



A series of zero-strain lithium insertion materials that undergo a non-topotactic reaction

Kazuhiko Mukai

Toyota Central Research & Development Laboratories, Inc., 41–1 Yokomichi, Nagakute, Aichi 480–1192, Japan



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ABSTRACT

Lithium titanium oxide spinel, $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO), is a zero-strain lithium insertion material, which indicates a virtually 0% change in lattice volume (ΔV) during the electrochemical reaction. We have performed systematic structural and electrochemical studies on $\text{Li}_{1/2+x/2}\text{Fe}_{5/2-3x/2}\text{Ti}_x\text{O}_4$ (LFTO) with $0 \leq x \leq 1.666$, where the LFTO formula forms a series of spinel compounds with $\text{Fe}[\text{Li}_{1/2}\text{Fe}_{3/2}]\text{O}_4$ and LTO via $\text{Li}_{1/2}\text{Fe}_{1/2}[\text{Li}_{1/2}\text{Fe}_{1/2}\text{Ti}]\text{O}_4$. The LFTO samples with $x < 0.875$ underwent a typical conversion reaction with large discharge capacities above $\sim 500 \text{ mAh g}^{-1}$, similar to nano-sized metal oxides. The LFTO samples with $0.875 \leq x < 1.666$ maintained their cubic lattice parameter (a_c) during the discharge and charge reactions. Since the Δa_c and ΔV values were lower than +0.2 and +0.5%, respectively, these LFTO samples are also regarded as zero-strain lithium insertion materials. Surprisingly, ex situ X-ray diffraction measurements revealed a reversible decrease/increase in the intensities of the 111 and 311 diffraction lines, indicating that Fe ions shuttle back and forth between the tetrahedral and octahedral sites of the spinel lattice. This reaction scheme differs from the so-called topotactic reaction, where only Li^+ ions are mobile and transition metal ions are immobile. Details of the non-topotactic reaction for LFTO are presented.

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1. Introduction

Lithium insertion materials for lithium-ion batteries (LIBs) are characterized by the ability to perform the reversible extraction/insertion of Li^+ ions, delivering or storing electricity, without destruction of their framework structures. Such reaction is called as “shuttlecock” or “rocking chair” in the early 1990s, however, the term “topotactic” is now widely accepted among LIB researchers [1–3]. Owing to the topotactic reaction, LIBs can be cycled more than one thousand times [1,4].

One lithium insertion material, $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO), crystallizes into a spinel structure with the formula $(\text{A})_{\text{tet}}[\text{B}_2]_{\text{oct}}\text{O}_4$ (SG: $Fd\bar{3}m$), in which the tetrahedral (tet) A site is occupied by Li^+ ions, and the octahedral (oct) B site is occupied by both Li^+ and Ti^{4+} ions (Fig. 1) [5–7]. In addition to the topotactic reaction, LTO exhibits a “zero-strain” character [7]; i.e., the change in lattice volume (ΔV) is virtually 0% during the charge and discharge reactions. The ΔV value of LTO is exceptionally small, compared with ΔV s of typical lithium insertion materials, such as LiCoO_2 and artificial graphite,

which display values for ΔV s of the order of $\sim 10\%$ [8–10]. X-ray diffraction (XRD) measurements and Raman spectroscopy clarified that the zero-strain character of LTO is achieved by local structural changes in the LiO_6 and TiO_6 octahedra [11–13].

Besides LTO, $\text{Li}[\text{CrTi}]\text{O}_4$ [14,15] and LiFeTiO_4 [15] are also zero-strain lithium insertion materials. In particular, the actual formula of LiFeTiO_4 is represented by $(\text{Li}_{1/2}\text{Fe}_{1/2})_{\text{tet}}[\text{Li}_{1/2}\text{Fe}_{1/2}\text{Ti}]_{\text{oct}}\text{O}_4$, and is characterized as the lithium insertion material that undergoes a “non-topotactic” reaction [15]. In the crystal lattice of LiFeTiO_4 , the A site is occupied by Li^+ and Fe^{3+} ions, whereas the B site is occupied by Li^+ , Fe^{3+} , and Ti^{4+} ions (Fig. 1) [15]. Since Li^+ ions are inserted into the spinel lattice through the A (tet) \rightarrow vacant octahedral site \rightarrow A (tet) pathway [12,13], the presence of immobile Fe^{3+} ions in the A site is expected to inhibit the insertion of Li^+ ions. However, as evidenced by XRD measurements, the Fe^{3+} ions in the A site are also mobile, providing the conduction pathway for the insertion of Li^+ ions into the lattice [15]. This reaction scheme is different from that of a topotactic process, where only Li^+ ions are mobile, whereas transition metal ions are immobile [1,3].

