Crystal Structures and Electrode Performance of Alpha-NaFeO₂ for Rechargeable Sodium Batteries

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ABSTRACT

Single phase, well-crystallized O3-type NaFeO₂ (alpha NaFeO₂) is prepared by a solid-state method. Electrode performance of O3-type NaFeO₂ is examined as positive electrode materials for rechargeable sodium batteries. O3-type NaFeO₂ can deliver 80–100 mAh g⁻¹ of reversible capacity with a nearly flat voltage profile at approximately 3.3 V vs. Na metal. The electrode performance is significantly deteriorated by oxidation beyond $x > 0.5$ in Na_{1-x}FeO₂. X-ray diffraction study reveals that loss of electrode reversibility originates from irreversible structural change, possibly accompanied by iron ion migration in layered host structures. The sodium ion insertion into the host structures would be disturbed by the irreversible structural change when charged beyond $x > 0.5$ in Na_{1-x}FeO₂. Acceptable cyclability is, therefore, achieved for O3-type NaFeO₂ as the positive electrode materials in the limited composition of $x = 0$ –0.45 in Na_{1-x}FeO₂.

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Keywords : Sodium Insertion, Iron Oxides, Sodium Batteries

1. Introduction

The demand for large scale batteries is now rapidly growing, especially for the load leveling in electrical grids, and the temporary storage of electricity generated by solar cells and wind turbines as renewable energy resources.¹ The elemental abundance in the Earth's crust is of primary importance to design electrode materials for such large-scale applications. Sodium-sulfur (NAS) batteries, which are mainly composed of the abundant elements in the Earth's crust, have been studied and commercialized for this purpose. The available energy and power density of the NAS batteries are, however, lower than that of state-of-the-art rechargeable lithium batteries as energy storage devices,¹ which are now used for automobile applications. Additionally, lowering operating temperature (typically ~300°C for the NAS batteries) is needed to reduce potential safety risk relating to molten sodium metal.

Recently, our group has reported rechargeable sodium batteries (Na-ion batteries), consisting of two different sodium insertion materials without the metallic sodium, which are operable at room temperature.^{2,3} Its energy storage mechanism is essentially the same with the commercial rechargeable lithium batteries (Li-ion batteries), except that sodium ions are substituted for lithium ions, which is undoubtedly less abundant element (approximately 20 ppm in the Earth's crust) and in fact classified as a minor metal.

Research interest on the sodium insertion materials is now completely renewed under these circumstances, even though once a study for energy storage applications almost disappeared. After 2010, new sodium insertion materials have been reported for the battery applications,^{4–10} and some of known layered materials have been revisited.^{8,11–13} Electrode performance of alpha-type sodium iron dioxide, NaFeO₂,¹¹ known as a conventional layered oxide consisting of a cubic-closed packed oxygen array, has been first reported by Okada and coworkers as possible candidates for the rechargeable sodium batteries. Alpha NaFeO₂ is also classified as "O3-type" layered structure following Delmas' notation.¹⁴ Surprisingly, O3-type NaFeO₂ is electrochemically active in a sodium cell, whereas a lithium counterpart, O3-type LiFeO₂, is known to be electrochemically inactive in a lithium cell.¹⁵ O3-type NaFeO₂ can

deliver approximately 80 mAh g⁻¹ of reversible capacity with a flat operating voltage profile at 3.4 V in the Na cell.¹¹ Approximately 1/3 of sodium ions are reversibly extracted/re-inserted from/into the crystal lattice of Na_{1-x}FeO₂. Theoretical capacity of NaFeO₂ reaches 241.8 mAh g⁻¹, assuming the Fe³⁺/Fe⁴⁺ redox reaction in the solid matrix without the destruction of crystal lattice, i.e., topotactic reaction.¹⁶ Moreover, the operating voltage could exceed 3.4 V vs. Na metal based on the possible Fe³⁺/Fe⁴⁺ redox.⁴ On the basis of elemental abundance in the Earth's crust, iron-based electrode materials^{4,9–11,17} are the promising candidates as the electrode materials for the battery applications, and among them, O3-type NaFeO₂ is of the most interest as the sodium-based insertion materials from the viewpoint of both gravimetric and volumetric energy density. Nevertheless, to the best of our knowledge, a study on O3-type NaFeO₂ as the electrode materials in the sodium cell is limited to some reports by Okada and coworkers.^{4,11}

