Mechanism of the Na-substituted Spinel Phase Generation in a Li$_4$Ti$_5$O$_{12}$ Electrode via Sodium-ion Battery Cycling

Mitsunori KITTA* and Masanori KOHYAMA

Research Institute of Electrochemical Energy, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

* Corresponding author: m-kitta@aist.go.jp

ABSTRACT

Spinel lithium titanate (LTO; Li$_4$Ti$_5$O$_{12}$) attracts much attention as a negative electrode material for a sodium-ion battery (SIB), while large volume changes in Na-insertion and extraction processes prevent practical applications of LTO-based electrodes. It is desirable to form a Na-substituted LTO phase as (Na$_3$)$_{8a}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$, which is expected to show excellent performance in a SIB, due to a small volume change from a Na-inserted phase (Na$_6$)$_{16c}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$, analogous to a strain-free LTO electrode in a LIB. In this work, we have discovered that such a Na-substituted phase is really formed via the discharge (Na-extraction) process from a Na-inserted LTO electrode consisting of two phases as (Na$_6$)$_{16c}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$ and (Li$_6$)$_{16c}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$. The Na-substituted phase generation occurs by the discharge with a high current density about 10 C rate, which induces high electrochemical polarization, exceeding the Li-extraction electrochemical potential in the discharging cell voltage. Thus both the Na-substituted LTO and pure LTO phases are formed due to the extraction of both Na$^+$ and Li$^+$ ions as an electrochemical equilibrium process. The present finding is a significant step toward practical application of the LTO-based electrode in a SIB.

© The Electrochemical Society of Japan, All rights reserved.

Keywords: Sodium-ion Battery, Li$_4$Ti$_5$O$_{12}$ Electrode, Na$_3$LiTi$_5$O$_{12}$ Phase Generation

1. Introduction

Spinel-type lithium titanate (LTO; Li$_4$Ti$_5$O$_{12}$) is widely used as a negative electrode material for lithium-ion batteries (LIBs), due to stable Li-insertion and extraction cycles with high-current density.\(^1^3\) This excellent electrochemical performance is originated from the structural stability of a LTO bulk crystal during Li insertion and extraction, expressed as follows.\(^4^5\)

$$\text{Spinel-Li}_3\text{Ti}_3\text{O}_4\rightarrow\text{Ordered rock-salt-Li}_2\text{Ti}_5\text{O}_4+(3\text{Li}^+ + 3\text{e}^-)$$

where superscripts of 8a, 16d, 16c and 32e represent the Wycko sites of spinel (Fd-3m) space group. In this process, only the Wycko site of Li$^+$ is altered and the basic-spinel framework is almost fixed with negligible lattice-volume changes, leading to the excellent electrode performance in a LIB.

Recently, LTO attracts much attention as an electrode material not only for a LIB but also for a sodium-ion battery (SIB).\(^5^10\) due to its high safety character such as non-flammable and no Na-metal deposition.\(^11^12\) Further, it shows flat electrochemical potential of Na insertion and extraction at 0.7–0.9 V vs. Na$^+$/Na, which is lower than the Li-insertion and extraction potential of 1.2–1.3 V vs. Na$^+$/Na (for 1.6–1.5 V vs. Li$^+$/Li). This lower electrochemical potential of Na insertion-extraction is beneficial for a negative electrode, and enables us to assemble 2 V-class sodium-ion cells\(^11^12\) as the same as a Li-ion cell using a LTO negative electrode.\(^5^13\)

Thus studies of LTO as an electrode material for a SIB are highly desired. Structural characterization such as ex-situ and in-situ X-ray diffraction (XRD)\(^5^14^15\) and microscopic observation\(^5^16\) was applied to LTO electrodes with Na insertion and extraction. It was revealed by XRD studies that the Na insertion in a LTO electrode leads to the separation into Na-rich and Li-rich phases, of which the mechanism is explained as follows.\(^5^14\)

$$2\text{(Li)}_{36}\text{(LiTi}_5\text{)}_{16d}\text{(O}_{12}\text{)}_{32e} + 6\text{Na}^+ + 6\text{e}^- \rightarrow \text{(Li)}_{36}\text{(LiTi}_5\text{)}_{16d}\text{(O}_{12}\text{)}_{32e} + (\text{Na})_{16c}\text{(LiTi}_5\text{)}_{16d}\text{(O}_{12}\text{)}_{32e}$$

