Effect of annealing on the electrochemical properties of ramsdellite-type lithium titanium oxide

Elly Setiawati*, Masahiko Hayashi, Masaya Takahashi, Takahisa Shodai, Keiichi Saito

NTT Energy and Environment Systems Laboratories, NTT Corporation, Japan

ABSTRACT

Lithium titanium oxide (LTO) with a ramsdellite structure is an advantageous anode for lithium ion secondary batteries, because of its positive potential, which is beneficial for safety reasons. In addition, compared with other titanate anodes, it has a superior theoretical capacity of $321\,\mathrm{mA\,h\,g^{-1}}$, which is close to the capacity of a practical carbonaceous anode. Our study showed that this ramsdellite-type LTO had a high discharge capacity that is stable at $250\,\mathrm{mA\,h\,g^{-1}}$ at a current density of $1\,\mathrm{mA\,cm^{-2}}$. However, this high capacity is only achieved by employing as-synthesized ramsdellite LTO powder. When the same powder was stored and the same evaluation was carried out, the resulting capacity was $200\,\mathrm{mA\,h\,g^{-1}}$, which is lower than the capacity of as-synthesized powder. An annealing applied to the ramsdellite LTO powder appeared to restore the capacity loss after storage. Annealing at $250\,^\circ\mathrm{C}$ for $5\,\mathrm{h}$ produced the best performance, which was even better than that obtained using the as-synthesized ramsdellite LTO powder. Moreover, we investigated the surface property of ramsdellite LTO and found that the presence of a carbon derivative is apparently responsible for blocking the Li ions insertion/extraction, and thus reducing the capacity.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Metal oxide materials are currently being researched as promising anodes for lithium ion batteries because of their relatively high potential (vs Li/Li⁺), which is beneficial for safe large-scale batteries. These kinds of materials with a relatively high potential (around 1.5 vs Li/Li⁺) are advantageous since they prevent the formation of dead lithium dendrites on the negative electrode, meaning that higher cycle numbers can be obtained. Of these materials, a series of titanium oxides is being promoted as one candidate for the negative electrodes of lithium ion batteries [1]. In particular, it was found that the spinel structure of this titanium series (LTO spinel) allows the lithium ion insertion/extraction to take place without significant structural changes. This material with a stable crystal structure, where the presence of Li ions in the structure does not influence the crystal lattice, is promising for realizing batteries with high cycle numbers. Moreover, compared with other metal elements in the transition metal group that are used as electrode materials, titanium is both naturally abundant and environmentally safe. For these reasons, titanium derived oxide has been studied intensively as an anode material.

Titanium oxides are reported to be present in several kinds of crystal structure as listed in Table 1. In general, they can be classified into two groups, namely structures with and without lithium. Compounds containing lithium, such as lithium titanium oxide (LTO) with spinel, ramsdellite, and hollandite structures, are being studied intensively as anode materials for lithium ion batteries. In this case, lithium ions have stable sites inside the structure. Thus, the number of lithium ions extracted/inserted during the charge/discharge process is fixed. On the other hand, lithium-free titanate oxides such as anatase, rutile, and brookite have no exact lithium ion sites inside the crystal, and thus the number of lithium ions that are inserted/extracted depends on the available space and the charge balance in the crystal. Theoretically, this kind of lithium free compound has a larger capacity than one with lithium. However, its electrochemical characteristics as an anode material are still unsatisfactory due to its low conductivity. So, many research groups have attempted using carbon coating and nanosize technology to exploit these compounds as anode materials for lithium ion batteries [1].

Recently, LTO with a spinel structure had been commercialized, and is expected to be used for a large-scale lithium ion battery, particularly because it overcomes the safety problem and provides high cycle numbers. However, the theoretical capacity of LTO with a spinel structure is only $175\,\mathrm{mA\,h\,g^{-1}}$, which is about half the value of the generally used graphite carbon ($372\,\mathrm{mA\,h\,g^{-1}}$), resulting a lower energy density. LTO with a ramsdellite structure, which has a theoretical capacity of $321\,\mathrm{mA\,h\,g^{-1}}$, has become a focus of

* Corresponding author at: 3-1, Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan. Tel.: +81 46 240 2692; fax: +81 46 270 2702.
E-mail address: setiawati.elly@lab.ntt.co.jp (E. Setiawati).

Table 1
Structural and capacity data for titanium oxide material.

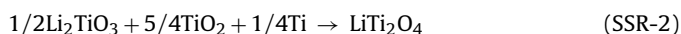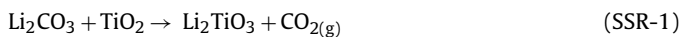| Structure	Chemical formula	Capacity (mA h g^{-1})	
		Theoretical	Experimental
Anatase [4]	TiO_2	335 (1e)	168
Brookite [1]	TiO_2	335 (1e)	200
Rutile [4]	TiO_2	335 (1e)	44
Bronze [1]	TiO_2	335 (1e)	160
Spinel [1]	$Li_4Ti_5O_{12}$	175 (3e)	173
Ramsdellite [4,8]	$LiTi_2O_4$	321 (2e)	235
	$Li_2Ti_3O_7$	298 (3e)	175
Holandite [1]	Ti_2O_4	160 (1e)	150

interest in an effort to find a stable anode that has a capacity larger than spinel LTO. Specifically, a larger capacity can be obtained because it has higher conductivity than the spinel structure [2,3]. This material has been reported to have a practical capacity as large as 235 mA h g^{-1} [2–10], which is about 1.5 mol of Li ion insertion/extraction during the charge–discharge process.

We studied ramsdellite LTO and found that the electrochemical characteristics of this material degraded, even when the powder was stored in a dry room where the dew point was kept constant at −50 °C. To overcome this electrochemical degradation during storage, we employed heat treatment for the stored LTO ramsdellite powder and found that its electrochemical characteristics were effectively improved. Furthermore, we investigated and discussed the degradation mechanism by characterizing such physical properties as their structural and surface characteristics.

