustion type spray pyrolysis exhibited the stable cycle performance.

4. Conclusion

Spray pyrolysis demonstrated that lithium transition metal oxide powders had spherical and porous particles which have a diameter of about 1 μm with narrow size distribution. As-prepared powders have high crystallinity and uniform chemical composition. The electrochemical measurement exhibited that the cathode materials had the higher rechargeable capacity and stable cycle performance. The rechargeable capacity decreased with increasing the charging rate, but the stability of cycle performance was maintained. The stability of cycle performance was also maintained at elevated temperature. It was found that the aerosol process was effective for the preparation of cathode materials. The electrochemical properties of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode materials obtained by internal combustion type spray pyrolysis were comparable with those obtained by spray pyrolysis.

Acknowledgement

This work was supported by Development of an Electric Energy Storage System for Grid-connection with New Energy Resources in New Energy and Industrial Technology Development Organization.

References

- [1] E. Karden, S. Ploumen, B. Fricke, T. Miller, K. Snyder, J. Power Sources 168 (2007) 2–11.
- [2] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Mat. Res. Bull. 15 (1980) 783-789.
- [3] D. Guyomard, J.M. Trascon, Solid State Ionics 69 (1994) 222-237.
- [4] Z. Pegeng, F. Huiqing, F. Yunfei, L. Zhuo, D. Yongli, Rare Metals 25 (2006) 100-104.
- [5] B. Markovsky, Y. Talyossef, G. Salitra, D. Aurbach, H.J. Kim, S. Choi, Electrochem. Commun. 6 (2004) 821-826.
- [6] Y. Idemoto, H. Sekine, K. Ui, N. Koura, Electrochemistry 70 (2004) 564-568.
- [7] S.H. Park, Y.K. Sun, Electrochimica Acta 50 (2004) 431-434.
- [8] N. Yabuuchi, T. Ohzuku, J. Power Sources 171 (2003) 119–121.
- [9] S.H. Park, C.S. Yoon, S.G. Kang, H.S. Kim, S.I. Moon, Y.K. Sun, Electrochimica Acta 49 (2004) 557-563.
- [10] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188-1194.
- [11] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224-A229.
- [12] S.L. Bewlay, K. Konstantinov, G.X. Wang, S.X. Dou, H.K. Liu, Mater. Lett. 58 (2004) 1788-1791.

- [13] J.D. Wilcox, M.M. Doeff, M.Marcinek, R.Kostecki, J. Electrochem. Soc. 154 (2007) A389-A395.
- [14] M.R. Yang, T.H. Teng, S.H. Wu, J. Power Sources 159 (2006) 307–311.
- [15] T.Ogihara, T.Yanagawa, N.Ogata, K.Yoshida, Y.Mizuno, S.Yonezawa, T.Takashima, N.Nagata, K.Ogawa, *Denki Kagaku*, 61 (1993) 1339-1341.
- [16] T.Ogihara, N.Ogata, S.Yonezawa, M.Takashima, N.Mizutani, *Denki Kagaku* 66 (1998) 1202-1205.
- [17] T.Ogihara, N.Ogata, K.Katayama, Y.Azuma, *Electrochemistry* 68 (2000) 162-166.
- [18] T.Ogihara, T.Ookura, T.Yanagawa, N.Ogata, K.Yoshida, *J. Mater. Chem.* (1991) 789-794 (1991).
- [19] K.Myojin, T.Ogihara, N.Ogata, N.Aoyagi, H.Aikiyo, T.Ookawa, S.Omura, M.Yanagimoto, M.Uede, T.Oohara, *Adv. Powder Technol.*, 15 (2004) 397-403.