In this paper, we report a systematic study of cut-off voltage dependency on the electrode performance of O3-type NaFeO₂ in the sodium cells. We first demonstrate that electrode performance highly correlates with irreversible structural transition accompanied with iron migration process in the crystal lattice when cut-off voltage is raised above 3.5 V. From these results, we discuss a possibility of O3-type NaFeO₂ as positive electrode materials for rechargeable sodium batteries.

2. Experimental

O3-type NaFeO₂ was prepared by a solid-state reaction from stoichiometric amount of Na₂O₂ (Sigma-Aldrich Co.) and Fe₃O₄ (Kanto Chemical Co.), which were selected according to a method described by Takeda et al.¹⁸ The starting materials were mixed using a mortar and pestle, and then pressed into a pellet. The pellet was heated in an electric furnace at 650°C for 12 h in air. The pellet was taken out from the furnace at 650°C without a cooling process, and then immediately transferred into an argon-filled glove box. The pellet cooled to room temperature in the glove box and was kept inside to avoid contact with moisture in air.

Figure 1. (Color online) A result of Rietveld analysis on SXR diffraction pattern of O3-type NaFeO₂. A schematic illustration of the crystal structure for O3-type NaFeO₂ drawn using the program VESTA³¹ is also shown (inset). Particle morphology was observed by SEM with different magnifications (bottom).

A synchrotron X-ray diffraction pattern of as-prepared NaFeO₂ was collected in SPring-8 (BL02B2¹⁹). An X-ray wavelength was calibrated to be 0.501 Å using a CeO₂ standard. The sample was filled into a glass capillary ($\phi = 0.5$ mm). The glass capillary was sealed by using resin in the argon-filled glove box to eliminate the sample exposure to air. Structural analysis was carried out using RIETAN-FP.²⁰ Crystal structures of Na_xFeO₂ samples after electrochemical tests were examined by using an X-ray diffractometer (MultiFlex, Rigaku Co.) with Cu K α radiation without air exposure by using a laboratory made attachment. Morphological feature of the sample was observed by using a field emission scanning electron microscope (SUPRA40, Carl Zeiss AG).

Coin-type cells (R2032 type) were assembled in the argon filled glove box (chamber: $< -70^\circ\text{C}$) to evaluate electrode performance of NaFeO₂.² Positive electrodes consisted of 80 wt% NaFeO₂, 10 wt% acetylene black, and 10 wt% poly(vinylidene fluoride), which were mixed with N-methylpyrrolidone and pasted on Al foil as a current collector, and then dried at 80°C in vacuum. Metallic sodium is used as a negative electrode. Electrolyte solution used was 1.0 mol dm⁻³ NaClO₄ dissolved in propylene carbonate (Kishida Chemical Co.) with 2 vol% of fluoroethylene carbonate (FEC) as an electrolyte additive.²¹ A glass fiber filter (GB-100R, ADVANTEC Co.) was used as a separator.

3. Results and Discussion

A result of Rietveld analysis on a synchrotron X-ray diffraction (SXR) pattern of as-prepared NaFeO₂ is shown in Fig. 1. All of Bragg diffraction lines of NaFeO₂ are nicely assigned to the O3-type layered oxide (space group: $R\bar{3}m$) without any diffraction lines from impurity phases. The refined structural parameters are summarized

Table 1. Crystallographic parameters of O3-type NaFeO₂ refined by Rietveld analysis.