2. Experimental

2.1. Synthesis of LTO powder with ramsdellite structure

LTO with a ramsdellite structure was synthesized by using a two solid-state reactions (SSR) method as described elsewhere [4–7]. The chemical reactions were as follows:

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_{2(g)} \qquad \text{(SSR-1)}$$

$$1/2Li_2TiO_3 + 5/4TiO_2 + 1/4Ti \rightarrow LiTi_2O_4 \qquad \text{(SSR-2)}$$

The first reaction is a substitution reaction where the powder forms of lithium carbonate (Kanto Chemical Co., Inc.) and TiO_2 (Anatase structure, Kanto Chemical Co., Inc.) were reacted in an alumina crucible after the starting powders had been thoroughly mixed in an agate mortar. The reaction continued for 10 h at a temperature of 750 °C. After the resulting powder had been ground and mixed in an agate mortar with a new reagent consisting of anatase TiO_2 (Kanto Chemical Co., Inc.) and metallic titanium (Kojundo High Purity Chemical Laboratory Co., Ltd., 99%) powder, it was further reacted in a N_2 gas flow furnace at 1150 °C for 10 h. The resulting powder was then stored in a dry room with a constant dew point of −50 °C.

2.2. Characterization of ramsdellite LTO

The powder was investigated by using an X-ray diffractometer (Rigaku, RINT2000) with CuKα radiation under a constant power of 30 kV and 100 mA. The structural phases of the synthesized powder were identified using the International Center for Diffraction Data (ICCD) database. The Rietveld refinement was carried using the PDXL software version 1.7.0.0 (Rigaku, Corp.). A measurement to determine the chemical composition

(Li/Ti) of the synthesized material was carried out by using inductively coupled plasma combined with atomic emission spectroscopy (ICP/AES, Seiko Instruments, SPS1700HVRS). The amount of oxygen was determined by the combustion-infrared absorption (combustion-IR absorption, LECO Corp., TC436) technique. The powder morphology was observed using scanning electron microscopy (SEM, JEOL JSM-890). Moreover, the surface properties of the oxide powder were examined through an elemental analysis of the surface binding energy (BE) using X-ray photoelectron spectroscopy (XPS, PHI XPS 5700), with an AlKα (1468.6 eV) anode as a target. The measurements were carried out in an ultra-high vacuum (UHV) chamber at a pressure below 10^{-7} Pa. The measurement area was kept at a diameter of 800 μm while the angle between the sample and the incident beam was kept at 45 deg.

The electrochemical characterizations were carried out using a coin test cell (type CR-2320). The electrode was prepared by mixing the active material (LTO powder) with acetylene black (AB) carbon as a conductive agent and PTFE as a binder with an active material:AB:PTFE weight ratio of 75:20:5. The mixture was first ground in an agate mortar and then roll-pressed into a 0.5 mm thick sheet to be assembled into a coin test cell as a working electrode. Lithium metal was used as a counter electrode. A microporous polypropylene film was inserted between them as a separator. The electrolyte was 1 mol L^{-1} of LiPF$_6$ in an equal volume of ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (Tomiyama Pure Chemical Industries, Ltd.).

The entire preparation and coin test assembly process was carried out in a dry room (dew point = −50 °C). The electrochemical evaluations were performed in a temperature-controlled chamber with a constant temperature of 20 °C. The electrochemical evaluation was conducted at a constant current density of 1 mA cm^{-2} in the 3.5–1 V range, with a rest period of 10 min between the charge and discharge steps.

Ex-situ characterizations were employed to examine any changes in such properties as structure and chemical composition after the electrochemical evaluation. This information is particularly useful for understanding the stability of an active material (ramsdellite LTO) during electrochemical evaluation. After performing a series of electrochemical evaluations, the cells were disassembled and the ramsdellite LTO pellet was carefully extracted from the measurement cell. The pellet was then carefully washed several times using a dimethylcarbonate (DMC) solution to remove the salt form that existed in the surface. After that, it was vacuum dried, and stored in a dry room for 12 h, before being subjected to structural and chemical composition characterizations using XRD and ICP-AES, respectively.

2.3. Annealing

The annealing is consisted a heat treatment that was applied to the ramsdellite LTO powder after it had been stored in a dry atmosphere for 1 year in a furnace chamber in a constant flow of nitrogen gas. The purpose of this heat treatment was to remove any contaminants that may have existed on the powder surface. Before annealing was started, the chamber was evacuated and purged with a N_2 gas flow. Annealing was carried out at constant temperatures of 150, 250, 350, and 450 °C to determine the optimum temperature. Moreover, at a fixed temperature of 350 °C we varied the treatment times of 1, 3, 5, and 10 h. The annealed sample was electrochemically characterized using the same procedures as described before for the as-synthesized powder. First, a pellet was prepared using the powder that had been treated at different temperatures, and the next step was to assemble the corresponding pellet into a coin test.
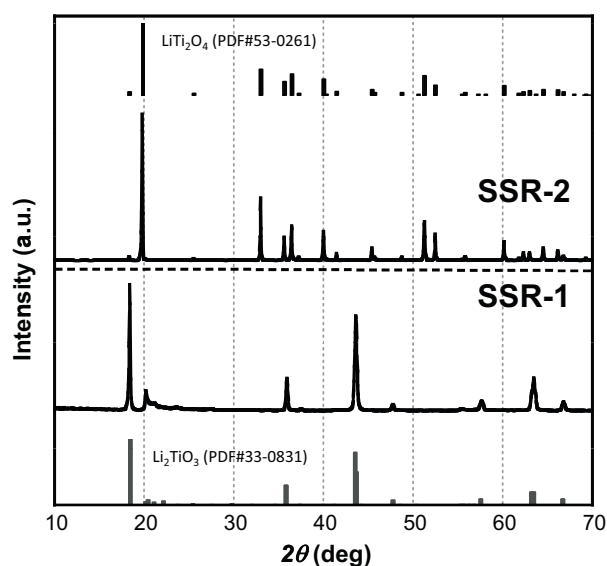
Fig. 1. XRD pattern of lithium titanium oxide powders synthesized by two solid-state reactions.

3. Results and discussion

3.1. Structure and surface characteristics

Fig. 1 shows the XRD pattern of the synthesized LTO powder. LTO powder obtained from the first reaction (SSR-1) through a substitution reaction was a one-dimensional layer with a chemical formula of Li_2TiO_3. The standard pattern of Li_2TiO_3 (PDF#33-0831) is given in the bottom part of the figure, and shows a good correlation with the resulting powder, indicating that the first reaction subsequently occurred. We also confirmed that the ratio of Li and Ti from the ICP/AES method gave a ratio Li/Ti value of 1.99, which is very close to its theoretical value of 2.

