Synthesis and electrochemical properties of Na$_{2/3}$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode materials for sodium ion battery by spray pyrolysis

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1. Introduction

Recently, lithium ion batteries are expected as the energy storage for electric vehicles, hybrid electric vehicles, and power supplies used for load leveling in wind power generation and solar power generation. Li$_2$MnO$_4$ and LiFePO$_4$ are regarded as promising cathode materials for large scale lithium ion batteries. One of the advantages of these cathode materials is that manganese and iron are abundance resources.

In sodium ion batteries, layered Na$_x$CoO$_2$, Na$_x$CrO$_2$, Na$_x$MnO$_2$, Na$_x$VO$_2$, Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$, Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$, and Na$_x$Fe$_{1/3}$Mn$_{2/3}$O$_2$ have been studied as cathode materials. Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$, Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$, and Na$_x$Fe$_{1/3}$Mn$_{2/3}$O$_2$ exhibited higher rechargeable capacity (150–200 mA h g$^{-1}$) compared with that of the other cathode materials. P2, O3, O3 and O6 structures are commonly known as the crystal structures of layered alkali transition metal oxide.

For example, P2-Na$_{2/3}$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode materials were approximately 150 mA h g$^{-1}$ at a rate of 0.1 C. Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cathode materials were also investigated.

2. Experimental procedure

Ultrasonic spray pyrolysis was used to prepare Na$_{2/3}$Fe$_{1/3}$Mn$_{2/3}$O$_2$ powders. NaNO$_3$, Fe(NO$_3$)$_3$·9H$_2$O and Mn(NO$_3$)$_2$·6H$_2$O were used as the starting materials. These compounds were dissolved in water at room temperature. The molar ratio of the metal component (Na$_x$Fe$_{1/3}$Mn$_{2/3}$) was set to 2/3:3/3:2/3 in the solution. The concentration of the starting solutions was 0.5 mol dm$^{-3}$. The starting solutions were converted to mists using an ultrasonic nebulizer at a frequency of 1.6 MHz. Air was used as the carrier gas during the preparation of Na$_{2/3}$Fe$_{1/3}$Mn$_{2/3}$O$_2$ powders. The generated mists were carried to an alumina tube (internal diameter, 30 mm; length, 2000 mm) that was heated by four electric furnaces, and then pyrolyzed. The flow rate of the carrier gas was 8 dm$^3$/min. The temperatures of two electric furnaces in the drying zone were both 400°C. The temperatures of two electric furnaces in the pyrolysis zone were both 600°C. The precursor powders were continuously collected using a cyclone system. Furthermore, the precursor powders were calcined from 700 to 1100°C for 2 h in an electric furnace under an air atmosphere. The heating and cooling rates were 5°C/min and 4°C/min, respectively. The crystal phase of the obtained powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuK$_\alpha$ radiation. The particle size and morphology of the obtained powders were determined by using a scanning electron microscope (SEM, JEOL, JSM-6390). In the SEM images, 200 particles were randomly sampled to determine the average particle size.

The electrochemical measurements were examined using a 2032 coin type cell. Na$_{2/3}$Fe$_{1/3}$Mn$_{2/3}$O$_2$ powders were mixed with acetylene black and a polyvinylidene difluoride powder in the weight ratio of 80:10:10 to make the N-methyl-2-pyrrolidone solution slurry. The prepared slurry was then coated on aluminum foil using a doctor blade and dried under vacuum at 120°C for 20 h. The electrochemical properties were examined using a three-electrode cell.
24 h. A thin plate of sodium was used as the counter electrode. A polypropylene sheet was used as a separator. 1 mol/dm² NaPF₆ in propylene carbonate (PC, Kishida chemical) were used as the electrolyte. 2032 coin type cell was built up in glove box under an argon atmosphere. The redox reactions of Na₂/₃Fe¹/₃Mn²/₃O₂ powders were investigated using cyclic voltammetry (CV, Hokuto Denko, HSV-100) at voltages between 1.5 and 5.0 V. Scans were performed at 1 mV/min. The rechargeable capacity and cycle stability of Na₂/₃Fe¹/₃Mn²/₃O₂ powders were measured with a battery tester (Hosen, BTS2004) at voltages between 1.5 and 4.8 V.