Space group: $R\bar{3}m$ (Hexagonal setting)						
$a_{\text{hex.}} = 3.025(1)$, $c_{\text{hex.}} = 16.112(3)$ Å						
$R_{\text{wp}} = 6.7\%$, $R_{\text{B}} = 2.7\%$.						
Atom	Wyckoff	g^*	x	y	z	$B/\text{\AA}^2$
Fe	3a	1.0	0	0	0	0.34(2)
Na	3b	1.0	0	0	0.5	0.88(5)
O	6c	1.0	0	0	0.2664(2)	0.40(2)

*not refined

Bond distance (Å)	
Na-O	2.374 ($\times 6$)
Fe-O	2.053 ($\times 6$)

in Table 1. Both R_{wp} and R_{B} , which are criteria of fit, are found to be reasonably small, indicating that the O3-type layered phase is the appropriate structural model for NaFeO₂. Both Fe and Na ions are accommodated at two distinct octahedral sites (3a and 3b sites in Table 1) in a distorted cubic-close-packed oxygen array. Interatomic distances of Fe-O and Na-O were calculated to be 2.05 and 2.37 Å on average, respectively. These values are also consistent with estimated values from the Shannon's ionic radii;²² 2.045 Å for Fe^{III}, O as a high-spin state and 2.42 Å for Na-O at the octahedral environment. As shown in Table 1, an isotropic displacement parameter of Na ions at 3b sites was refined to be 0.88 Å², which is a reasonably small value, suggesting that no vacancy exists at 3b sites in as-prepared NaFeO₂. Moreover, it is intuitively expected from the experimental observation that the intensity of (003)_{hex.} diffraction line, located at $2\theta = 5.3$ degrees, is clearly smaller than that of (104)_{hex.} diffraction line, located at $2\theta = 13$ degrees. Note that NaFeO₂ is easily damaged even by a trace of moisture in air, because of the proton ion-exchange for sodium and/or incorporation of water molecules between layers. The coexistence of two layered phases with peak profile broadening was observed by XRD after the exposure to air.

From the SEM observation, primary particle size of as-prepared NaFeO₂ ranges from approximately 0.5 to 1 μm, and the morphology is found to be rectangle-shaped particles. Synthesis at higher temperature ($> 650^\circ\text{C}$) easily resulted in growth of NaFeO₂ particles to several micrometers in size with plate-like morphology. In addition, the phase transition into beta-type NaFeO₂ as a high-temperature polymorph was observed above 760°C, which agrees with the previous result.²³

Electrochemical reversibility of sodium extraction/insertion processes for the single phase of O3-type NaFeO₂ was examined in aprotic sodium cells. The reversibility as the electrode materials is significantly influenced by cut-off conditions upon charge (sodium extraction) process as shown in Fig. 2. Although charging capacity, corresponding to the amount of sodium extracted from crystal lattice, increases as a function of the cut-off voltage, the reversible capacity obviously decreases when charged beyond 3.5 V. Excellent reversibility with small polarization was observed with the cut-off voltage of 3.4 V. Reversible capacity observed reaches 80 mAh g⁻¹, indicating that approximately 0.3 mole of Na is reversibly extracted from NaFeO₂ and inserted into the Na_{0.7}FeO₂ host structures as electrode materials. Charge/discharge current efficiency in the first cycle is calculated to be 83% when the Na cell is charged to 3.4 V, and increases to approximately 97% from 2nd cycles. Note that the charge/discharge current efficiency in the first cycle was significantly lower ($< 70\%$) when FEC-free electrolyte was used,

Figure 2. Initial charge/discharge curves of Na/NaFeO₂ cells with different cut-off voltage at a rate of 12 mA g⁻¹.

associated with the oxidation of sodium propyl carbonate generated at metallic Na electrode side.²¹ The reversibility seems to be gradually deteriorated by increasing cut-off voltage beyond 3.5 V. Polarization on electrochemical cycles drastically increases after charge to 4.0 V or higher, and thus reducing the reversible capacity. Approximately 70% of Na is extracted from O3-type NaFeO₂ by oxidation to 4.5 V by assuming that all current passed is consumed by the sodium extraction without any side reactions. The sample, however, becomes almost completely inactive as electrode materials as shown in Fig. 2.