LiFeTiO_4 forms two series of spinel compounds with LTO and $\text{Fe}[\text{Li}_{1/2}\text{Fe}_{3/2}]\text{O}_4$ (LiFe_5O_8), respectively [16,17]; namely, compounds with the composition $(\text{Li}_{3x/4-1/4}\text{Fe}_{5/4-3x/4})_{\text{tet}}[\text{Li}_{3/4-x/4}\text{Fe}_{5/4-3x/4}]_{\text{oct}}\text{O}_4$.

E-mail address: e1089@mosk.tytlabs.co.jp.

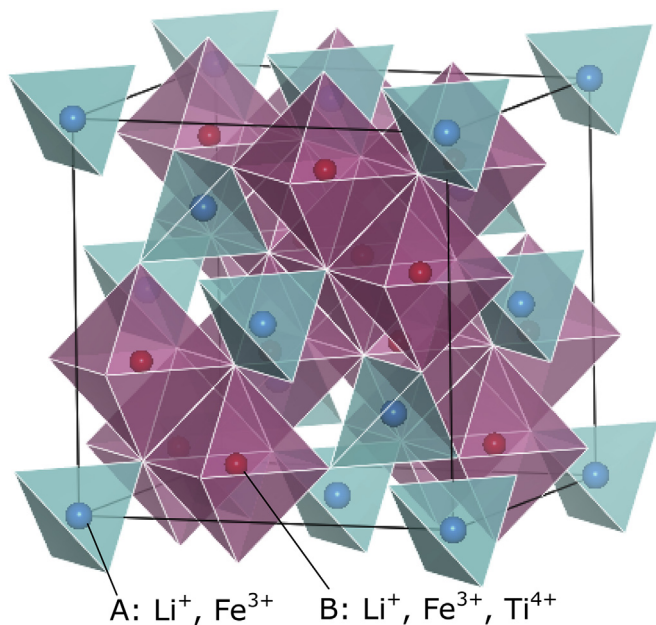


Fig. 1. Crystal structure of $\text{Li}_{1/2+x/2}\text{Fe}_{5/2-3x/2}\text{Ti}_x\text{O}_4$ (LFTO) with $0 \leq x \leq 1.666$. LFTO crystallizes into a spinel structure, in which tetrahedral A site is occupied by Li^+ and Fe^{3+} ions, and octahedral B site is occupied by Li^+ , Fe^{3+} , and Ti^{4+} ions. The space group for the $x < 1.6$ samples is $P4_332$, due to 1:3 the cation order at the B site. The space group for the $x = 1.6$ and 1.666 samples is $Fd\bar{3}m$.

$4\text{Ti}_x\text{O}_4$ at $1 \leq x \leq 1.666$ and compounds with the composition $(\text{Li}_{x/2}\text{Fe}_{1-x/2})_{\text{tet}}[(\text{Li}_{1/2}\text{Fe}_{3/2-x}\text{Ti}_x)_{\text{oct}}\text{O}_4$ at $0 \leq x \leq 1$. Hereafter, we denote these spinel compounds as $\text{Li}_{1/2+x/2}\text{Fe}_{5/2-3x/2}\text{Ti}_x\text{O}_4$ (LFTO) with $0 \leq x \leq 1.666$, ignoring the site occupancies of the A and B sites. The electrochemical properties of some LFTO compounds (those for which $x = 0, 1, 1.2, 1.3$, and 1.666) have already been reported [5–7], [15,18,19]. However, due to the lack of systematic structural and electrochemical studies, the reaction schemes for LFTO compounds other than those with $x = 1$ (LiFeTiO_4) and 1.666 (LTO), and whether zero-strain or not, are currently unknown. We recently clarified the site occupancies of LFTO by using synchrotron radiation XRD measurements, and found that two types of 1:3 cation order exist in the wide x range between 0 and 1.55 [20]. Such cation orders would be helpful to understand the reaction schemes of LFTO, leading to providing crucial information on the relationship between electrochemical properties and crystal structures of LIB materials.

In this paper, we performed the systematic structural and electrochemical studies on LFTO compounds with $0 \leq x \leq 1.666$. Consequently, we found that a zero-strain character is observed for compounds for which the x values range between 0.85 and 1.666. We also found that, except for the reaction scheme for $x = 1.666$, the electrochemical reaction proceeds along two different types of non-topotactic routes.