3. Results and discussion

3.1 Powder characteristics

The effect of changing the calcination temperature on the powder characteristics of the obtained powders was investigated. The calcination temperatures were from 700 to 1100°C. The crystal phases of the obtained powders were observed by using the XRD. Figure 1 shows the XRD patterns of the powders obtained by changing the calcination temperature. The precursor powders were not crystallized, because the pyrolysis temperature in spray pyrolysis process was low. However, the precursor powders were crystallized by the calcination over 700°C and then had the layered structures. In addition, the diffraction patterns of the calcined powders were in good agreement with that of layered Na₂/₃Ni¹/₃Mn²/₃O₂ powders.²¹ The crystal phase of the powder obtained at 700°C were in agreement with P2 structure (space group: P6₃/mmc), but the phase of P3 structure (space group: R3m) was also observed. On the other hand, it was observed that the diffraction patterns of the powders obtained from 800 to 1100°C were in good agreement with P2 structure, and the other phases were not observed. This suggested that it is necessary to calcine over 800°C in order to obtain a homogeneous crystal phase of P2-Na₂/₃Fe¹/₃Mn²/₃O₂. The lattice parameters of P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders were calculated using the XRD data. The lattice parameters were \( a = 0.28964 \) and \( c = 1.1233 \) nm for P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained at 800°C, \( a = 0.28958 \) and \( c = 1.1226 \) nm for P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained at 900°C, and \( a = 0.28988 \) and \( c = 1.1271 \) nm for P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained at 1000°C. The lattice parameters of P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained from 800 to 1000°C were similar to that of P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders.¹⁴

Figure 2 shows the SEM images of the precursor powders and Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained by changing the calcination temperature. The precursor powders obtained by ultrasonic spray pyrolysis exhibited spherical morphology and were non-aggregated. The average particle size of the precursor powders was approximately 1 μm. P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained at 800°C also exhibited spherical morphology with 1 μm. On the other hand, when the calcination temperature was from 900 to 1100°C, irregularly shaped particles were formed. The average particle sizes of P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders obtained at 900, 1000 and 1100°C were approximately 1.5, 1.7 and 3.5 μm, respectively. The precursor powders were sintered by the calcination over 900°C. This resulted in changing the particle morphology and the average particle size of Na₂/₃Fe¹/₃Mn²/₃O₂ powders.

3.2 Electrochemical properties

The electrochemical properties of P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders as cathode for sodium battery were examined. Figure 3 shows the rechargeable curves of the P2-Na₂/₃Fe¹/₃Mn²/₃O₂ cathodes at a rate of 0.1 C in the voltage range 2.0–4.5 V. The P2-Na₂/₃Fe¹/₃Mn²/₃O₂ cathodes were prepared by mixing P2-Na₂/₃Fe¹/₃Mn²/₃O₂ powders, acetylene black and a polyvinyliden difluoride powder. The rechargeable capacity of the P2-Na₂/₃Fe¹/₃Mn²/₃O₂ cathode was compared with that of the cathode that
used the calcined powders obtained by calcining at different temperature. The discharge capacities of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathodes obtained at 800, 900, 1000 and 1100°C was 150, 156, 162 and 148 mAh g$^{-1}$, respectively. The rechargeable capacity of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathodes obtained at 900 and 1000°C was high in comparison to that of the other cathodes. In addition, the discharge capacity of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathodes was similar to that of the P2-Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cathode.

Figure 4 shows the relation between cycle number and discharge capacity of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathodes obtained at 900 and 1000°C in the voltage range 2.0–4.5 V (at a rate of 0.1 C). The rechargeable rate was 0.1 C. The rechargeable test was conducted with up to 100 cycles at 25°C. The discharge capacity of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 900°C after 100 cycles was maintained at approximately 70% of the initial discharge capacity. On the other hand, the discharge capacity of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 1000°C after 100 cycles was maintained at approximately 12% of the initial discharge capacity. It was found that the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 900°C exhibited good cycle stability.

Figure 5 shows the rechargeable curves of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 900°C and 1000°C in the voltage range 2.0–4.5 V. The rechargeable rate was 0.1 C. The rechargeable test was conducted with up to 100 cycles at 25°C. The P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 900°C exhibited good cycle stability, regardless of the rechargeable rate.

Figure 6 shows CV curve of the P2-Na$_2$Fe$_{1/3}$Mn$_{2/3}$O$_2$ cathode obtained at 900°C. The voltage ranged from 1.5 to 5.0 V. At voltages between 1.5 and 4.0 V, the peaks in charge process were observed at approximately 1.75 and 3.0 V. The peaks in discharge process were observed at approximately 2.0 and 3.25 V. It is
considered that the intercalation and deintercalation reaction of Na resulted in the occurrence of peaks at voltages between 1.5 and 4.0 V. Several peaks also occurred from 4.0 to 5.0 V in charge process, but these peaks did not have a pair in discharge process. This suggested that the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C can react reversibly at voltages between 1.5 and 4.0 V.

**Figure 8** shows the rechargeable curves of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C for a range of rechargeable voltages, as indicated in the figure. The rechargeable rate was 0.1 C. When the voltage ranged from 2.0 to 4.0 V, the charge and discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C were 66 and 63 mAh g⁻¹, respectively. When the voltage ranged from 1.5 to 4.0 V, the charge and discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C increased to 150 and 144 mAh g⁻¹, respectively. It was found that the rechargeable efficiency of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C was high.

The discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C was maintained at approximately 35% of the initial discharge capacity. On the other hand, the discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode at 900°C after 20 cycles was maintained at approximately 90% of the initial discharge capacity.

