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Effect of oxygen content on CO_2 absorption characteristics of Li_2TiO_3

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ABSTRACT

In order to investigate the CO_2 absorption characteristics of the low- and high-density Li_2TiO_3 samples, X-ray diffraction (XRD), non-Rutherford backscattering spectroscopy (NRBS) and elastic recoil detection (ERD) analyses have been performed. Crystallographic structure of a sintered and CO_2 exposed samples is decided by the XRD analysis, and the NRBS and ERD analyses have evaluated the amount of CO_2 absorption and H content quantitatively. The CO_2 absorption characteristics of the non-stoichiometric Li_2TiO_3 sample are investigated. It is found that the CO_2 absorption rate of the non-stoichiometric Li_2TiO_3 sample is much larger than that of the stoichiometric sample. The Li_2TiO_3 sample (80%T.D.) has a good tritium release characteristics, and we find also that the sample sintered at temperatures higher than 1,428 K absorb very little CO_2 under high humidity conditions. The amount of CO_2 absorption of the low-density Li_2TiO_3 samples is found to increase with increase in the humidity. This seems to be a catalytic effect of water vapor on CO_2 absorption at the Li_2TiO_3 surface.

1. Introduction

Li_2TiO_3 has excellent chemical properties such as non-reactivity with H_2O and relatively good T breeding properties among the solid blanket materials [1–9]. However, our research showed that Li_2TiO_3 material absorbed CO_2 at room temperature [10–12]. The C contamination of a blanket material should be minimized. It has been reported that C atoms included in a blanket material can form a tritiated hydrocarbon in a T recovery process [13,14]. Therefore, if a blanket material has C contamination, the T recovery efficiency would be decreased, because additional process of isotope separation would be required. However, the CO_2 absorption characteristics of Li_2TiO_3 have not been fully studied yet [15].

We have been investigating the CO_2 absorption characteristics of Li_2TiO_3, and showed that CO_2 absorption of the low-density sample (39%T.D. −41%T.D.) at room temperature was observed at the dry CO_2 gas, the atmospheric, the dry air and the moist air exposures. On the other hand, the CO_2 absorption of the high-density sample (91%T.D.) was not appreciable. The low-density Li_2TiO_3 sample has more defects such as vacancies and micro-pores in the crystal grains of the sample compared with the high-density sample.

In the present work, we investigate the CO_2 absorption characteristics of a non-stoichiometric Li_2TiO_3 sample with defects of O and Li deficiencies caused by re-sintering the sample under an Ar gas atmosphere using an electric tube furnace. The sample is exposed to the dry CO_2 gas and the amount of CO_2 absorption with respect to the exposure time is investigated.

A suitable density of Li_2TiO_3 sample for a good T release property is about 80% T.D. [16–19]. We investigate materials which have good T release characteristics and do not absorb CO_2.

We have investigated the dependence of CO_2 absorption in the low-density Li_2TiO_3 sample on exposure time to the atmosphere, the dry air and the moist air. In this work, we measure the amount of H content and absorbed amount of CO_2 in the sample with ERD and NRBS analyses, and investigate the influence of the humidity in the exposure environment on CO_2 absorption.

In order to investigate the CO_2 absorption properties, X-ray diffraction (XRD) in addition to the non-Rutherford backscattering spectroscopy (NRBS) and the elastic recoil detection (ERD) analyses mentioned above are carried out to the samples before and after the exposures, and crystallographic structure of the exposed samples and the amount of CO_2 absorption and H content in the Li_2TiO_3 sample are investigated.

2. Experimental

The Li_2TiO_3 sample used in the present work was prepared by a solid phase reaction method with Li_2CO_3 and TiO_2 powders. The molded sample was sintered at temperatures from 973 K to 1,500 K using an electric furnace. The sintering conditions for the samples are

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Table 1
Sintering parameters and heat treatment conditions of the Li_2TiO_3 samples.