The cyclability of O3-type NaFeO₂ with different cut-off voltage as electrode materials in sodium cells was further compared in Fig. 3. Na/NaFeO₂ cells were charged to different voltage of 3.4–4.5 V and then discharged to 2.5 V at a rate of 12.1 mA g⁻¹ [Fig. 3(a)]. When the cut-off voltage is limited to 3.4 V, relatively good capacity retention is found with 80 mAh g⁻¹ of initial reversible capacity. Reversible capacity retention reaches approximately 75% after 30 charge/discharge cycles as plotted in Fig. 3(b). The reversible capacity for first cycle increases to 100 mAh g⁻¹ by raising the cut-off voltage to 3.5 V. The capacity retention is, however, slightly worse compared with that of the 3.4 V cycle. Moreover, poor capacity retention is noted with the cut-off voltage of 4.0 V or higher, which is consistent with the data in Fig. 2.

To study a mechanism of the poor reversibility as electrode materials with higher cut-off voltage, changes in crystal structures were examined using an ex-situ X-ray diffraction (XRD) technique. Figure 4 compares XRD patterns of the electrochemically cycled Na_{1-x}FeO₂ electrodes in sodium cells with different cut-off voltage. All data in Fig. 4 were collected in the discharged state (2.5 V) after charge to 3.4, 4.0, or 4.5 V vs. Na metal. When the cut-off voltage is limited to 3.4 V, sodium ions are extracted reversibly based on the topotactic manner. Since intensity of (003)_{hex.} diffraction line increases relative to that of (104)_{hex.} diffraction line after the cycle test in a range between 3.4 and 2.5 V, some of sodium ion vacancies are formed at 3b octahedral sites. This fact is consistent with the observation of irreversible capacity (~15 mAh g⁻¹) in the initial charge/discharge cycle in Figs. 2 and 3(a). Such structurally (crystallographically) reversible process in this voltage range is also supported by the observation of relatively good capacity retention as shown in Fig. 3. For O3-type sodium layered compounds, O3-P3 phase transition is often observed during sodium extraction processes; $x > 0.1$ in Na_{1-x}MeO₂ (Me = Cr,²⁴ Mn,^{8,25} Co,²⁶ Ni,²⁴ Fe_{1/2}Mn_{1/2},¹⁰ and Ni_{1/2}Mn_{1/2}).²⁷ The phase transitions associated with the sodium/vacancy ordering in 3b sites result in stepwise voltage change (except Na[Fe_{1/2}Mn_{1/2}]O₂)¹⁰ by the galvanostatic oxidation/reduction. In contrast to these O3(O'3)-type layered

Figure 3. (a) Charge/discharge curves of the Na/NaFeO₂ cells with the different cut-off voltage at a rate of 12 mA g⁻¹. Discharge capacity retention for 30 cycles is compared in (b).

Figure 4. XRD patterns of Na_{1-x}FeO₂ composite electrodes before and after initial charge/discharge cycle with the different cut-off voltage. The electrodes were charged (oxidized) to 3.4, 4.0, or 4.5 V, and then discharged to 2.5 V at a rate of 12.1 mA g⁻¹.

materials, cell voltage of Na_{1-x}FeO₂ monotonically increases by sodium extraction as shown in Figs. 2 and 3. Takeda and coworkers reported sodium extraction process from Na_{1-x}FeO₂ ($0 < x < 1$) in “lithium” cells.²⁸ They have reported that formation of distorted O'3-type Na_{0.5}FeO₂ phase associated with the existence of Jahn-Teller active Fe⁴⁺ ions. They have also reported that two phases, seemingly O'3-type Na_{0.5}FeO₂ and O3-NaFeO₂, coexist during charge for $0 < x < 0.5$ in Na_{1-x}FeO₂.²⁸ In contrast, we did not

confirm the formation of distorted O'3-type $\text{Na}_{0.5}\text{FeO}_2$ during charge in sodium cells for $x < 0.5$ in $\text{Na}_{1-x}\text{FeO}_2$, and a single phase reaction was observed in a range of $0 < x < 0.5$ in $\text{Na}_{1-x}\text{FeO}_2$ (not shown). This inconsistency could simply originate from the difference in experimental conditions; Li vs. Na cells, because Li ions are, in part, possibly ion-exchanged for Na ions in Li cells.