Table 1 SSA of lithium transition metal oxide powders prepared by spray pyrolysis

Sample	SSA(m ² /g)
LiAl _{0.05} Mn _{1.95} O ₄	2
LiNi _{0.5} Mn _{1.5} O ₄	1.6
LiCo _{1/3} Ni _{1/3} Mn _{1/3} O ₂	1
LiFePO ₄	4

Table 2 Chemical composition of lithium transition metal oxide powders prepared by spray pyrolysis

	Atomic concentration (moler ratio)						
	Li	Al	Mn	Co	Ni	Fe	P
LiAl _{0.05} Mn _{1.95} O ₄	1	0.05	1.95				
LiNi _{0.5} Mn _{1.5} O ₄	1		1.5		0.5		
LiCo _{1/3} Ni _{1/3} Mn _{1/3} O ₂	1		0.34	0.33	0.33		
LiFePO ₄	1					1	1

Figure 1

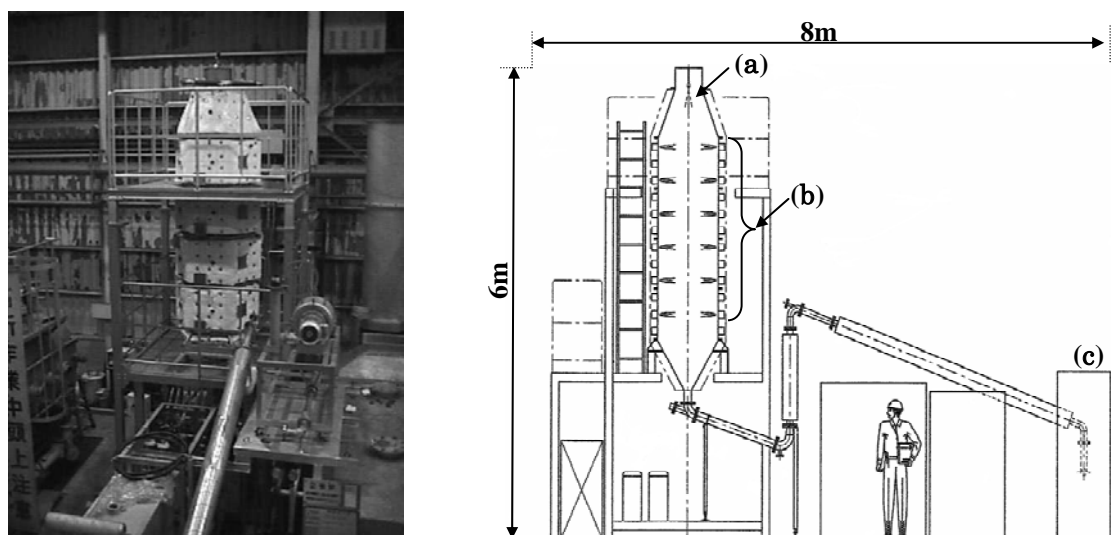


Fig.1 Picture and schematic diagram of internal combustion types spray pyrolysis apparatus, (a) two-fluid nozzle atomizer, (b) combustion furnace, (c) powder collection box