LTO with a three-dimensional ramsdellite structure was obtained from the 2nd solid state reaction (SSR-2). The ramsdellite structure is known to have an orthorhombic unit cell with a space group *Pbnm (62)* [4,5]. It is worth noting that several standard patterns for the LTO ramsdellite structure with different chemical formulas have already been reported [8,9]. To determine the chemical formula of a unit cell LTO crystallite with a ramsdellite structure, we evaluated its chemical composition using ICP/AES and a combustion-IR technique. The Li to Ti ratio was determined as 2.04 from an ICP/AES measurement, while the amount of oxygen (weight %) obtained from the combustion IR absorption was 36.4, that is equivalent to 3.7 amount of O in one unit cell. On this basis, we consider that the SSR-2 product has a chemical formula of $LiTi_2O_4$ in one unit cell.

We refined the pattern above by employing the Rietveld method using a standard pattern of PDF#53-0261. The refinement result is shown in Fig. 2, with an inserted table showing the lattice constant values of our refined powder that are in a good agreement to the corresponding reference values. Quantitatively, as indicator to measure how close the observed XRD pattern, we used the R_{wp} and S values to indicate the accuracy and the standard differences to the standard XRD pattern, respectively. Our refinement resulted the R_{wp} value of ∼12.88% and the S value of 1.23. These values are in a good agreement with those of a typical refinement process, where the R_{wp} value is around 10% and the S value is close to 1, and verifying that the synthesized powder is having a ramsdellite LTO with the chemical formula of $LiTi_2O_4$, to give a good accordance with the ICP/AES results.

Fig. 3 shows the particle morphology of the as-synthesized samples. The particle size was varied in the 1–10 μm range. From the main XRD peak, we estimated the crystallite size using the Scherrer equation, which gave an average value of less than 1 μm. This implies that one particle consisted of one to several crystallites.

3.2. Electrochemical performance of typical ramsdellite type LTO

The electrochemical evaluation of LTO with ramsdellite structure was expressed in terms of a charge–discharge curve and cycle performance, which are shown in Fig. 4(a and b), respectively. The typical charge–discharge curve for the 1st, 3rd and 5th cycles gives an almost stable capacity of 250 mA h g^{-1} as shown in Fig. 4(a). The charge–discharge curve for ramsdellite LTO shows that the discharge curve has two regions: a quarter cycle region with a stopping voltage value exceeding 1.3 V and a flat region corresponding to a stopping voltage of 1.3 V. In more detail, three kinds
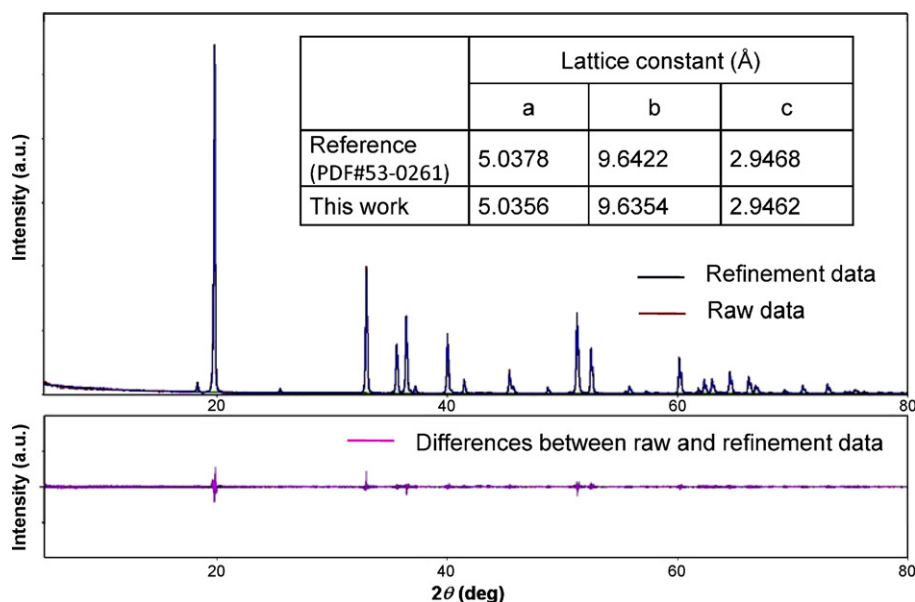

	Lattice constant (Å)		
	a	b	c
Reference (PDF#53-0261)	5.0378	9.6422	2.9468
This work	5.0356	9.6354	2.9462

Fig. 2. Refinement result for lithium titanium oxide with ramsdellite structure by Rietveld method.
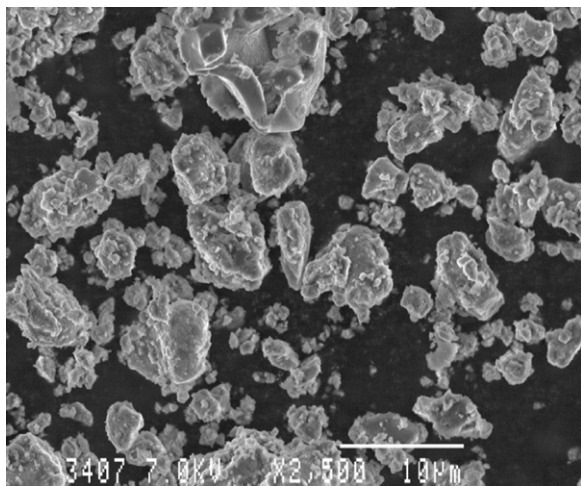
Fig. 3. SEM images of synthesized LTO with ramsdellite structure.

of electrochemical reactions (2.1; 1.3; and 0.6 V) were involved as described elsewhere [4–7]. The typical electrochemical reactions for ramsdellite oxide were take place at approximately 1.3 V and 2.1 V. Particularly, the reaction at 1.3 V for first cycles, which is the standard reduction potential of $Ti^{4+}/Ti^{3+} = 1.33$ V, was observed at lower potential (1.2 V), indicating a mixture valence of Ti ions existed in the initial condition. This is also confirmed from the XPS data given in Fig. 7(a), where the oxide was dominated with Ti

3+. Moreover, a small plateau around 0.6 V that was only observed in first cycle might indicate a formation of an interface layer that reduced a barrier between electrolyte and electrode to accommodate the Li insertion/extraction which is beneficial for the Li ions transport. This kind of small plateau was existed in all samples and thus explained a large capacity drop happened in the early cycles.