Li_2CO_3 : TiO_2 (molar ratio)	Pre-sintering condition		Press condition	Main sintering condition			Sample density [%T.D.]
	Temperature [K]	Time [h]		Temperature [K]		Time [h]	
1.0 : 1.0			40 MPa 3min	1,000		5	39
							40
							41
	1,000	5		1,173		8	76
				1,250			85
	973			1,473		40	91
							94
	1,000			Heat treatment conditions	1st:1,500	8	80
					2nd:1,000	10	
		10			873(Ar gas)	24	39

summarized in Table 1. The low-density Li_2TiO_3 samples were made by sintering for 5 h at temperatures of 1,000 K. As theoretical mass density of Li_2TiO_3 is 3.43 g/cm^3, the ratio of the sample mass density to the theoretical mass density was 0.40, which we call “40%T.D.”.

The high-density sample was made by re-sintering the presintered low-density samples as the starting materials. After pulverizing the presintered samples again and molding them, we sintered the samples at 1,473 K for 40 h to get high density up to 94%T.D. To prepare a non-stoichiometric Li_2TiO_3 sample, the low-density Li_2TiO_3 sample (39% T.D.) was re-sintered in Ar gas atmosphere at 873 K for 24 h using an electric tubular furnace. The sintered samples were disk-shaped with thickness of 2 mm and diameter of 15 mm. We measured the sample mass with a microbalance and the volume with a vernier caliper to calculate the density.

The samples were put in a vacuum chamber evacuated to a pressure of 1 Pa, and were exposed at room temperature to the dry CO_2 gas, the atmosphere or the moist air at 1 atm. In the case of exposure to the moist air, we set a beaker filled with water in the chamber kept at high humidity (> 34,000 ppm). A digital thermo-hygrometer FL-02 was set in the vacuum chamber. The humidity during exposure to the dry CO_2 gas and the dry air was less than 5,000 ppm, while that during exposure to the atmosphere was 20,000–30,000 ppm.

Samples used in this work were Li compounds, Li_2TiO_3. The NRBS analysis is highly sensitive to Li isotopes, and is very effective for blanket material analysis [20]. The ERD analysis is suitable for measuring H distribution from sample surface region. Placing the sample at the center of the target vacuum chamber, the NRBS analysis was performed using 2.6-MeV-proton beams and a silicon surface barrier detector (SSBD) located at 165° while for ERD analysis 3.0-MeV-He^{2+} beams and SSBD located at 30° with respect to the direction of the beam incidence. The energy resolution (FWHM) of the NRBS measurement system is 30 keV for C(p,p) and 80 keV for Ti(p,p), which corresponds to the depth resolution of 100 nm and 150 nm, respectively, while the ERD resolution is 80 keV for H(He,p) corresponding to 140 nm.

The crystallographic structure of the prepared Li_2TiO_3 samples was investigated by XRD analysis using RINT2000 (Rigaku) with Cu-Kα X-ray at room temperature. The simulation of powder XRD patterns was performed using a Rietveld-analysis program RIETAN and the crystal data for Li_2TiO_3, Li_2CO_3, and TiO_2.

3. Results and discussion

3.1. CO_2 absorption characteristics in the non-stoichiometric composition of a Li_2TiO_3 sample with defects of O and Li deficiencies

Our previous studies have shown that high-density Li_2TiO_3 samples with 90% to 95% T. D. hardly absorb CO_2. In order to prepare reference data on CO_2 absorption characteristics, Li_2TiO_3 samples with low-density (39–41% T.D.) were mainly used in this section. The dry CO_2 gas exposure of the low-density Li_2TiO_3 sample (39%T.D.) was performed in the dry CO_2 gas- filled vacuum chamber at 1 atm at room temperature. The exposure time was 2,000 h at the maximum.

XRD analysis was performed on the low-density Li_2TiO_3 samples (39%T.D.) after exposure to the dry CO_2 gas in order to investigate crystallographic structure change of Li_2TiO_3. Fig. 1 shows the powder XRD spectra in comparison with the typical as-sintered Li_2TiO_3 sample (39%T.D.), where X-ray intensity is recorded as a function of the diffraction angle 2θ. Simulation spectra of Li_2TiO_3, Li_2CO_3 and TiO_2 are also shown in this figure.