Figure 2

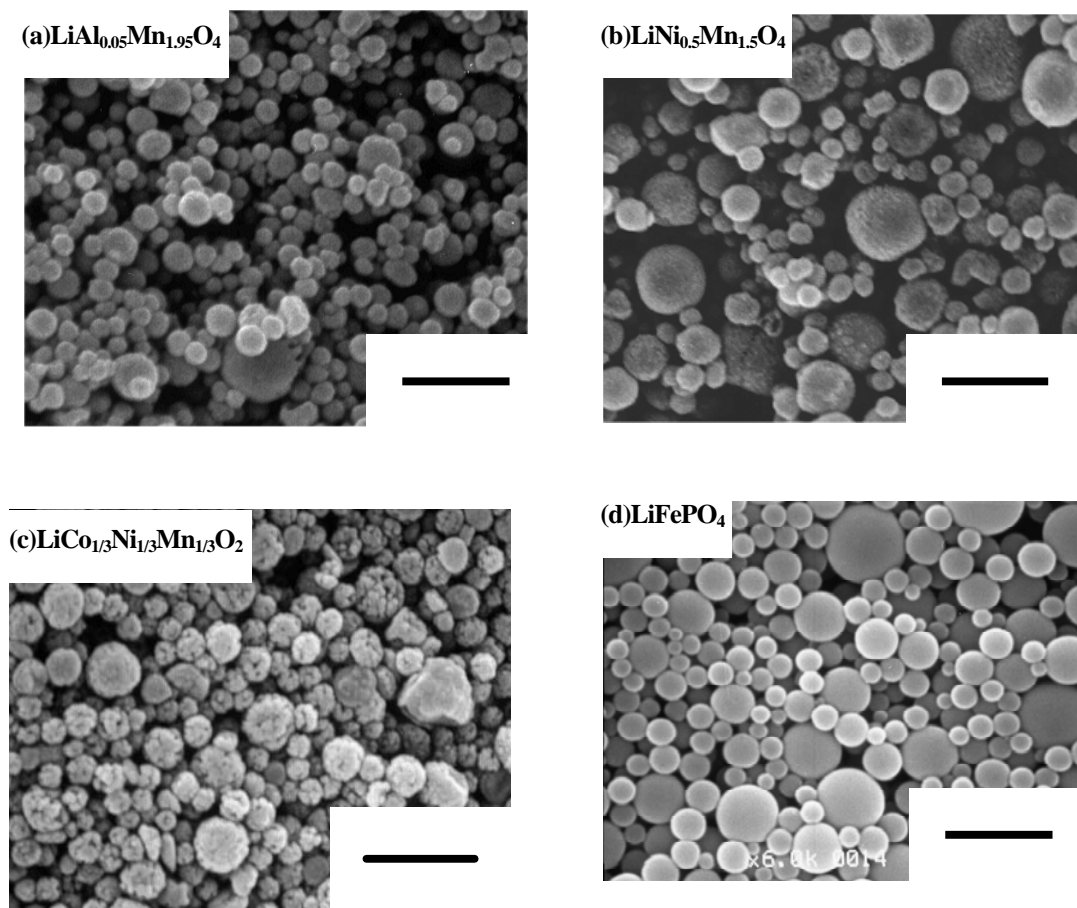


Fig.2 SEM photographs of lithium transition metal oxide powders prepared by spray pyrolysis (bar=5μm).