2. Experimental

LFTO samples with $0 \leq x \leq 1.666$ were prepared by a solid-state reaction technique as reported previously [15,20]. Powder samples of $\text{LiOH} \cdot \text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.), $\alpha\text{-FeOOH}$ (Koujyundo Chemical Laboratory Co., Ltd.), and TiO_2 anatase (Wako Pure Chemical Industries, Ltd.) were mixed together carefully with a mortar and pestle, and then pressed into a pellet with a diameter of 23 mm and a thickness of ~ 5 mm. This pellet was pre-heated at 400°C in air for 12 h, then ground and re-pressed into a pellet, and

finally heated at 750°C in air for 12 h. The powder obtained was characterized by powder XRD measurements equipped with a source of Fe-K α radiation (D8 ADVANCE, Bruker AXS, Inc.) and scanning electron microscopy (SEM, S-3600N, Hitachi High-Technologies Co., Ltd.). Rietveld analyses were performed using the RIETAN-FP program [21], and schematics of crystal structures were drawn by the VESTA program [22].

The electrochemical reactivity of LFTO was examined in a nonaqueous lithium cell. A black slurry consisting of 88 wt% of LFTO powder, 6 wt% of acetylene black (Denka Company Ltd.), and 6 wt% of polyvinylidene fluoride (Kureha Corp.) was cast onto copper foil with 10 μm in thickness and 16 mm in diameter using an *N*-methyl-2-pyrrolidone (NMP, Nacalai Tesque, Inc.) solution. The copper foil instead of aluminum foil was chosen as the current collector, to avoid the reactions around 0.5 V vs. Li^+/Li for the alloying of lithium with aluminum [23]. NMP was evaporated under vacuum at 120°C for 12 h. A lithium metal sheet pressed onto a stainless steel plate (19 mm ϕ) was used as the counter electrode, while 1 M LiPF_6 dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) solution (EC/DEC = 1/1 by volume, Kishida Chemical Co., Ltd.) was used as the electrolyte. A polypropylene membrane with 25 μm in thickness (TonenGeneral Sekiyu K. K.) were used as the separator. The lithium cells were fabricated in an argon-filled glove-box. Charge and discharge cycle tests were carried out at a current of 0.5 mA ($\approx 0.25 \text{ mA cm}^{-2}$) in the voltage range between 0.5 and 3.0 V. The temperature at which the electrochemical measurements were conducted was 25°C . Open circuit voltage (OCV) measurements were also carried with an intermittent current of 0.5 mA for 0.5 h (or 1 h for the LFTO sample with $x < 0.875$) and a relation time of 5 h. To clarify the change in crystal structure and the value of ΔV for each LFTO sample, ex situ XRD measurements were also performed during the charge and discharge reactions. Here, the 2θ range for in situ and *operando* XRD measurements is still too narrow ($10\text{--}20^\circ$) to determine such structural changes, although in situ and *operando* XRD measurements provide fundamental insights into the process of a phase transition [24]. Each lithium cell was de-constructed in the argon-filled glove-box, and then the electrodes were covered with a polyethylene film or a Kapton tape to avoid undesired reactions with the moist air.

3. Results and discussion

3.1. Particle morphologies

Fig. 2 shows the SEM images for the LFTO samples with (a) $x = 0$ and (b) $x = 1.4$ at the 1 μm scale. The SEM images at the 10 μm scale are also shown in Fig. S1. The average size of primary particles is approximately 0.2–0.3 μm , regardless of x . However, some primary particles of $x = 0$ indicate a rectangular shape with the long side of $\sim 0.4 \mu\text{m}$ and the short side of $\sim 0.1 \mu\text{m}$, whereas the primary particles for $x = 1, 1.4$ and 1.666 show a non-uniform or spherical shape. Numerous primary particles aggregate together, forming a large secondary particle with the size of $\sim 10 \mu\text{m}$.

3.2. Electrochemical properties

Fig. 3 shows the discharge (reduction) and charge (oxidation) curves of the LFTO/Li cells with (a) $x = 0$, (b) $x = 0.4$, (c) $x = 0.7$, (d) $x = 0.875$, (e) $x = 1$, (f) $x = 1.2$, (g) $x = 1.4$, and (h) $x = 1.666$. Discharge and charge curves of the LFTO/Li cells with $x = 0.25, 0.5, 0.625, 1.1, 1.3, 1.5$, and 1.6 are also shown in Fig. S2. For the $x = 0$ sample, the cell voltage rapidly decreases to ~ 0.8 V at the beginning of the discharge reaction, and then maintains almost constant voltage at around 0.8 V up to a discharge capacity (Q_{dis}) of $\sim 800 \text{ mAh g}^{-1}$. The subsequent charge curve differs significantly

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