It is noted that irreversible structural change is found when the charging voltage is raised above 4.0 V ($x > 0.5$ in $\text{Na}_{1-x}\text{FeO}_2$). Although irreversible capacity significantly increased by charge to 4.5 V (much more vacancies were presumably formed at 3b sites) in Figs. 2 and 3a, intensity of $(003)_{\text{hex}}$ diffraction line is clearly decreased in comparison to that of $(101)_{\text{hex}}$ and $(104)_{\text{hex}}$ diffraction lines. The results presumably suggest iron migration process from 3a to 6c (face-shared tetrahedral sites to 3a sites) and/or 3b (octahedral sites in Na layers) sites if we assume no oxygen release from samples. A sodium conduction path could suffer from the migration in the host structures, leading to the significant deterioration of the electrode performance. A similar phase transition, associated with the migration of transition metals to Na sites, was also reported in $\text{Na}_{1-x}\text{TiO}_2$.²⁹ In addition, the iron migration process upon charge was reported in the lithium system, e.g., $\text{Li}[\text{Co}_{1-x}\text{Fe}_x]\text{O}_2$.³⁰ From the results, we conclude that the suppression of irreversible structural change could be of primary importance to retain the electrode performance of iron-based layered materials. Indeed, such irreversible structural change was not observed in the O3-type $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and P2-type $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$.¹⁰ Systematic studies on the O3-type and P2-type iron-based layered materials are in progress in our group to further improve the energy density of rechargeable Na-ion batteries in the future.

4. Conclusions

We have prepared single phase and well-crystallized O3-type NaFeO_2 by a solid-state method. Electrode performance of O3-type NaFeO_2 was systematically examined by changing the cut-off voltage in sodium cells. When the cut-off voltage is limited to 3.4 V in sodium cells, Na/ NaFeO_2 cells show good capacity retention with 80 mAh g^{-1} of reversible capacity with nearly flat voltage profile at 3.3 V. The electrode reversibility is, however, significantly deteriorated by charge to higher voltage above 3.5 V. Ex-situ XRD studies suggest the irreversible structural change upon charge to high voltage, and thus the loss of Na conduction path in the host structures. The irreversible structural change restricts the reversibility of O3-type NaFeO_2 as electrode materials. The results shown in this paper provide some implications for the further development of NaFeO_2 -based electrode materials. The suppression of the irreversible phase transition, e.g., by metal substitution for iron, possibly improves the reversibility of NaFeO_2 -based electrode materials for Na-ion batteries.

Acknowledgments

This study was partly supported by NEXT Program of Japan Society for the Promotion of Science (JSPS) and Grant-in-Aid for

Young Scientists (B) (No. 24750186) from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT). The synchrotron X-ray diffraction experiments were made possible through the support of MEXT, Nanotechnology Support Project (Proposal No. 2011B1729) with the approval of Japan Synchrotron Radiation Research Institute (JASRI).