The Na-rich phase, (Na$_6$)$_{16c}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$, was confirmed as a Fd-3m based ordered rock-salt phase with a larger lattice constant, \(a = 8.72\ \text{Å} \).\(^5^14\) The two-phase separation feature was also confirmed by high-resolution transmission electron microscopy observation.\(^5^17\) In contrast, for the Na-extraction process from a Na-inserted LTO electrode, two types of reactions were observed. Na-inserted LTO was completely reverted to a pure LTO phase in some studies,\(^6^14^15^17\) while a Na-contained spinel phase was partly generated irreversibly from Na-inserted LTO in other studies.\(^12^18\) The former means only Na ions participate in the oxidation reaction of Na-inserted LTO, and the latter means both Li and Na ions participate in the oxidation. Of course, the occurrence of each type of reaction should depend on some reaction conditions, and the understanding on such conditions is crucial because the Na-extraction reaction seriously affects successive electrochemical reactions in the SIB cycles. However, the mechanism of the Na-extraction reaction and the conditions dominating the reaction mode have not yet investigated clearly.

In the present study, we investigate the Na-extraction reaction for a Na-inserted LTO electrode during electrochemical SIB cycling by using XRD characterization. Especially, we focus on the effects of discharge (Na-extraction) rates ranging from 0.1 C to 10 C. As will be shown, we have found that resultant phases after the Na extraction are seriously dependent on the discharge rate. This rate-dependent feature is analyzed by the competitive extraction of Na and Li, dominated by the discharge voltage profiles. We have also found that a high discharge rate generates a Na-substituted LTO phase as (Na$_3$)$_{8a}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$ with a lattice constant similar to that of the Na-inserted phase (Na$_6$)$_{16c}$(LiTi$_5$)$_{16d}$(O$_{12}$)$_{32e}$, which is expected to show excellent performance in a SIB, due to a small lattice-volume change in Na-insertion and extraction, analogous to the strain-free LTO electrode for a LIB.
2. Experimental

Li4Ti5O12 electrode material, ENERMIGHT® LT-106, was purchased by ISIHARA SANGYO KAISHA, LTD. The Basic properties of the LTO powder are presented in elsewhere (https://www.iskweb.co.jp/eng/products/battery.html). Then the active material (LTO), acetylene black (AB) and PolyVinylidene DiFluoride (PVDF) were mixed at weight ratio of 90:5:5 and dispersed in N-methylpyrrolidone solvent to form the electrode slurry. The composite slurry was mounted on aluminum foil and dried in a dry-air filled box (−80°C d.p.) for 3 days. The electrode sheet was punched out for φ16 mm of disk. The SIB was assembled by a test-type cell (HS-cell, Hoshen Corp.) with an LTO sheet as a positive electrode and Na-metal foil as a negative electrode. 1 M NaPF6 dissolved in mixed carbonate solvent [ethylene carbonate (EC): diethyl carbonate (DEC) = 1:1] was used for electrolyte. Electrodes were separated by a micro-porous polypropylene film and a glass-filter. All the cell assembling was performed under dry-air atmosphere (−80°C d.p.). Electrochemical experiments were performed by a BLS charge/discharge system (Keisokuki Center). As-assembled cells show 2.2–2.5 V of open circuit potential. Then the cells were charged (Na-insertion) to 0.3 V with 0.1 C of constant current (CC) experiment and held at 0.3 V with constant voltage (CV) experiment until the charge capacity was reached over 150 mAh g−1 to complete the Na insertion. For the Na-extraction experiment, we examined three types of different discharge rates such as A) discharged at 2.0 V for 0.1 C rate with CC-mode then held at 2.0 V with CV-mode, B) discharged at 2.0 V for 1.0 C rate and held to 2.0 V, and C) discharged at 2.0 V for 10 C rate and held at 2.0 V. Total discharge capacity was reached up to 150 mAh g−1 for all the cells.