The cycle performance shown in Fig. 4(b) reveals that the capacity of the 1st cycle was ∼310 mA h g^{-1}, and this decreased to an almost stable 250 mA h g^{-1} after the 3rd cycle. The amount of electron transfer is a useful parameter to estimate the electrochemical reaction during Li ions insertion/extraction. However, the electron transfer is evaluated from the 3rd reaction, because of the formation of interface layer that was observed in first cycle. By assuming an active material with a chemical formula of $LiTi_2O_4$ as the standard with a molecular weight of 166.68 g mol^{-1}, we estimated that the 3rd cycle occurred as the result of about 1.6 electrons transfer. However, the capacity degradation that was observed for the next cycle implies a reduction in the number of electrons taking part in the reaction. The number of electrons included in the reaction was estimated to be 1.6, and this implies that the ramsdellite LTO was still partly occupied by Li ions.

It is well known that the capacity decay can originate from two factors; the presence of blocking contaminants molecules and the practical conductivity of the active material. The particle size, the ratio of active material to carbon, and the current density are several factors that significantly influence the conductivity. These factors were not optimized in this study. However, the kind of capacity decay that occurs in the first 5 cycles has been reported [4] to
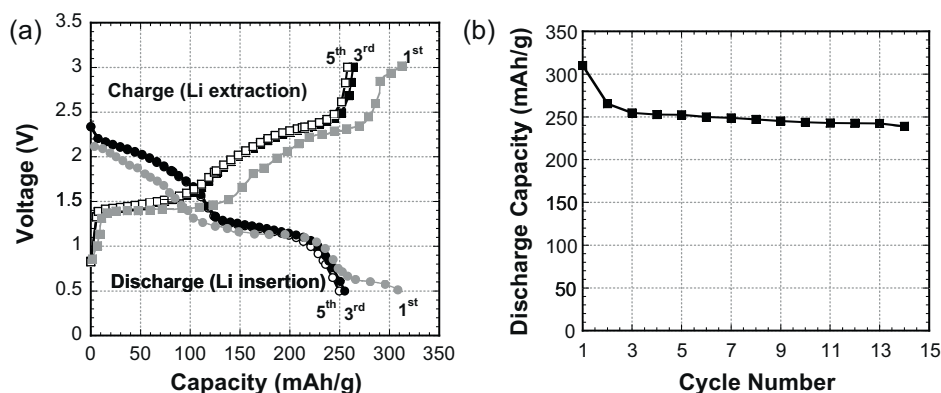

Fig. 4. (a) Typical charge–discharge curves for ramsdellite LTO taken at 3rd, 5th, and 15th cycles. (b) Cycle performance of ramsdellite LTO evaluated at 0.2 C.
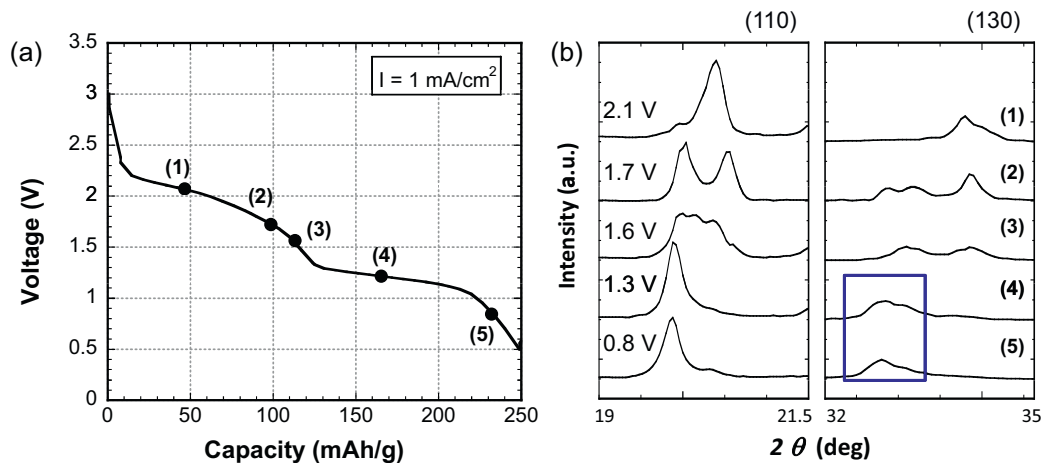

Fig. 5. (a) Discharge curves plotted with stopping voltage value for ex-situ evaluation. (b) Ex-situ XRD pattern for sample measured at six different points given in Fig. 5. The left side shows the corresponding chemical formula obtained from ICP/AES evaluation.

be closely influence by conductivity. The typical charge–discharge curve and the stable cycle performance show that the synthesized ramsdellite LTO is in a good agreement with those that described in previous reports [4–7], and suggested that ramsdellite LTO is promising for use as the anode of lithium ion batteries.

To determine the number of lithium ions that participated in the charge–discharge process, we prepared five test cells and evaluate their electrochemical behavior under the same condition for 5 cycles. After that, they were discharged at five different stopping voltages as shown in Fig. 5(a). Ex-situ XRD measurements were carried on those samples and the resulting patterns are shown in Fig. 5(b). Additionally, the chemical compositions corresponding to stopping voltages of 2.1 V and 0.8 V were evaluated by ICP/AES to estimate the total number of Li ions in the ramsdellite LTO that participated in the electrochemical reaction. By assuming that the number of Ti ions in the ramsdellite LTO is constant, we can directly convert the Li to Ti ratio obtained from ICP/AES to the number of Li ions in the ramsdellite LTO. Accordingly, the valence number of the Ti ions was calculated with a charge balance equation, to give a value that represents the number of electrons that took part in the electrochemical reaction.

