

Effects of Li_4TiO_4 Structure on Tritium Release Kinetics from Lithium-Enriched $\text{Li}_{2+x}\text{TiO}_3$

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The release kinetics of tritium for $\text{Li}_{2+x}\text{TiO}_3$ ($x = 0, 0.2, 0.4$) and Li_4TiO_4 were studied by means of Thermal Desorption Spectroscopy (TDS). Tritium-TDS spectrum at the heating rate of 0.5 K / min for $\text{Li}_{2+x}\text{TiO}_3$ irradiated with thermal neutron consisted of two release stages at 480 K and 580 K, namely Peaks 1 and 2, respectively. The activation energy of Peak 1 was estimated to be around 0.37 eV, while that of Peak 2, about 0.63 eV. The latter corresponded to the activation energy of tritium diffusion in Li_2TiO_3 . For Li_4TiO_4 exposed to tritium-deuterium mixture gas, two tritium release stages named as Peaks A and B were also observed at 450 K and 600 K, respectively, in tritium-TDS spectrum at the heating rate of 0.5 K / min. As the release temperature regions of Peak 1 and Peak A were almost the same, tritium releases of these peaks were considered to be originated from a same process. O-T bonds formed on the surface of Li_4TiO_4 were decomposed as Peak B in TDS spectra.

1. Introduction

For the development of D-T fusion reactors, it is important to establish an effective fuel recycling system and a comprehensive model of tritium migration processes in solid tritium breeding materials. In the test blanket module for ITER, lithium titanate (Li_2TiO_3), one of ternary lithium oxides, is a candidate of tritium breeding materials because of good tritium release property, chemical stability, and so on [1]. During the operation of D-T fusion reactor, energetic tritium is generated by the reactions of ${}^6\text{Li}(n, \alpha)\text{T}$ and ${}^7\text{Li}(n, n\alpha)\text{T}$ in Li_2TiO_3 and lithium will be consumed by these reactions, resulting in lithium-depletions in Li_2TiO_3 . As lithium-depletion in Li_2TiO_3 induces lower tritium generation rate, the lithium-depleted tritium breeding materials will be replaced after certain periods of operations.

The use of $\text{Li}_{2+x}\text{TiO}_3$ ($x=0.2, 0.4$), which is the lithium-enriched Li_2TiO_3 , is proposed recently to improve the life cycle of tritium breeding materials with respect to tritium generation property [2-4]. $\text{Li}_{2+x}\text{TiO}_3$ consists of Li_2TiO_3 structure and excess lithium: i.e. Hara *et al.* [5], reported that both of $\text{Li}_{2.2}\text{TiO}_3$ and $\text{Li}_{2.4}\text{TiO}_3$ were the mixture of Li_2TiO_3 and Li_4TiO_4 structures, indicating that excess lithium induced the formation of Li_4TiO_4 structure in Li_2TiO_3 structure during fabrication.

In our previous study, tritium release behaviors and their kinetics for $\text{Li}_{2+x}\text{TiO}_3$ irradiated with thermal neutron were investigated by means of TDS [6]. Tritium-TDS spectrum for $\text{Li}_{2.0}\text{TiO}_3$ at the heating rate of 0.5 K/min consisted of

single release stage at around 580 K. An additional release stage was observed at around 480 K for the tritium-TDS spectra for $\text{Li}_{2.2}\text{TiO}_3$ and $\text{Li}_{2.4}\text{TiO}_3$, although the major release stage was located at 580 K, which was assigned to the tritium release controlled by tritium diffusion in Li_2TiO_3 structure from kinetic analyses. In addition, the amount of tritium released at 480 K was increased with increasing lithium concentration. It was considered that this additional tritium release stage would be associated with excess lithium, that is, Li_4TiO_4 structure. However, the effects of Li_4TiO_4 structure on tritium release for $\text{Li}_{2+x}\text{TiO}_3$ are still unclear because tritium release mechanisms for Li_4TiO_4 have not been studied in detail. Therefore, in this study, tritium release behavior for Li_4TiO_4 was studied by means of TDS. Tritium was generated in Li_4TiO_4 by thermal neutron irradiation or introduced by thermal tritium gas absorption. The tritium release kinetics for $\text{Li}_{2+x}\text{TiO}_3$ irradiated with thermal neutron was also evaluated for comparison.

2. Experimental

Powders of Li_4TiO_4 and $\text{Li}_{2+x}\text{TiO}_3$ purchased from Kaken Co. were used as samples. The average grain diameters of Li_4TiO_4 , $\text{Li}_{2.0}\text{TiO}_3$, $\text{Li}_{2.2}\text{TiO}_3$ and $\text{Li}_{2.4}\text{TiO}_3$ measured by SEM (Scanning Electron Microscope) were 12, 3.0, 1.0 and 1.0 μm , respectively. For thermal neutron irradiation experiments, 0.3 g of these samples were introduced into