Figure 3

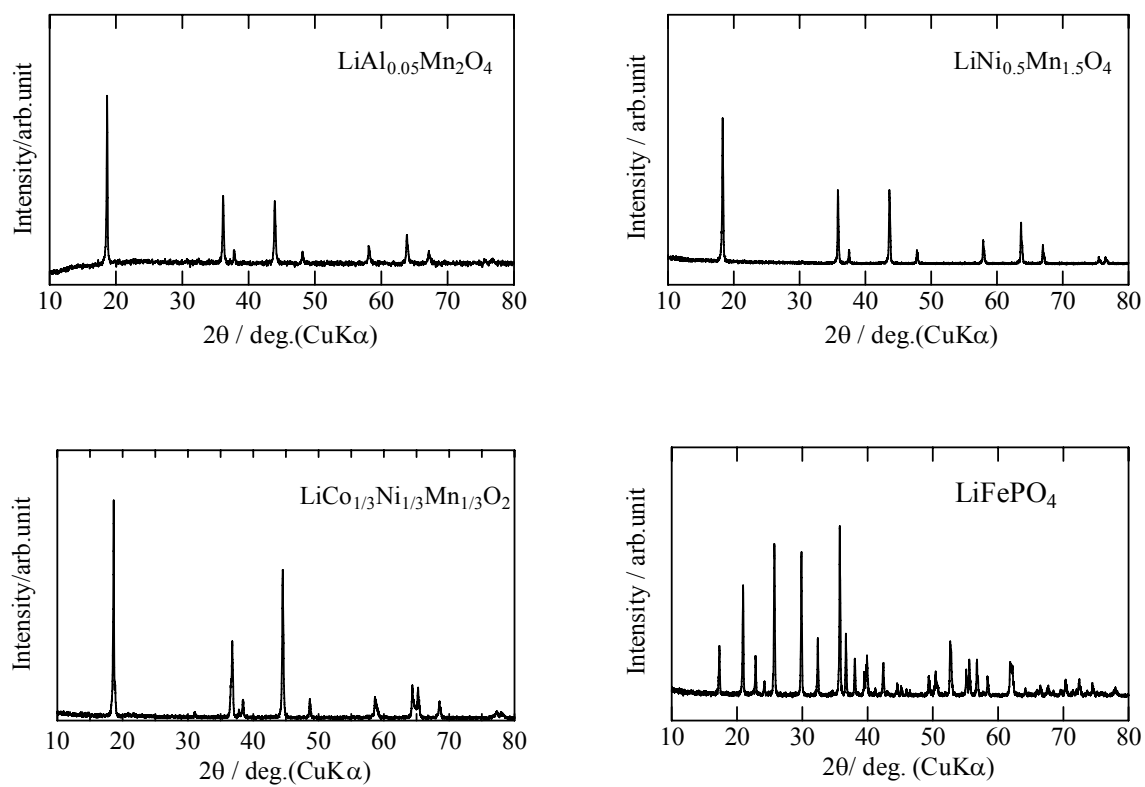


Fig.3 XRD patterns of lithium transition metal oxide powders prepared by spray pyrolysis