The powder XRD spectral pattern of the as-sintered sample is in good agreement with the simulation spectrum; peaks are observed at 2θ = 19°, 36°, 44°, 48°, 58°, 63° and 67°, which indicates that the sintered samples are converted almost perfectly to Li_2TiO_3. In the spectrum of the low-density Li_2TiO_3 sample after the exposure to the dry CO_2 gas for 2,000 h, the XRD peaks of Li_2CO_3 are observed at 2θ = 21°, 31°, and 32°. This clearly indicates that Li_2TiO_3 absorbs CO_2 and then forms Li_2CO_3 and TiO_2 by the dry CO_2 gas exposure.

A non-stoichiometric composition Li_2TiO_3 sample (39%T.D.) was prepared in an Ar gas atmosphere using an electric tube furnace. The NRBS spectra of the non-stoichiometric composition Li_2TiO_3 sample

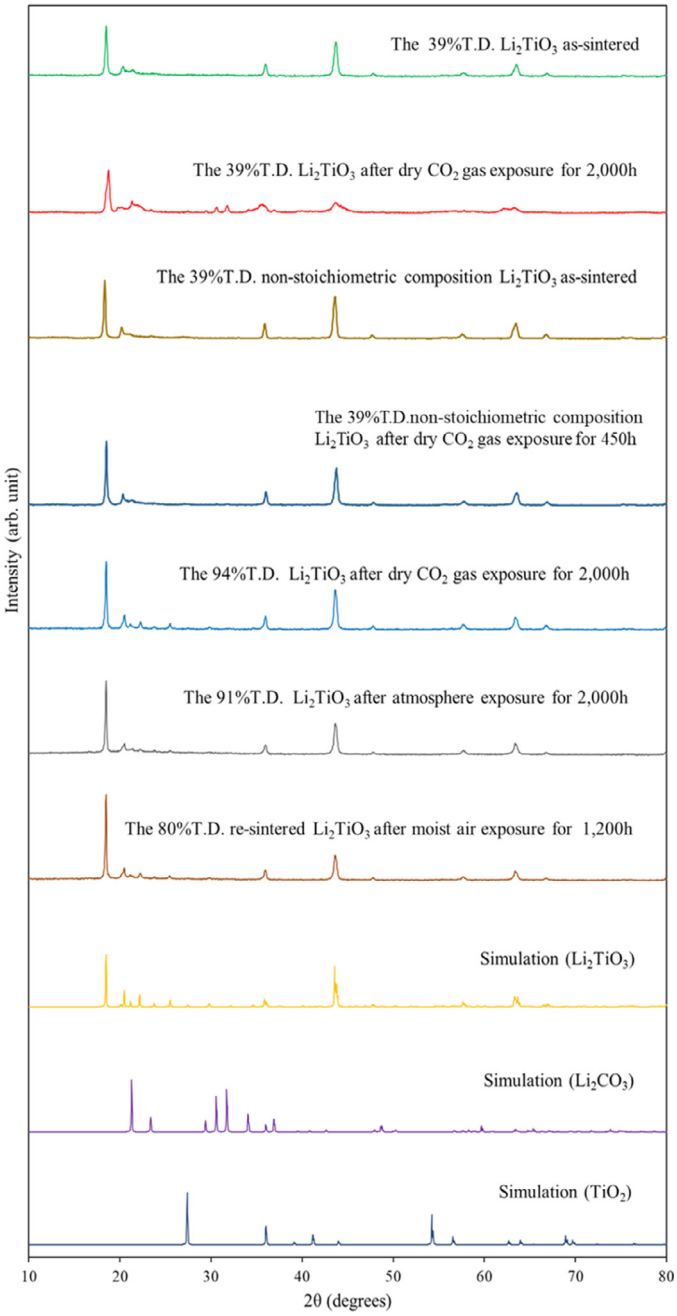

Fig. 1. XRD patterns of the as-sintered low-density and high-density Li_2TiO_3 samples and changes of XRD patterns after exposures to the dry CO_2 gas, the atmosphere and the moist air.

(39%T.D.) before and after the dry CO_2 gas exposure for 800 h was shown in Fig. 2a. In this figure, the scattered particle yield is plotted as a function of energy. For comparison, the NRBS spectrum of this sample before exposure (as-sintered sample) is also shown. The edge energies of Ti, O, C, and Li spectra are about 2.4, 2.0, 1.8, and 1.5 MeV, respectively. A C(p,p) proton spectral peak, which was absent before the dry CO_2 gas exposure, appeared, and the O(p,p) yield increased after the dry CO_2 gas exposure.