After the electrochemical experiment, cells were dismantled in dry-air atmosphere, and LTO electrodes were washed with dimethyl carbonate (DMC) solvent to eliminate the electrolyte component. Then LTO electrodes were well dried and pasted on the sample holder of XRD measurement. The XRD experiment was performed by desktop type X-ray diffractometer (MiniFlex 600R, Rigaku) with Cu-Ka X-ray source (λ1 = 1.54059 Å and λ2 = 1.54432 Å) in 0.03 deg of scan step. The measurement was performed in the air atmosphere and 15 deg−75 deg of scan range with 1 deg min−1 of scan rate for 20 cycles. All the XRD data were averaged with 20 cycle scanning. Powder diffraction simulation was performed by VESTA program.19

3. Results and Discussion

Figure 1 shows XRD spectra of Na-extracted LTO electrodes with various discharge rates. Blue, green and red solid lines represent the results by discharge rates of 0.1 C, 1 C and 10 C, respectively. Clear sharp peaks assigned as an ordinary LTO (Li4Ti5O12) phase can be observed in all the samples at similar diffraction angles, as indicated by black dot lines, which means that all the resultant LTO electrodes contain the Li4Ti5O12 phase with a fixed lattice constant (a = 8.36 Å). These peak positions are in good agreement with the powder diffraction simulation of a pure LTO (Li4Ti5O12) phase.11,12,14-16 The lattice volume of all the resultant LTO electrodes are not common in the three samples. In the sample with the discharge rate of 0.1 C, the side peaks are almost negligible, except for only slight shoulders at some peaks. Hence, the Na extraction from the Na-inserted LTO electrode with the discharge rate of 0.1 C leads to the recovery of almost pure Li4Ti5O12 phase, as previously reported.11,14-16 For the sample with the discharge rate of 1 C, these shoulders at the lower-angle sides are substantially enhanced, which means the presence of local lattice expansion in LTO by some mixture of Na+ ions as discussed later.

However, the features of the lower-angle side of each LTO peak are greatly different for the sample with the discharge rate of 10 C. There clearly exist new peaks, marked by arrows, positioned at all the lower 2θ angle side of the LTO diffraction. These sharp peaks are originated from a definite spinel phase with a larger lattice constant than that of LTO, which was correctly calculated as a = 8.69 Å for spinel Fd-3m pattern fitting of their diffraction peak positions. In previous work, we observed generation of Na-contained spinel phases with various lattice constants in the range of a = 8.45–8.50 Å during SIB cycles.18 However, the present phase has an apparently fixed value of the lattice constant, 2–3% larger than previously reported, indicating that the present phase contains more amount of Na with a rather fixed composition. Therefore the present Na-contained spinel phase should be a newly found one, and completely different from the Na-contained phases and any other Na-doped LTO phase as previously reported.18-25 In the XRD pattern of this sample, the 220 diffraction peak is more clearly observed for the new Na-contained phase than the other Li4Ti5O12 phase. As the 220 diffraction of spinel structure is originated only from the ordering of 8a site species, this feature indicates that the spinel 8a site of this new phase should be occupied by some element with a larger X-ray scattering factor, instead of Li. Generally, titanium cations hardly occupy oxygen 8a tetrahedral sites, and therefore we can conclude that the spinel 8a site of this phase is occupied by Na+, as a Na-substituted spinel phase of (Na13)8a(Li16dTi5)32e(O12)32e. A powder diffraction simulation pattern of (Na13)8a(Li16dTi5)32e(O12)32e, provided by VESTA, is also shown by magenta solid lines. The parameters of this crystal model are provided in Fig. S1 in Supporting Information (SI). The agreement between the simulated (magenta) and observed (red) peak profiles proves that the Na-substituted spinel phase, (Na13)8a(Li16dTi5)32e(O12)32e, is really formed. Interestingly, the lattice constant of the present Na-substituted phase (a = 8.69 Å) is rather similar to that of the Na-inserted phase (Na8.72a(Li16dTi5)32e(O12)32e (a = 8.72 Å),14 The lattice volume difference is almost 1%, indicating that the (Na13)8a(Li16dTi5)32e(O12)32e phase would possibly work as an electrode showing strain-free Na insertion and extraction in a SIB, just like the LTO electrode in a LIB. Of course, the Na-substituted phase is an oxidized phase containing only Ti4+, in contrast to the Na-inserted phase as a reduced phase with both Ti3+ and Ti4+.
and Ti$^{4+}$. Indeed, the Na-substituted phase was stable under air-atmosphere for 20 hours in XRD measurement, while the Na-inserted phase was quickly disappeared in the same condition, as shown in Fig. S2 in SI.