References

1. B. Dunn, H. Kamath, and J.-M. Tarascon, *Science*, **334**, 928 (2011).
2. S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, and K. Fujiwara, *Adv. Funct. Mater.*, **21**, 3859 (2011).
3. S. Komaba and N. Yabuuchi, *Electrochemistry*, **80**, 93 (2012).
4. S. Okada and J. Yamaki, in *Lithium Ion Rechargeable Batteries* (Ed. K. Ozawa), WILEY-VCH, Weinheim, p. 57 (2009).
5. N. Recham, J. N. Chotard, L. Dupont, K. Djellab, M. Armand, and J. M. Tarascon, *J. Electrochem. Soc.*, **156**, A993 (2009).
6. P. Senguttuvan, G. Rousse, V. Seznec, J.-M. Tarascon, and M. R. Palacin, *Chem. Mater.*, **23**, 4109 (2011).
7. D. Kim, S. H. Kang, M. Slater, S. Rood, J. T. Vaughan, N. Karan, M. Balasubramanian, and C. S. Johnson, *Adv. Energy Mater.*, **1**, 333 (2011).
8. S. I. Park, I. Gocheva, S. Okada, and J. Yamaki, *J. Electrochem. Soc.*, **158**, A1067 (2011).
9. Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai, and S. Komaba, *Electrochemistry*, **80**, 80 (2012).
10. N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, and S. Komaba, *Nat. Mater.*, **11**, 512 (2012).
11. S. Okada, Y. Takahashi, T. Kiyabu, T. Doi, J. Yamaki, and T. Nishida, *ECSS Meeting Abstracts*, **602**, 201 (2006).
12. S. Komaba, C. Takei, T. Nakayama, A. Ogata, and N. Yabuuchi, *Electrochem. Commun.*, **12**, 355 (2010).
13. C. Didier, M. Guignard, C. Denage, O. Szajwaj, S. Ito, I. Saadoun, J. Darriet, and C. Delmas, *Electrochem. Solid-State Lett.*, **14**, A75 (2011).
14. C. Delmas, C. Fouassier, and P. Hagenmuller, *Physica B+C*, **99**, 81 (1980).
15. K. Ado, M. Tabuchi, H. Kobayashi, H. Kageyama, O. Nakamura, Y. Inaba, R. Kanno, M. Takagi, and Y. Takeda, *J. Electrochem. Soc.*, **144**, L177 (1997).
16. T. Ohzuku and A. Ueda, *Solid State Ionics*, **69**, 201 (1994).
17. S. Komaba, T. Mikumo, and A. Ogata, *Electrochem. Commun.*, **10**, 1276 (2008).
18. Y. Takeda, J. Akagi, A. Edagawa, M. Inagaki, and S. Naka, *Mater. Res. Bull.*, **15**, 1167 (1980).
19. E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata, and N. Ikeda, *Nucl. Instrum. Methods Phys. Res., Sect. A-Accel. Spectrom. Deut. Assoc. Equip.*, **467–468**, 1045 (2001).
20. F. Izumi and K. Momma, *Solid State Phenom.*, **130**, 15 (2007).
21. S. Komaba, T. Ishikawa, N. Yabuuchi, W. Murata, A. Ito, and Y. Ohsawa, *ACS Appl. Mater. Interfaces*, **3**, 4165 (2011).
22. R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
23. J. Thery and Collongue, *Comptes Rendus Hebdomadaires Des Seances De L'Academie Des Sciences Serie C*, **247**, 2003 (1958).
24. J. J. Braconnier, C. Delmas, and P. Hagenmuller, *Mater. Res. Bull.*, **17**, 993 (1982).
25. A. Mendiboure, C. Delmas, and P. Hagenmuller, *J. Solid State Chem.*, **57**, 323 (1985).
26. C. Delmas, J. J. Braconnier, C. Fouassier, and P. Hagenmuller, *Solid State Ionics*, **3–4**, 165 (1981).
27. S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takada, A. Hokura, and I. Nakai, *ECSS Trans.*, **16(42)**, 43 (2009).
28. Y. Takeda, K. Nakahara, M. Nishijima, N. Imanishi, O. Yamamoto, M. Takano, and R. Kanno, *Mater. Res. Bull.*, **29**, 659 (1994).
29. A. Maazaz, C. Delmas, and P. Hagenmuller, *J. Inclusion Phenom. Macrocyclic Chem.*, **1**, 45 (1983).
30. H. Kobayashi, H. Shigemura, M. Tabuchi, H. Sakaebe, K. Ado, H. Kageyama, A. Hirano, R. Kanno, M. Wakita, S. Morimoto, and S. Nasu, *J. Electrochem. Soc.*, **147**, 960 (2000).
31. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, **41**, 653 (2008).