Fig. 2b shows depth distribution of Li, C, O and Ti deduced from the energy spectra. The reason for the apparent non-zero densities in the negative depth region and the finite width of the up edges at the surface is a finite energy resolution of the detection system. The spectra are not corrected for the energy dispersion due to finite energy resolution. Anyway, integrating the density over the depth from −0.2 to2.0 μm, we

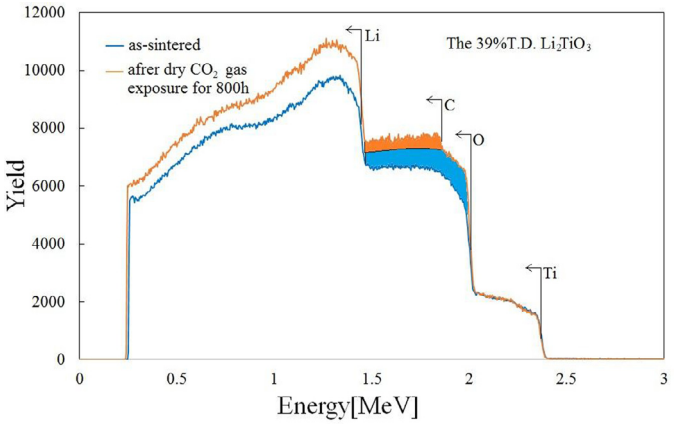

Fig. 2a. The NRBS spectra measured with a 2.6-MeV proton beam for non-stoichiometric composition Li_2TiO_3 sample (39%T.D.) after exposure to the dry CO_2 gas for 800 h. The NRBS spectra of the as-sintered Li_2TiO_3 sample of the non-stoichiometric composition are also shown for comparison.

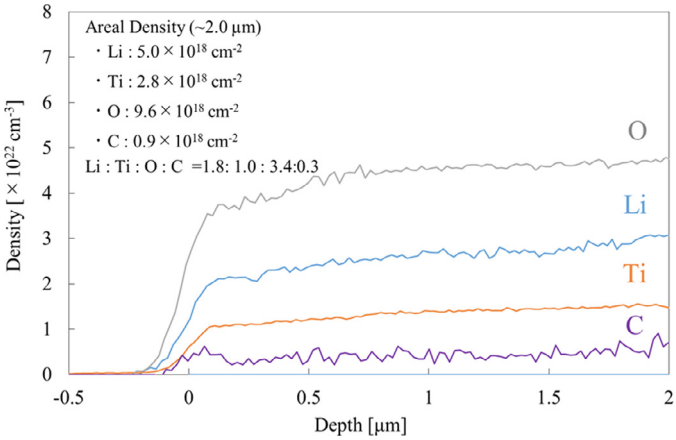

Fig. 2b. Depth distribution of Li, C, O and Ti in the non-stoichiometric composition Li_2TiO_3 sample (39%T.D.) exposed to the dry CO_2 gas for 800 h.

obtain the areal densities of Li, C, O and Ti near the surface layers (~2.0 μm) as $N_{Li} = 5.0 \times 10^{18}$ cm^{-2}, $N_C = 0.9 \times 10^{18}$ cm^{-2}, $N_O = 9.6 \times 10^{18}$ cm^{-2} and $N_{Ti} = 2.8 \times 10^{18}$ cm^{-2}, respectively. The composition ratio of Li:Ti:O:C is then 1.8:1.0:3.4:0.3. And the composition ratio of Li:Ti:O before exposure (as-sintered 39%T.D.sample) was 1.8: 1.0: 2.8, which shows O and Li are lost in this sample during sintering in Ar gas atmosphere.