**Figure 9** shows the relationship between the cycle number and discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C for a range of rechargeable voltages, as indicated in the figure. The rechargeable rate was 0.1 C. The rechargeable test was conducted with up to 20 cycles at 25°C. The discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C after 20 cycles was maintained at approximately 35% of the initial discharge capacity, when the voltage ranged from 1.5 to 4.8 V. On the other hand, the retention rate of the P2-Na2/3Fe1/3Mn2/3O2 cathode discharge capacity was approximately 90% at the voltage range 1.5–4.0 V. It was found that the discharge properties of the P2-Na2/3Fe1/3Mn2/3O2 cathode obtained at 900°C exhibited excellent cycle stability, when the voltage ranged until 4.0 V. From CV curve (Fig. 7), the reversible reaction at voltages between 1.5 and 4.0 V led to an improvement in cycle stability.

### 4. Conclusions

P2-Na2/3Fe1/3Mn2/3O2 powders were successfully prepared by spray pyrolysis. The calcination temperature influenced the crystal phase and particle morphology. XRD revealed that the homogeneous crystal phase of P2 type Na2/3Fe1/3Mn2/3O2 was obtained by calcining from 800 to 1100°C. P2-Na2/3Fe1/3Mn2/3O2 powders were well crystallized. Electrochemical analysis indicated that the P2-Na2/3Fe1/3Mn2/3O2 cathode had a high rechargeable efficiency and rechargeable capacity. In addition, the rechargeable voltage influenced the cycle stability of the P2-Na2/3Fe1/3Mn2/3O2 cathode. The P2-Na2/3Fe1/3Mn2/3O2 cathode exhibited excellent cycle stability at the voltage range 1.5–4.0 V. The discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode was approximately 150 mAh g⁻¹ at a rate of 0.1 C. The discharge capacity of the P2-Na2/3Fe1/3Mn2/3O2 cathode after 20 cycles was maintained at approximately 90% of the initial discharge capacity.

### References

1. R. Berthelot, D. Carlier and C. Delmas, *Nat. Mater.*, 10, 74–80 (2011).
2. M. D’Arienzo, R. Ruffo, R. Scotti, F. Morazzoni, C. M. Maria and S. Polizzii, *Phys. Chem. Chem. Phys.*, 14, 5945–5952 (2012).
3. S. Komaba, C. Takei, T. Nakayama, A. Ogata and N. Yabuuchi, *Electrochem. Commun.*, 12, 355–358 (2010).
4. X. Xia and J. R. Dahn, *Electrochem. Solid-State Lett.*, 15, A1–A4 (2012).
5. A. Caballero, L. Hernan, J. Morales, L. Sanchez, J. Santos Pena and M. A. G. Aranda, *J. Mater. Chem.*, 12, 1142–1147 (2002).
6. F. Sauvage, L. Laffont, J. M. Tarascon and E. Baudrin, *Inorg. Chem.*, 46, 3289–3294 (2007).
7. R. Stoyanova, D. Carlier, M. Sendova-Vassileva, M. Yoncheva, E. Zhecheva, D. Nihitianova and C. Delmas, *J. Solid State Chem.*, 183, 1372–1379 (2010).
8. X. Ma, H. Chen and G. Ceder, *J. Electrochem. Soc.*, 158, A1307–A1312 (2011).
9. O. Szajwaj, E. Gaudin, F. Weill, J. Darriet and C. Delmas, *Inorg. Chem.*, 48, 9147–9154 (2009).
10. D. Hamani, M. Afi, J.-M. Tarascon and P. Rozier, *Electrochem. Commun.*, 13, 938–941 (2011).
11. J. M. Paulsen and J. R. Dahn, *Sol. St. Ion.*, 126, 3–24 (1999).
12. Z. Lu and J. R. Dahn, *J. Electrochem. Soc.*, 148, A1225–A1229 (2001).
13. S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takeia, S.
Takada, A. Hokura and I. Nakai, *ECS Trans.*, 16, 43–55 (2009).

14) N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada and S. Komaba, *Nat. Mater.*, 11, 512–517 (2012).

15) C. Delmas, J.-J. Braconnier, C. Fouassier and P. Hagenmuller, *Sol. St. Ion.*, 3–4, 165–169 (1981).

16) C. Delmas, J.-J. Braconnier, A. Maazzaz and P. Hagenmuller, *Rev. Chim. Min.*, 19, 343–351 (1982).

17) C. Delmas, J.-J. Braconnier and P. Hagenmuller, *Mater. Res. Bull.*, 17, 117–123 (1982).

18) A. Mendiboure, C. Delmas and P. Hagenmuller, *Mater. Res. Bull.*, 19, 1383–1392 (1984).

19) Z. Lu and J. R. Dahn, *Chem. Mater.*, 13, 1252–1257 (2001).

20) G. L. Messing, S. C. Zhang and G. V. Javanthi, *J. Am. Ceram. Soc.*, 76, 2707–2726 (1993).

21) T. Kodera, T. Ogihara, N. Ogata and K. Nakane, *J. Soc. Powder Technol., Japan*, 43, 348–354 (2006).

22) Z. Lu, R. A. Donaberger and J. R. Dahn, *Chem. Mater.*, 12, 3583–3590 (2000).