In Fig. 1, the XRD pattern of the sample with the discharge rate of 1 C shows apparent shoulder peaks at the lower-angle side of each LTO peak, indicating that the discharge rate of 1 C leads to a Na-contained spinel phase with various lattice constants around $a = 8.48$–8.67 Å. This Na-contained phase should not be the same as that formed by the discharge rate of 10 C, because broadened shoulders of the LTO peaks indicate inhomogeneous expansion of the LTO lattice due to locally varied Na-ion contents, quite differently from the definite Na-substituted phase with the larger lattice constant of $a = 8.69$ Å. It seems that the Na-extraction rate of 1 C generates a solid-solution like phase expressed as $(Na, Li)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$. The variations of the resultant phases by the Na extraction, remarkably depending on the discharge rate, should be concerned with the oxidation process of the Na-inserted LTO electrode, initially consisting of the two phases as $(Li)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$ and $(Na)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$. The oxidation process means the removal of electrons to change Ti$^{3+}$ into Ti$^{4+}$ for 60% of total amount of Ti ions in each phase, which is compensated by the removal of Na$^+$ or Li$^+$, and the sum of amounts of removed Na$^+$ or Li$^+$ ions corresponds to the total amount of removed electrons. Here the competitive Li-extraction is possible even in the SIB cell as discussed later. Thus if a substantial amount of Li$^+$ is extracted, we obtain the Na-contained or Na-substituted LTO phases. The Li-extraction from a Na-inserted LTO electrode should be dominated by the electrochemical potential of Li-extraction reaction. Generally the Li-extraction potential in a LIB cell is 1.5–1.6 V vs. Li$^+$/Li, which is equal to 1.2–1.3 V vs. Na$^+$/Na for a SIB cell. Note that the standard electrode potentials of Li and Na are $E_{Li} = -3.03$ V and $E_{Na} = -2.713$ V, and the electrochemical potential of electrode materials is about 0.32 V lower in a SIB half-cell than in a LIB half-cell. Therefore, when the voltage profile of discharge is higher than 1.2 V, both Li and Na ions should be extracted, competitively.