In addition, the dry CO_2 gas exposure followed by NRBS analysis was also performed on the stoichiometric Li_2TiO_3 sample (39% T.D.). Dependence of the C areal density on the exposure time of the dry CO_2 gas for the non-stoichiometric low-density Li_2TiO_3 sample (39%T.D.) and the stoichiometric low-density Li_2TiO_3 sample (39%T.D.) is shown in Fig. 3. NRBS analysis was carried out every 200 h. Exposure time of the dry CO_2 gas was 800 h for the non-stoichiometric sample (39% T.D.) and up to 2,000 h for stoichiometric sample (39% T.D.).

Under the dry CO_2 gas exposure conditions, the C areal density of the non-stoichiometric sample (39% T.D.) was 7.5×10^{17} cm^{-2}, 8.6×10^{17} cm^{-2} and that of the stoichiometric sample was 1.8×10^{17} cm^{-2}, 4.1×10^{17} cm^{-2} at an exposure time of 200 h and 400 h, respectively. The non-stoichiometric Li_2TiO_3 sample with defects of O and Li deficiencies has 2 to 4 times greater amount of CO_2 absorbed at the same exposure time compared to the stoichiometric Li_2TiO_3 sample. The C areal density of the stoichiometric sample saturates at about 1,200 h, while that of the non-stoichiometric sample (39% T.D.) at about 450 h with almost the same saturation value of 9×10^{17} cm^{-2}. Therefore, it is considered that the non-

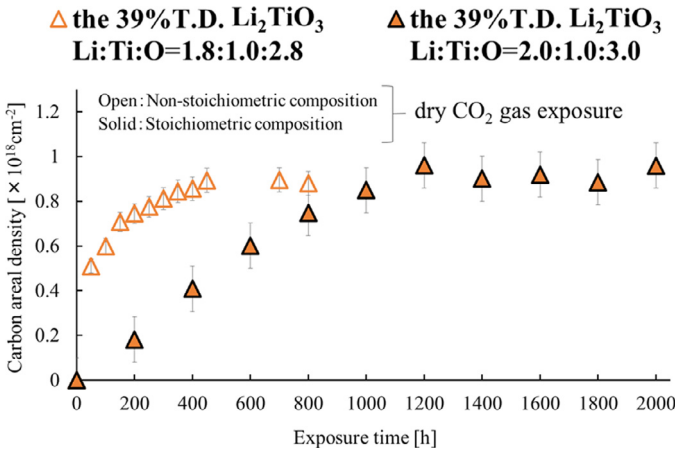

Fig. 3. Dependence of C areal density on the exposure time of the dry CO_2 gas for the non-stoichiometric composition Li_2TiO_3 sample (39%T.D.) and the stoichiometric Li_2TiO_3 sample (39%T.D.).

stoichiometricality increases CO_2 absorption rate due to defects of O and Li.

3.2. CO_2 absorption characteristics of the Li_2TiO_3 sample with the optimum density for a blanket material

In order to improve the tritium release characteristics as a blanket material, Li_2TiO_3 sample with about 80% T.D. is considered to be good [16–19]. In our previous experiments, it was found that CO_2 is hardly absorbed by the high-density Li_2TiO_3 samples with above 90% T.D. under the atmospheric and the moist air exposures. However, Li_2TiO_3 samples with 76%T.D. and 85% T.D. absorbed CO_2 in the moist air and the atmospheric exposures. Both exposure atmospheres contained CO_2 with a fraction of 0.035 vol.% .

The high-density Li_2TiO_3 sample (91% T.D.) sintered at a temperature above 1,428 K for 40 h absorbed little amount of CO_2 under the atmospheric exposure for 2,000 h; the crystal structure of the Li_2TiO_3 can be seen from the XRD spectrum of this sample after the exposure as shown in Fig. 1. A high-density sample sintered at above 1,428 K was crushed with a crucible and re-sintered at 1,000 K for 10 h. As a result, the 80%T.D. Li_2TiO_3 sample was obtained.