Figure 4

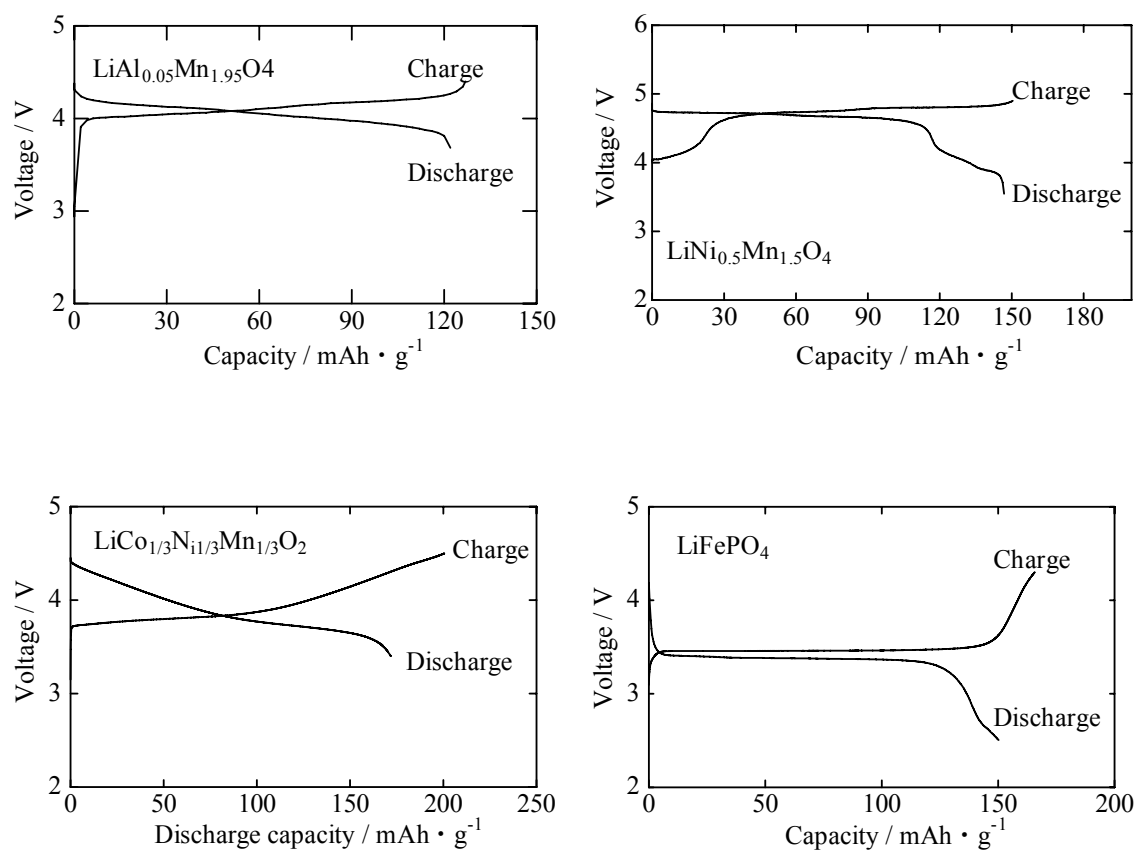


Fig.4 Charge and discharge curves of cathodes at rate of 1 C

Figure 5

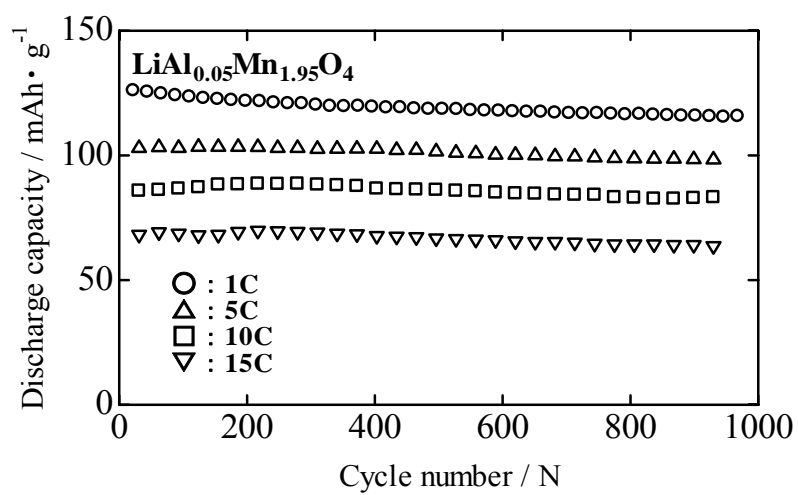


Fig.5 Relation between cycle number and discharge capacity of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode at rate from 1C to 15C.

Figure 6

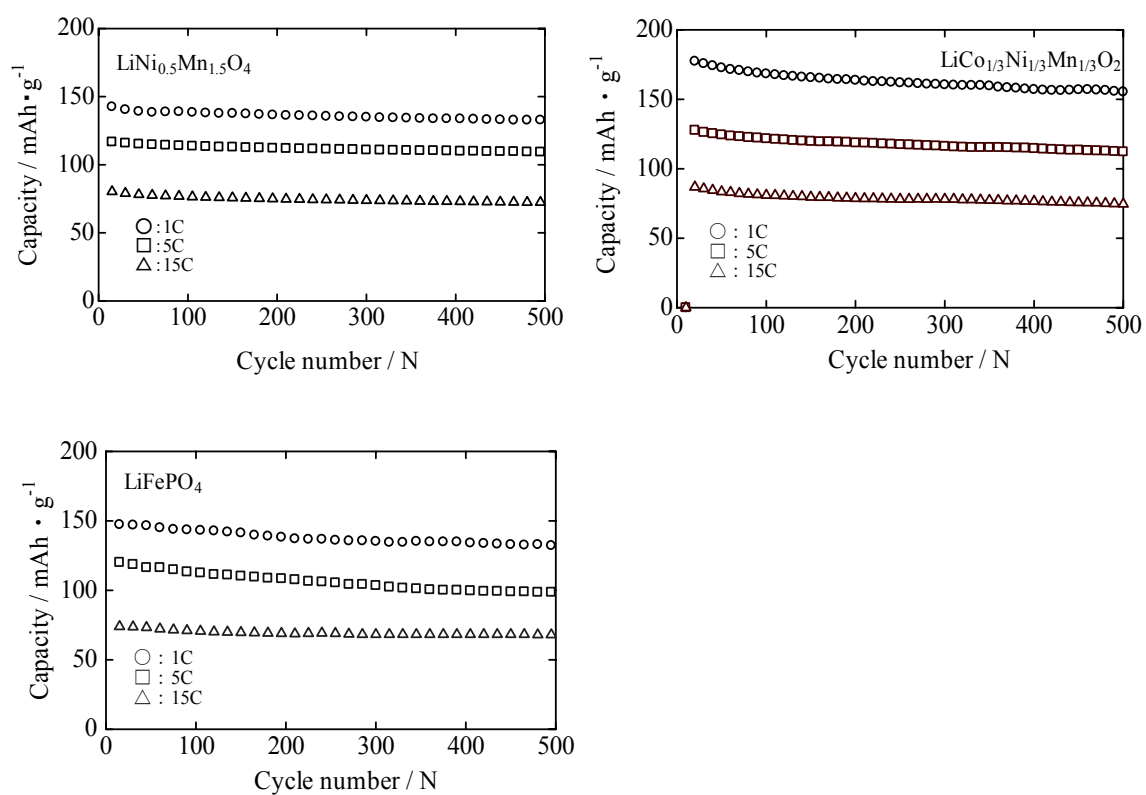


Fig.6 Relation between cycle number and discharge capacity of cathode at rate from 1 C to 15 C.