Figure 2 shows the discharge voltage profiles for various discharge rates. A black dot line shows the Li-extraction potential, 1.2 V in a SIB cell. Na-extracting potential, 0.75 V vs. Na$^+$/Na was also shown as dot line in Fig. 2. In the profile of the discharge rate of 0.1 C, shown by a blue solid line, the voltage is lower than 1.2 V in the most region of discharge capacity. Therefore at this discharge rate, Na$^+$ ions should be mainly extracted from the Na-inserted LTO electrode, resulting in the recovery of the pure LTO phase with negligible Na-contained phases, as observed in the XRD pattern in Fig. 1. For the discharge rate of 1 C, the voltage profile is below 1.2 V for the first half region of capacity, and exceeds it for the latter half. This means that Na$^+$ ions are mainly extracted in the former process, while both Li$^+$ and Na$^+$ ions are competitively extracted in the latter process. Thus, the solid-solution like Na-contained phase $(Na, Li)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$ as well as the LTO phase are generated in the LTO electrode as shown in Fig. 1. For the discharge rate of 10 C, the voltage profile exceeds the electrochemical potential of Li-extraction during the whole process, meaning that 10 C rate current density should easily induce electrochemical polarization of Li-extraction for the whole discharge capacity region. Therefore, both Li$^+$ and Na$^+$ are extracted from the Na-inserted LTO electrode in whole the process of discharge, leading to the clear generation of both $(Na_3)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$ and $(Li_3)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$ phases from the initial two phases $(Li_3)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$ and $(Na_3)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$, respectively, as confirmed in the XRD pattern. We performed pattern fitting of the XRD data of 10 C rate discharged sample of Fig. 1 with the two basic crystal models described in Fig. S1 in SI. Components of Li$_5$Ti$_3$O$_9$ and Na-substituted phases were 52% and 48%, respectively. This means that almost equal amounts of Li and Na ions were extracted during the discharging process, because the amounts of initial two phases in the Na-inserted LTO electrode are estimated to be equal.6,14 We would like to emphasize that the dominant factor to decide the resultant phases is the relation between the discharge voltage profile and the Li-extraction potential for a LTO electrode in a SIB cells. Actually, as shown in Fig. S3 in SI, no Na-contained phase was confirmed in the XRD pattern for a sample discharged by a constant voltage below the electrochemical potential of Li-extraction, (1.1 V vs. Na$^+$/Na). This means that no Li-extraction should occur in this voltage condition. A low discharge voltage below the Li-extraction potential leads to only the Na-ion extraction. Only when the discharge voltage exceeds the Li-extraction potential, there occurs both Na$^+$ and Li$^+$ ion extraction, leading to the Na-substituted spinel LTO phase generation in the half part of the crystal. Thus the present reaction is understood as a thermodynamical equilibrium one, instead of a rate-dependent one.

The mechanism to decide the resultant phases via various discharge rates from a Na-inserted LTO single particle is summarized in Fig. 3. In the low-rate discharge process as 0.1 C, shown in Fig. 3(a), the voltage profile is lower than the Li-extraction potential, and thus only Na extraction occurs. Na$^+$ ions are extracted from the initial Na-rich phase, $(Na_3)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$ (abbreviated as Na$_3$), in the Na-inserted LTO, and Li$^+$ ions migrate from the Li-rich phase, $(Li_3)_{16c}(LiTi_5)_{16d}(O_{12})_{32e}$ (abbreviated as Li$_3$), toward the Na-contained phase. Finally all the phases become oxidized LTO phases as $(Li_3)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$ (abbreviated as Li$_3$, as previously reported.6,14 In the middle-rate discharge process as 1 C, shown in Fig. 3(b), the discharge voltage is lower than the Li-extraction potential in the latter half of the process. Thus initially Na extraction occurs dominantly, while both Na$^+$ and Li$^+$ ions are extracted in the latter half of the process. Differently from the case of Fig. 3(a), Na$^+$ ions remain in the initial Na-rich phase, and a solid-solution like phase as $(Na, Li)_{38a}(LiTi_5)_{16d}(O_{12})_{32e}$ is formed there, while the initial Li-rich phase becomes the oxidized LTO phase (Li$_3$ phase), due to the Li-extraction or migration toward the Na-contained phase. The distribution of remained Na$^+$ ions should be inhomogeneous, leading to a broadened range of expansion in the Na-contained regions as observed in Fig. 1. For the fast discharge rate (10 C) as shown in Fig. 3(c), the voltage exceeds the Li-extraction potential from the initial stage of oxidation, and thus both Li$^+$ and Na$^+$ ions are extracted from the Li$_3$ and Na$_3$ phases, respectively, during the whole process, leading to the generation of Li$_3$ and $(Na_3)_{8a}(LiTi_5)_{16d}(O_{12})_{32e}$ (abbreviated as Na$_3$) phases with keeping

**Figure 2.** Cell voltage profiles of discharge process. Blue, green and red solid lines show the processes with discharge rates of 0.1 C, 1 C and 10 C, respectively. All the discharge profiles were held at 2.0 V vs. Na$^+$/Na till the discharge capacity reached 150 mAh g$^{-1}$. A black dot lines show the Li$^+$ and Na$^+$ extraction potential in a Na-ion half-cell.
Na+, Na+, Li+

blue and red colors, respectively. Resultant (Li3)8a(LiTi5)16d(O12)32e extraction of both Li+(Na6)16c(LiTi5)16d(O12)32e (abbreviated as Li6 and Na6), are shown by high current density, and the potential pro much higher electrochemical polarization should be induced under a XRD pattern in Fig.1. If we operated much higher discharge rate, a con with the powder di was clearly observed in addition to the LTO phase. Comparing extra new phase with a larger lattice constant than LTO, peak. For the sample with a high discharge rate of 10 C, however, an causing broadened shoulders at the lower-angle side of each LTO phases, with various discharge rates by using XRD measurement.