The re-sintered 80% T.D. sample was exposed for 1,200 h to the moist air. Fig. 4 shows the dependence of the C areal density in the samples on the exposure time. The re-sintered sample had the C areal density lower than the detection limit in the NRBS measurement for

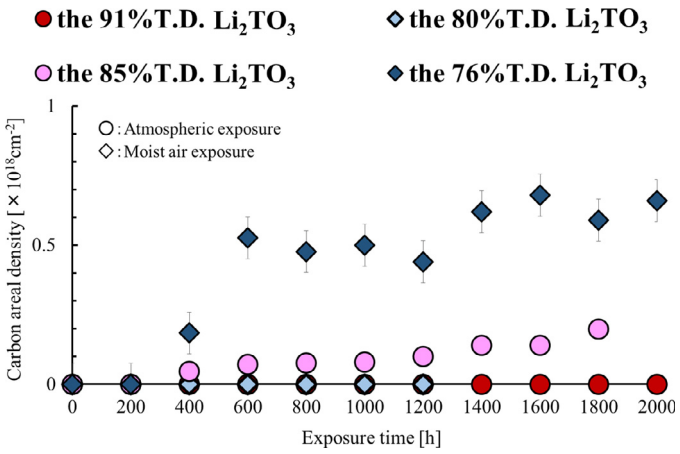

Fig. 4. Dependence of C areal density on the exposure time of the atmosphere, and the moist air for the medium- and high-density samples and of the moist air for the sample re-sintered above 1,428 K.

exposure times up to 1,200 h. On the other hand, the C areal density of the 85% T.D. and 76% T.D. Li_2TiO_3 samples prepared by sintering at 1,250 K for 8 h and at 1,173 K for 8 h shows 1.0×10^{17} cm^{-2} and 4.4×10^{17} cm^{-2}, respectively, at the atmospheric and the moist air exposure for 1,200 h.

The 85% T.D. Li_2TiO_3 sample sintered at 1,250 K has a higher apparent sample density than the 80% T.D. Li_2TiO_3 sample. There is a report by Kleykamp that crystal structure changed from monoclinic to cubic in the Li_2TiO_3 sample sintered at above 1,428 K [21]. Taking this into account, Li_2TiO_3 was sintered at a temperature above 1,428 K. It is supposed that the crystal structure of Li_2TiO_3 turns into cubic one and then turns back to monoclinic one due to the gradual decrease in temperature in the electric furnace. This crystal structure change occurs with rearrangements of the particles and the crystal grains, leaving very few defects such as vacancies and pores, which is supposed to reduce CO_2 absorption. The XRD peaks in the 80%T.D. sample spectrum have smaller FWHMs compared with others as shown in Fig. 1, which implies the higher crystallinity of the sample.

In summary, CO_2 absorption is largely influenced by the presence or absence of defects in the Li_2TiO_3 sample, and it is suggested that CO_2 absorption can be greatly suppressed in the sample having very few defects.

3.3. Catalytic effect of water vapor on CO_2 absorption in the low-density Li_2TiO_3 sample

Influence of water vapor on the CO_2 absorption of the low-density Li_2TiO_3 sample has been investigated in a similar manner. The low-density Li_2TiO_3 samples (39–41%T.D.) were exposed to the dry air (< 5,000 ppm), the atmosphere (20,000 to 30,000 ppm) and the moist air (> 34,000 ppm) containing 0.035 vol.% CO_2 at the room temperature for 2,000 h. ERD analysis was performed every 200 h during exposure to the atmosphere (for 1,800 h), the dry air (800 h) and the moist air (600 h).

The dependence of H areal density on the exposure time of the atmosphere, the dry air and the moist air is shown in Fig. 5. The H areal densities from the sample surface to the depth of 0.5 μm in the 39%T.D. Li_2TiO_3 (atmospheric exposure), the 40%T.D. (dry air exposure) and the 41%T.D. (moist air exposure) samples are compared. Although the data scattering is rather large especially for the 39%T.D. sample, it is clear that the value at the moist air exposure is the lowest. In spite of the lower humidity in the dry air and the atmosphere than in the moist air, the H content in the sample with the moist air exposure is the lowest. Therefore, the increase in H content in the sample is not related to the amount of water vapor.