Upon discharge to a lower voltage from 2.1 to 0.8 V, the number of Li ions increases from 1.3 to 3 mol; where approximately 1.7 mol Li ions are inserted into the ramsdellite LTO. In other words, approximately 1.7 mol of Li ions take part in the electrochemical reaction. Thus the overall electrochemical reaction in the charge–discharge process is estimated to be as follows:

$$\mathrm{Li}_{(1+x)}\mathrm{Ti}_2\mathrm{O}_4 \leftrightarrow \mathrm{LiTi}_2\mathrm{O}_4 + x\mathrm{Li}^+ + xe^-$$

where the maximum value of x is equal to 1.7.

It should be noted that the capacity can be calculated from the molecular weight of the active material and the number of Li ions that participate in the electrochemical reaction. The molecular weight of the synthesized active material with a chemical formula $\mathrm{LiTi}_2\mathrm{O}_4$ is 166.68 g mol^{-1}, so theoretically the calculated capacity for 1.7 electrons is 273 mA h g^{-1}. However, we obtained a discharge capacity for the 3rd cycle of 250 mA h g^{-1}, which is equal to about 1.6 electrons. This result suggests that about 0.1 mol of the mobile Li ions did not participate in the reaction. We considered that these Li ions might be trapped inside the structure and so unable to participate in the reactions. Noting the structural characteristic of ramsdellite LTO with a (2×1) tunnel space [4,5], it can be considered that keeping the Li ions partly inside the structure is useful for protecting the structure from collapse, and thus obtaining a high cycle number.

Khun et al. [4] mentioned that in $\mathrm{Li}_2\mathrm{Ti}_3\mathrm{O}_7$ ramsdellite, the Li ions in the crystal are distributed into two tetrahedral sites: Li1 and Li2. The Li1 sites are energetically more stable because they do not share a face with the TiO_6 octahedron. They estimated that about 60% of the Li ions in the ramsdellite crystal were distributed in the Li1 site, while the rest occupied the less stable Li2 site. Although the same condition has not been reported for $\mathrm{LiTi}_2\mathrm{O}_4$, it can be assumed since they have a similar crystal structure. In this case, for one unit crystal of ramsdellite LTO with 2 mol Li ions, the stable sites should be occupied by 1.2 mol Li ions, with the remaining 0.8 mol occupying the less stable one. According to this estimation, when all of the Li ions occupying stable sites in the ramsdellite LTO contributed to the reaction, the capacity would be 192 mA h g^{-1}. As our experiment showed a capacity of 250 mA h g^{-1}, the Li ions occupying both stable and less stable sites contributed to the reaction. A detailed structural analysis is needed to explain which kind of Li ion participated in the electrochemical reaction.

Table 2
The lattice constant of Li-rich ramsdellite LTO resulted from Rietveld refinement.

No cell	Stage	Stopping voltage (V)	wt% Li$_x$Ti$_2$O$_4$		Lattice constant (Å)		
			$x=0.14$	$x=1$	a	b	c
1	I	2.1	90	10	4.814	9.92	3.099
2	II	1.7	46	54	–	–	–
3	II	1.6	34	66	–	–	–
4	III	1.3	9	91	5.0387	9.634	2.9499
5	III	08.8	4	96	5.043	9.645	2.9516

The ex-situ XRD pattern (Fig. 5(b)) shows two kinds of structure with ramsdellite LTO that has different numbers of Li ions in the structure with two main peaks corresponding to (1 1 0) and (1 3 0). Akimoto et al. [2,3] reported that the number of Li ions inside a ramsdellite LTO structure influence the lattice constant of one unit crystal. Changes in the lattice constant can be easily observed by carefully examining the main diffraction peaks. A higher 2θ peak is generally sensitive to the structural property, and thus the change in the lattice constant can be predicted.

The two structures seen in Fig. 5(a) correspond well with the typical discharge curves shown in Fig. 5(b). To simplify the explanation, five coin cells with different stopping voltages are divided into three stages (I for 2.1 V, II for 1.7 and 1.6 V and III for 1.3 and 0.5 V). Accordingly, the discharge curve can be divided into two regions, one with a semicircular curve that covers stages I and II, and one with a flat area that covers stage III. Stages I and III had a single phase of ramsdellite LTO with low and high Li ion concentrations, respectively; while the ramsdellite LTO in stage II consisted of two phases, with both high and low Li concentrations. The two phases contributed to a discharge reaction that resulted in a half-cycle, and the flat discharge curve suggested that they were conducted under different reaction, and thus the charge–discharge reaction in the ramsdellite LTO is considered to be a two-phase reaction. Each reactions contributed to about half of the overall capacity. Therefore, theoretically, in each phase approximately 1 mol of Li ions contributed to the electrochemical reaction, so that in total 2 mol Li ions take part in the discharge reaction.

The Li rich regions with stopping voltages of 0.5 and 1.3 V in Fig. 5(b) show that they have an identical main peak for (1 1 0) existed at $2\theta = \sim 19.8$ deg. In addition, those two stopping-voltage values have a minor peak of (1 3 0) at a higher 2θ value around 33 deg. It is generally known that a higher 2θ value is more sensitive to the properties of the structure. Specifically, the condition of the lattice space could be predicted by observing any shift of the minor peak that appeared at a high degree of 2θ value. The (1 3 0) peak shown in Fig. 5(b) for the Li medium to rich region that corresponds to a 2θ value of ~ 33 deg for a stopping voltage from 1.6 to 0.8 V is shifted to a lower 2θ value. The shift of minor (1 3 0) peak to a lower 2θ value implies an expansion of lattice constant occurred, suggesting that the lattice constant was expanded by discharging to a lower stopping voltage. At the same time, we applied Rietveld analysis to estimate their lattice constant values (Table 2) to give a larger lattice constant value for lower stopping voltage that indicate a lattice expansion occurred with the Li insertion. The refinement was carried out by assuming that two kinds of ramsdellite, high and low Li concentrations were existed. Similar evaluation to estimate the lattice constant of samples with low Li concentrations using Rietveld analysis were omitted because the broadening of main 2θ peak.

Based on the above discussion, upon discharge, Li ions were inserted easily into the structure, and began by filling up the less occupied sites. At some points, where the sites were almost fully occupied (stopping voltage below 1.3 V), the insertion of any additional Li ions led to the expansion of the lattice constant. It is worth

noting that the discharged LTO at the stopping voltage of 0.5 V contained more Li ions compare to the as synthesized one. So that any lattice expansion happened at this point is reasonably thought originated by a further insertion of Li ions from its initial as synthesized amount.