For the sample with a slow discharge rate of 0.1 C, the XRD pattern inserted LTO electrode, consisting of Na-rich and Li-rich spinel was clearly observed in addition to the LTO phase. Comparing extra new phase with a larger lattice constant than LTO, peak. For the sample with a high discharge rate of 10 C, however, an causing broadened shoulders at the lower-angle side of each LTO phases, with various discharge rates by using XRD measurement.

Figure 3. Mechanism of various phase generation by Na extraction from a Na-inserted LTO single particle via sodium-ion battery cycling. Discharge processes with a low rate (0.1 C), a middle rate (1.0 C) and a fast rate (10 C) are presented in (a), (b) and (c), respectively. Initial two phases, (Li6)16c(LiTi5)16d(O12)32e and Li6 Na6 (abbreviated as Li6 and Na6), are shown by blue and red colors, respectively. Resultant (Li3)8a(LiTi5)16d(O12)32e and (Na3)8a(LiTi5)16d(O12)32e phases (abbreviated as Li3 and Na3) are shown by light cyan and magenta colors, respectively.

the initial two-phase distribution. Therefore, the clear phase separation between the Li3 and Na3 phases was observed in the XRD pattern in Fig. 1. If we operated much higher discharge rate, a much higher electrochemical polarization should be induced under a high current density, and the potential profile quite easily exceeds the Li-extraction potential (1.2 V vs. Na+/Na) leading to easy extraction of both Li+ and Na+ ions in a wider discharge capacity region, resulting in the Na-substituted phase generation.

4. Conclusions
We have studied the Na-extraction mechanism from a Na-inserted LTO electrode, consisting of Na-rich and Li-rich spinel phases, with various discharge rates by using XRD measurement. For the sample with a slow discharge rate of 0.1 C, the XRD pattern showed the presence of an ordinary LTO phase with negligible Na-contained phases, indicating an almost reversible reaction. For the sample with a moderate discharge rate of 1 C, a solid-solution like Na-contained phase was observed in addition to the LTO phase, causing broadened shoulders at the lower-angle side of each LTO peak. For the sample with a high discharge rate of 10 C, however, an extra new phase with a larger lattice constant than LTO, a = 8.69 Å, was clearly observed in addition to the LTO phase. Comparing with the powder diffraction pattern simulation, this extra phase was confirmed as a Na-substituted phase with (Na3)8a(LiTi5)16d(O12)32e structure, never been reported. The present phenomena are essentially dominated by the voltage profile, depending on the discharge rate, to decide extracted alkali species, because of different electrochemical potential for Li+ and Na+ in a SIB cells. Thus the present phenomenon is understood as a thermodynamic equilibrium one, instead of a rate-dependent one. The present results should contribute to preparing various LTO electrodes with various phases via SIB cycling. Especially, the finding of generation of the Na-substituted spinel phase with 8a-site substitution is significant, because this phase is expected to show excellent performance in a SIB, due to the small volume change from the Na-inserted phase, (Na3)8a(LiTi5)16d(O12)32e, analogous to the strain-free LTO electrode in a LIB. Of course, we have to settle several issues to prepare the pure phase and to practically apply it to a SIB, which will be reported in the near future.

Supporting Information
The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.18-00029.

Acknowledgments
The authors thanks Dr. Nobuhiko Takechi (AIST) for XRD analysis and also thanks Dr. Riki Kataoka (AIST) and Chie Fukada (AIST) for beneficial assistance of electrode preparation and XRD measurement.