Figure 7

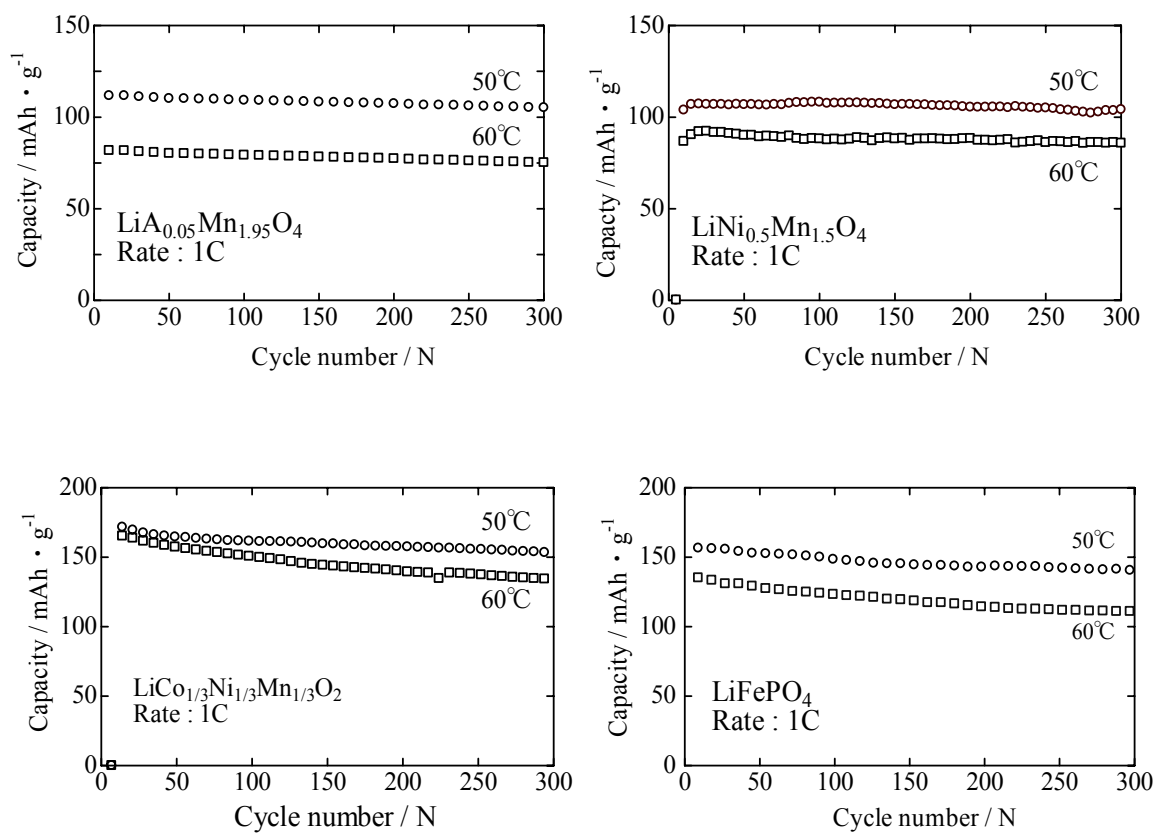


Fig.7 Relation between capacity and cycle number at temperature indicated.