3.3. Surface degradation during storage

We evaluated the electrochemical properties of a sample prepared from ramsdellite LTO powder after being stored in a dry atmosphere, and we found that there was a capacity retardation. The capacity of the stored sample was ~200 mA h g^{-1} lower than that for the as-synthesized sample (~250 mA h g^{-1}), as seen in Fig. 6. The lower capacity obtained after the ramsdellite LTO powder had been stored indicated that fewer Li ions contributed to the reaction. Since they originated from the same production lot, this capacity reduction must be the result of a change in their intrinsic properties, such as their surface properties, that occurred during storage.

Titanium oxide is particularly well known for its typical non-stoichiometric behavior [11–13]. This behavior can be studied by evaluating the surface properties of oxide to find whether there was any change or shift in the elemental binding energy (BE). The elemental binding energy information represents the valence number of the elements in the compound, and thus is useful for
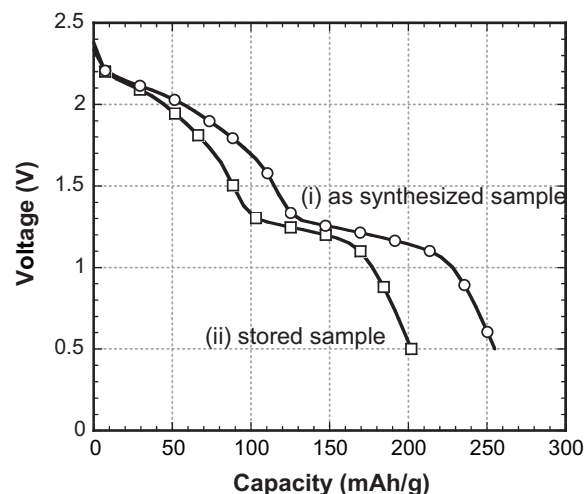

Fig. 6. The 3rd cycle discharge curves for ramsdellite LTO: (i) as-synthesized and (ii) those powders after storage in dry atmosphere.

predicting the existence of any adsorbed molecules. In this study, we compared the binding energy of Ti2p for the as-synthesized and stored oxide as shown in Fig. 7(a) in a gray solid line and black solid line, respectively. The Ti2p binding energy is in a good
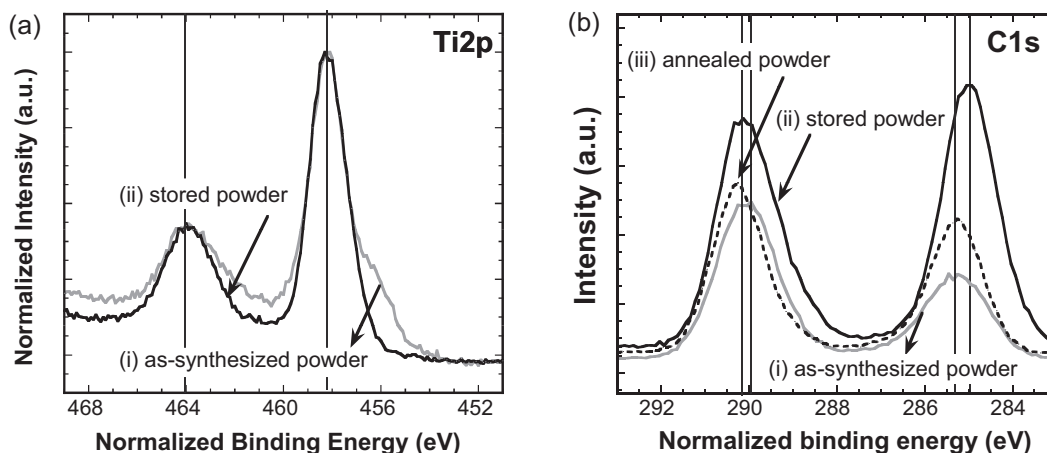

Fig. 7. (a) XPS spectra ofTi2p binding energy for: (i) as-synthesized and (ii) after stored and ramsdellite-LTO powders. (b) XPS spectra of C1s binding energy for: (i) as-synthesized, (ii) after stored and (iii) after annealed ramsdellite-LTO powder.
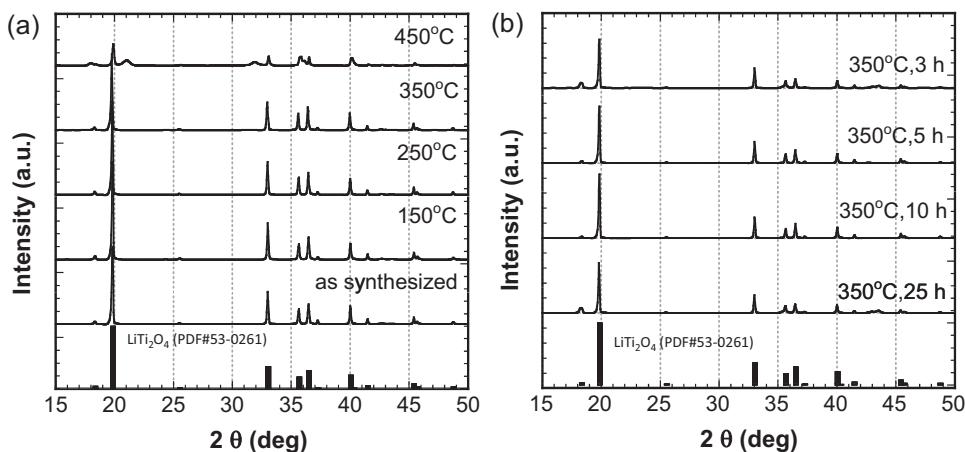

Fig. 8. (a) XRD pattern for annealed-ramsdellite LTO powder at various temperatures for 5 h. A structural transformation takes place with 350 °C treated powder. (b) Effect of annealing time on LTO ramsdellite structure.
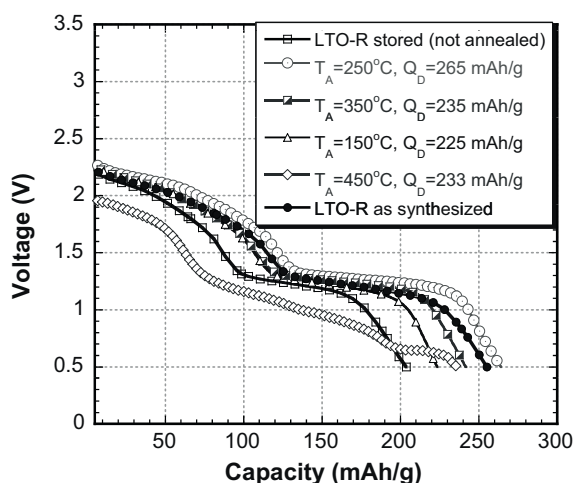
Fig. 9. Typical discharge curves for ramsdellite LTO after annealing.