References
1. M. Majima, S. Ujije, E. Yagasaki, K. Koyama, and S. Inazawa, J. Power Sources, 101, 53 (2001).
2. K. Nakahara, R. Nakajima, T. Matsushima, and H. Majima, J. Power Sources, 117, 331 (2003).
3. N. Takami, H. Inagaki, Y. Tatebayashi, H. Saruwatari, K. Honda, and S. Egusa, J. Power Sources, 244, 469 (2013).
4. T. Ohnuki, A. Ueda, and N. Yamamoto, J. Electrochem. Soc., 142, 1431 (1995).
5. K. Ariyoshi, R. Yamato, and T. Ohnuki, Electrochem. Acta, 51, 1125 (2005).
6. L. Zhao, H.-L. Pan, Y.-S. Hu, H. Li, and L.-Q. Chen, Chin. Phys. B, 21, 028201 (2012).
7. M. Dahlbä, N. Yabuuchi, K. Kubota, K. Tokiwa, and S. Komaba, Phys. Chem. Chem. Phys., 16, 15007 (2014).
8. N. Yabuuchi, K. Kubota, M. Dahlbä, and S. Komaba, Chem. Rev., 114, 11636 (2014).
9. H. Kim, H. Kim, Z. Ding, M. H. Lee, K. Lim, G. Yoon, and K. Kang, Adv. Energy Mater., 6, 1600943 (2016).
10. J.-Y. Hwang, S.-T. Myung, and Y.-K. Sun, Chem. Soc. Rev., 46, 3529 (2017).
11. M. Kitta, K. Kuratani, M. Tabuchi, R. Kataoka, T. Kiyobayashi, and M. Kohyama, Electrochemistry, 83, 899 (2015).
12. S. Ivanova, E. Zhecheva, R. Kukeva, N. Dhiptanov, L. Mihaylov, G. Atanasova, and R. Stoyanova, ACS Appl. Mater. Interfaces, 8, 17321 (2016).
13. N. Takami, H. Inagaki, Y. Harada, Y. Fujita, and K. Hoshina, J. Electrochem. Soc., 156, A128 (2009).
14. Y. Sun, L. Zhao, H. Pan, X. Lu, L.-G. Wang, Y.-S. Hu, H. Li, M. Armand, Y. Ikukara, L. Chen, and X. Huang, Nat. Commun., 4, 1870 (2013).
15. Y. Yu, H. Pan, W. Fan, C. Ma, J. Bai, Q. Meng, S. N. Ehrlich, Y.-S. Hu, and X.-Q. Yang, Nano Lett., 13, 4721 (2013).
16. K.-T. Kim, C.-Y. Yu, C.-S. Yoon, S.-J. Kim, Y.-K. Sun, and S.-T. Myung, Nano Energy, 12, 725 (2015).
17. M. Kitta, R. Kataoka, and M. Kohyama, Phys. Chem. Chem. Phys., 18, 19888 (2016).
18. M. Kitta, K. Kuratani, M. Tabuchi, N. Takechi, T. Akita, T. Kiyobayashi, and M. Kohyama, Electrochim. Acta, 148, 175 (2014).
19. K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272 (2011).
20. S.-H. Lee, H.-K. Kim, Y.-S. Yun, J. R. Yoon, S.-G. Lee, and Y.-H. Lee, Int. J. Hydrogen Energy, 39, 16569 (2014).
21. C. W. Xiao, Y. Ding, J. T. Zhang, X. Q. Su, G. R. Li, X. P. Gao, and P. W. Shen, J. Power Sources, 248, 323 (2014).
22. T.-F. Yi, S.-Y. Yang, X.-Y. Li, J.-H. Yao, Y.-R. Zhu, and R.-S. Zhu, J. Power Sources, 246, 505 (2014).
23. Z. Liu, L. Sun, W. Yang, J. Wang, S. Han, D. Chen, Y. Liu, and X. Liu, Solid State Sci., 44, 39 (2015).
24. P. Lu, X. Huang, Y. Ren, J. Ding, H. Wang, S. Zhou, Y. Chenc, and X. Ding, RSC Adv., 6, 90455 (2016).
25. F. Zhao, P. Xue, H. Ge, L. Li, and B. Wang, J. Electrochem. Soc., 163, A690 (2016).