Fig. 6 shows dependence of C areal density on the exposure time to

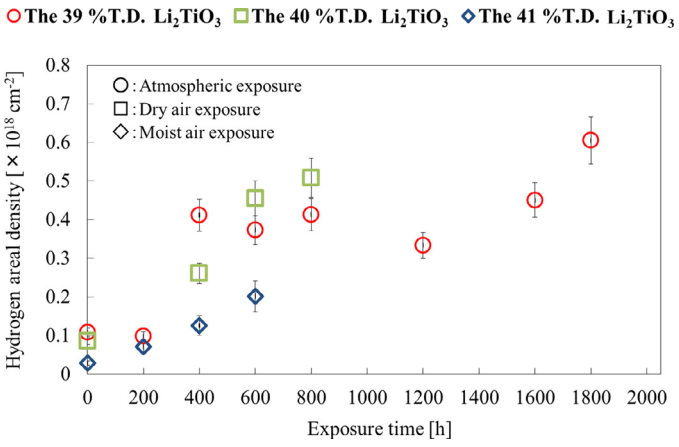

Fig. 5. Dependence of H areal density on the exposure time of the dry air, the atmosphere and the moist air for the low-density samples.

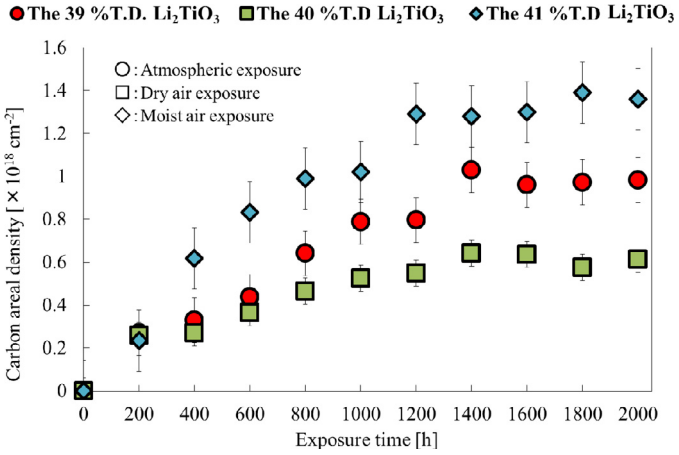

Fig. 6. Dependence of C areal density on the exposure time of the atmosphere, the dry air and the moist air for the low-density samples.

the atmosphere, the dry air and the moist air for the samples. The C areal densities were determined by the NRBS measurement. The C areal densities gradually increased with exposure time until 1,000 h with the saturation values of 1.3×10^{18} cm^{-2} (moist air), 1.0×10^{18} cm^{-2} (atmosphere) and 0.6×10^{18} cm^{-2} (dry air). It is found that the amount of the C areal density under the moist air exposure is the largest.

There is no correlation between the amount of the H areal density and that of the C areal density. This result means that the H_2O absorbed in the sample does not exert any effect on CO_2 absorption, while the adsorbed H_2O on the sample surface has catalytic effect to promote CO_2 absorption into the Li_2TiO_3 sample.

4. Conclusions

Dry CO_2 gas exposures of the non-stoichiometric Li_2TiO_3 sample with O and Li deficiencies (39%T.D.) and the stoichiometric low-density Li_2TiO_3 sample (39%T.D.) have been performed. The XRD analysis shows that in both low-density Li_2TiO_3 samples composition of a part of the Li_2TiO_3 samples has changed to a mixture of Li_2CO_3 and TiO_2. The NRBS analysis of the samples shows that C areal density is increased with exposure time and saturated at about 450 h for the non-stoichiometric sample which is much shorter than 1,200 h for the stoichiometric sample. It is concluded that defects of O and Li deficiencies in the Li_2TiO_3 sample promote the CO_2 absorption.

CO_2 absorption could be greatly suppressed in the sample without defects. We have found a process to prepare a Li_2TiO_3 sample that has 80%T.D., the suitable density as the blanket material, and capable of absorbing very little amount of CO_2 even in high humidity environment.

Next, in order to investigate the influence of water vapor on CO_2 absorption, exposure experiments have been carried out by changing humidity. ERD measurements have shown that there is no correlation between the H distribution near the Li_2TiO_3 sample surface region and the humidity in the atmosphere. On the other hand, NRBS measurements have shown that the amount of the C areal density of the sample exposed to moist air was largest among three exposure conditions. There is no correlation between the amount of H content and the C areal density. It is inferred that adsorbed H_2O on the sample surface provides catalytic action for absorption of CO_2.

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