accordance with typical spectra, consisted of two sharp peaks of 464 and 458.4 eV. Both of those spectra were normalized to the reference value of Ti2p$_{3/2}$ at 458.5 eV [14,15], so that the difference can be clearly seen. This compensation was used to eliminate the charge-up phenomenon that occurred when the sample was irradiated with X-rays during measurement, which shifted the measured binding energy from its true value. In many cases, the C1s reference value is used to correct the binding energy, because carbon is generally present as a very thin contaminant layer on the sample surface. However, in this case we avoid using C1s as a reference because our measured C1s peaks differed from the typical C1s peak originating from carbon contamination.

It is generally known that peak broadening in the lower BE (458.4 eV) informs the oxidation number of Ti ions [16,17]. According to Huflund et al. [17], the oxidation number of Ti ions in the as-synthesized oxide, which Ti2p$_{3/2}$ peak broadened at BE = 456 eV, are in a mixed of 4+ and 3+ oxidation state. On the other hand, a sharp BE observed for stored oxide indicate that the Ti4+ dominantly existed. This result is consistent showing that upon storage, the powder is oxidized, so that the Ti ions reach their stable state at 4+ oxidation number. On the other hand, it was reported that titanium oxide surface is more likely to adsorb molecules and atoms whether it is organic or inorganic [16]. These molecules occur in the surface via two routes, namely, through physical and chemical adsorption. With physical adsorption, no new chemical bond is

formed, so the molecules can be easily introduced to or removed from the surface.

3.4. Annealing for stored ramsdellite LTO powder

Using the elemental binding energy described above as a basis, we employed annealing for ramsdellite LTO powder that had been stored for approximately 1 year in a dry room. Fig. 8(a and b) shows the crystal structure of powder after annealed at various temperatures and for various time periods. Fig. 8(a), which shows the structure of powder annealed at a temperature below 350 °C, confirms the existence of a single phase of LTO with a ramsdellite structure. However, when the treatment temperatures exceeded 350 °C, a structural transformation was observed. Moreover, we varied the treatment time at the maximum temperature of 350 °C. At this temperature, we confirmed that, whatever the treatment time, all the powder was in a single ramsdellite structure and there was no phase transformation.

Although the ramsdellite structure was formed at a relatively high temperature of more than 1100 °C, a structural transformation still occurred with relatively low temperature (above 350 °C) treatment. Akimoto et al. [8,9] has reported that ramsdellite type LTO is very reactive in air. A noticeable change in their lattice parameters and therefore the Li ion content was observed in a unit crystal. Moreover, they indicated that the ramsdellite type is a meta-stable phase, which transformed to TiO$_2$ with a pseudo brookite structure upon additional heating to 367 °C. However, there was no detailed explanation regarding the driving force that causes phase transformation. These data correspond well with our result showing that a structural transformation occurred in the 350–450 °C temperature range.

The phase transformation phenomenon after annealing can be explained by assuming that some kinds of contaminant molecules might be adsorbed into the particles during storage. When those contaminant molecules receive any additional energy in the form of heat, they may induce a reaction that drives a phase transformation. At an appropriate temperature, a sufficient energy is given to break and decompose the molecules bond. So that, the optimum annealing temperature revealed the decomposition temperature of the contaminant adsorbent. The decomposition temperature of the contaminant adsorbent makes it possible to assume that it is a kind of organic molecule, however such a conclusion is premature. At a certain temperature (350 °C), which must be their decomposition temperature, the contaminants can be effectively removed from the powder. The process for removing all of this contaminant depends on the adsorption site. The deeper the site of the adsorbed contaminant is in a particle, the longer the annealing treatment time
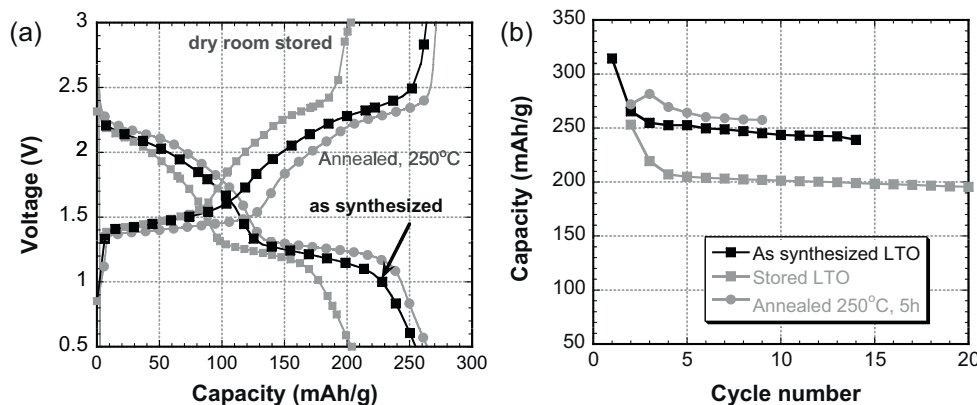

Fig. 10. Charge and discharge curves of powder annealed at optimum temperature (250 °C) compared with as-synthesized and dry room stored samples. (b) Cycle performance for as-synthesized, stored and annealed samples.

that is required. Further experiments regarding the treatment time and the effectiveness of contaminant removal must be performed to confirm this.