Figure 8

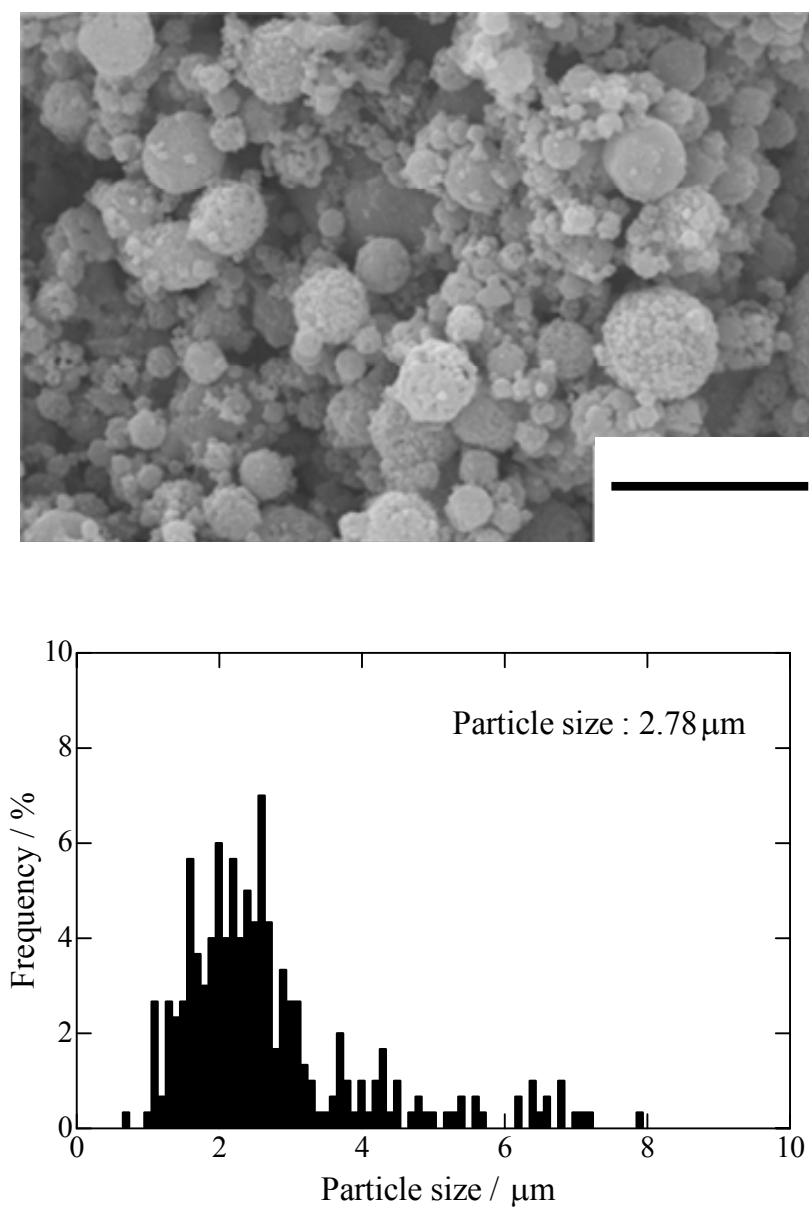


Fig.8 SEM photograph and particle size distribution of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders obtained by internal combustion type spray pyrolysis (bar=10μm)

Figure 9

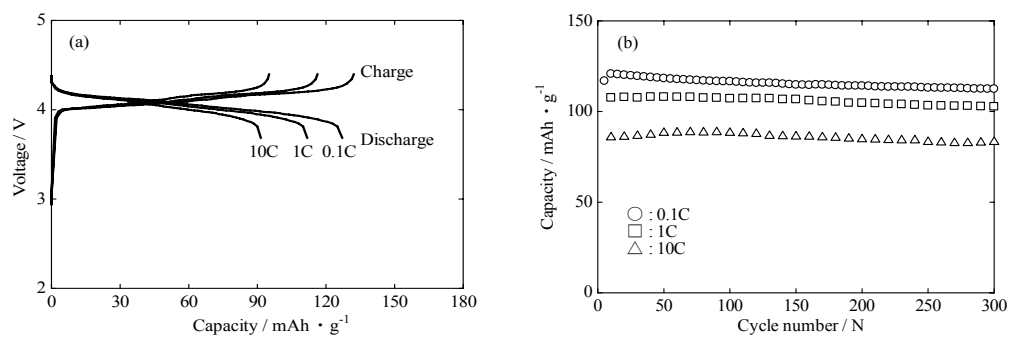


Fig.9 Rechargeable curves (a) and cycle performance (b) of $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode at rate indicated.