Again, the XPS study was applied to evaluate the surface condition to find any information about the contaminant molecules in a surface level. Fig. 7(b) shows the BE for C1s of three different oxide; as-synthesized, stored and annealed one; without normalizing their intensity. The BE of C1s are existing in two peaks for all samples, representing lower and higher BE values with peaks at 285.6 and 291.3 eV, respectively. The former peak is a native carbon that generally observable in many kinds of sample, while the latter peak is observed only in particular case. Since there is almost no significant difference between those samples in the latter peak, we can neglect this peak. One clear difference observable for those samples is that the former peak has a lower intensity for the as-synthesized powder (gray line) compared with the spectra for the stored powder (black line) and annealed powder (black, dot line). It is still difficult to clarify what kind of carbon derivative was observed in the XPS spectra, particularly because there is a BE shift that observed in for each peaks. However, the literature on the XPS database shows that those kinds of carbon are close to the saturated hydrocarbon peak that contained aromatic carboxylic and its derivatives [11,13]. More intense saturated hydrocarbon peak on the stored powder suggested that upon storage, the active surface sites of the ramsdellite LTO tends to adsorb carboxylic carbon and thus those kinds of molecules might existed in the surface. At this point, we found an indication of an irregular carbon-derived compound (Fig. 7(a)) in the surface states of the powder stored in a dry environment that might responsible to result electrochemical degradation.

We studied the effect of treatment temperature on improving the electrochemical properties of ramsdellite LTO. The discharge curves for ramsdellite LTO after annealing are shown in Fig. 9. The same typical discharge profiles were obtained for all samples that were treated at temperatures below 450 °C. Moreover, the discharge capacities of annealed powder increased as the annealing temperature increased. We can clearly see that the 250 °C annealed powder exhibits the optimum discharge capacity of 265 mAh g^{-1}, which is larger than that of the as-synthesized powder. The low capacity for the sample treated at temperatures below 250 °C appears to suggest that in this temperature range the organic contaminant adsorbent is still partly present in the powder. In other words, the decomposition temperature for those contaminants is around 250 °C.

On the other hand, the discharge curve for a sample post annealed at a high temperature of 450 °C has different characteristics from those of other samples. Specifically, the voltage dropped about 0.2 V and a slope was observed instead of the flat curves that were seen for other samples. Also, there was a short flat curve at around 0.65 V. Moreover, we confirmed that even when the discharge capacity for 450 °C annealed sample was high, it decreased after several cycles. We think that changes observed in the discharge curves is due to the structure transformation (Fig. 8(a)).

The charge–discharge curves of the annealed sample after treatment and their cycle performance are shown in Fig. 10(a and b), respectively. The as-synthesized sample and the sample stored in a dry atmosphere (degraded) plotted together to provide a comparison. We can see clearly that after annealing, the capacity of the degraded sample was restored, and moreover exhibited a higher capacity than the as-synthesized sample. The capacity of this treated sample was stable at 265 mAh g^{-1}, which is more than 85% of the theoretical capacity. At this point, we can estimate that 1.6 electrons participated in the reaction. Even though the number of participating electrons has been increased, no significant drop

was observed in their capacity during cycling as seen in Fig. 10(b). The cycle performance is still being examined experimentally. To date, a stable cycle has been achieved for more than 10 cycles. More detailed characterizations are under way to explain the mechanism that leads to the improved capacity after annealing. Our concern is to evaluate surface properties, such as the binding energy before and after treatment.

4. Conclusions

LTO with a ramsdellite structure was synthesized using two solid-state reactions (SSR) method and an electrochemical evaluation showed that only 1.5 mol of the Li ions participated in the charge–discharge process. As a result, the total capacity of this synthesized ramsdellite LTO was 250 mAh g^{-1}, which is only 80% of the theoretical capacity. Furthermore, we found that the electrochemical properties of the ramsdellite LTO had degraded to about 200 mAh g^{-1} after being stored even in a dry room with a constant dew temperature of −50 °C, although all the preparation and coin-cell assembly procedures were carried out in the same way as for the as-synthesized sample.

Annealing was employed with the above powder (ramsdellite LTO stored in a dry atmosphere). We found that suitable annealing is effective in restoring the electrochemical properties of the as-synthesized sample. Specifically, the optimum electrochemical properties were achieved (discharge capacity of 265 mAh g^{-1}) with treatment at 250 °C for 5 h. According to the XPS evaluation, we found that the surface properties directly influence the electrochemical properties. In addition, the XPS evaluation suggested that a derivative of carbonate molecules physically adsorbed on the surface during storage might be responsible for degrading the electrochemical characteristics. A further detailed examination is required to determine the identity of the adsorbed molecule.

References

[1] H. Noguchi, Encyclopedia of Electrochemical Power Source, vol. 21, Elsevier, 2009, pp. 4–224.
[2] J. Akimoto, Y. Gotoh, Y. Oosawa, N. Nonose, T. Kumagai, K. Aoki, J. Solid State Chem. 113 (1994) 27.
[3] J. Akimoto, Y. Gotoh, M. Sohma, K. Kawaguchi, Y. Oosawa, J. Solid State Chem. 110 (1994) 150.
[4] A. Khun, R. Armandi, F.G. Alvardo, J. Power Source 92 (2001) 221.
[5] A. Kuhn, C. Baehtz, F.G. Alvarado, J. Power Source 174 (2007) 421.
[6] R.K.B. Gover, J.R. Tolchard, H. Tukamoto, T. Murai, J.T.S. Irvine, J. Electrochem. Soc. 146 (1999) 4348.
[7] R.K.B. Gover, J.T.S. Irvine, J. Solid State Chem. 141 (1998) 365.
[8] M.E. Arroyo, E. Moran, A. Varez, F.G. Alvarado, Mater. Res. Bull. 32 (1997) 993.
[9] M.E. Arroyo, A. Varez, F.G. Alvarado, J. Solid State Chem. 153 (2000) 132.
[10] C.J. Chen, M. Greeblatt, Mater. Res. Bull. 20 (1985) 1347.
[11] U. Diebold, Surf. Sci. Rep. 48 (2003) 53.
[12] H. Onishi, Surf. Sci. 193 (1988) 33.
[13] G. Lu, A. Linsebigler, J.T. Yates Jr., J. Phys. Chem. 98 (1994) 11733.
[14] G. Beamson, High Resolution XPS of Organic Polymers, John Willey & Sons, England, 1992.
[15] Perkin-Elmer Corporation, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, USA, 1992.
[16] W. Gopel, Surf. Sci. 139 (1984) 333.
[17] G.B. Huflund, H.L. Yin, A.L. Grogan, D.A. Asbury, Langmuir 4 (1988) 346.