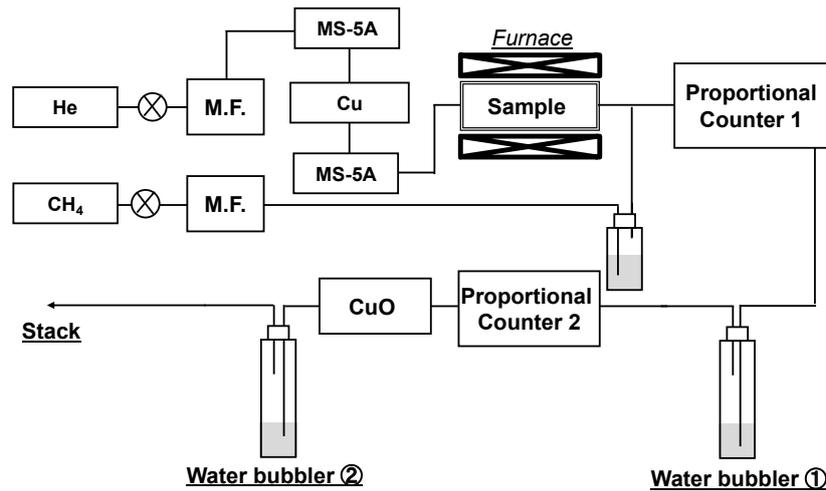


Fig. 1 Schematic drawing of TDS system

quartz tubes individually and annealed at 1073 K for Li_4TiO_4 and 1173 K for $\text{Li}_{2+x}\text{TiO}_3$ under He gas with the pressure of less than a few Pa for 3 h. After heating, these tubes were sealed under vacuum. Thermal neutron irradiations were conducted at Pneumatic tube 2 (Pn-2) of Research Reactor Institute, Kyoto University (KURRI). The thermal neutron flux was $5.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The thermal neutron irradiation was carried out for 10 min, corresponding to the thermal neutron fluence of $3.3 \times 10^{15} \text{ n cm}^{-2}$. The temperatures of the samples during irradiation were estimated to be lower than 350 K.

For hydrogen isotope gas exposure, Li_4TiO_4 sample was heated at 1073 K for 3 h in vacuum under the pressure around 10^{-5} Pa, then sample temperature was kept at 673 K. Thereafter, the tritium-deuterium mixture gas consisting of D_2 and DT ($\text{T/D} = 0.005$) or the pure D_2 (isotopic purity: 99.4%) gas was introduced into the sample with the total pressure of 200 Pa for 1 day. After the hydrogen isotope gas exposure, the sample was quickly cooled down by water and liquid nitrogen.

Out-of-pile tritium release experiments were performed in tritium-TDS system at Shizuoka University as shown in Fig. 1. The sample put in Mo crucible was set in quartz tube surrounded by a ceramic furnace. The He gas at the flow rate of 15 sccm was introduced into MS-5A and a heated Cu at 623 K to exclude impurities such as water and oxygen in He gas, and then purged into the system during experiments. The released tritium is recovered by purge gas and is carried to the first proportional counter (PC1). The volume of PC is 30 cm^3 , and the voltage of 2.4 kV was applied to PC during measurement. After PC1, purge gas with tritium passes through first water bubbler (WB1) to trap the water-form tritium such as HTO and T_2O , named as “oxidized T”. The second proportional counter (PC2) set after WB1 measures gas-form tritium such as HT and T_2 , named as “reduced T”. Thereafter, the reduced T are oxidized by heated CuO at 623 K after PC2 and trapped by second water bubbler (WB2). The amounts

of oxidized T and reduced T trapped in WB1 and WB2, respectively, are quantified by a Liquid Scintillation Counter (ALOKA LSC-5100). The CH_4 gas at the flow rate of 25 sccm was used as a counting gas for the proportional counters. The CH_4 gas was humidified by passing through another water bubbler for reduction of memory effect in proportional counters. The humidified CH_4 gas was converged to He gas flow just before PC1 so that humidified CH_4 is not purged directly to Mo crucible with sample during heating. The quartz tube, stainless tubing of this system and the proportional counters were also heated at around 373 K to reduce the memory effect.

In the tritium-TDS experiments, the samples were heated up to 1173 K. Isothermal heating experiments were also conducted around 600-700 K.

FT-IR (Fourier Transform Infrared Spectroscopy) measurements were also carried out for Li_4TiO_4 exposed to pure D_2 gas at Shizuoka University to reveal chemical states of deuterium in Li_4TiO_4 . Changes of crystal structure of Li_4TiO_4 by D_2 gas exposure were also investigated by X-ray diffraction (XRD) technique at University of Toyama.

3. Results and discussion

Fig. 2 shows the tritium-TDS spectra for $\text{Li}_{2+x}\text{TiO}_3$ at the heating rate of 0.5 K / min measured by PC1, representing the overall release of tritium. These spectra can be separated into two release stages, namely Peak 1 at 480 K and Peak 2 at 580 K. The TDS spectra for $\text{Li}_{2.0}\text{TiO}_3$ consisted of one release stage as Peak 2, although additional release stage of Peak 1 was also found for $\text{Li}_{2.2}\text{TiO}_3$ and $\text{Li}_{2.4}\text{TiO}_3$. The amount of tritium for Peak 1 was increased with increasing lithium concentration. To understand the tritium release kinetics for these peaks, the heating rate dependence experiments were carried out. In this analysis, Kissinger-Akahira-Sunose (KAS) model-free-kinetics method [6] which has been widely applied to analyze TDS spectra was adopted in the present

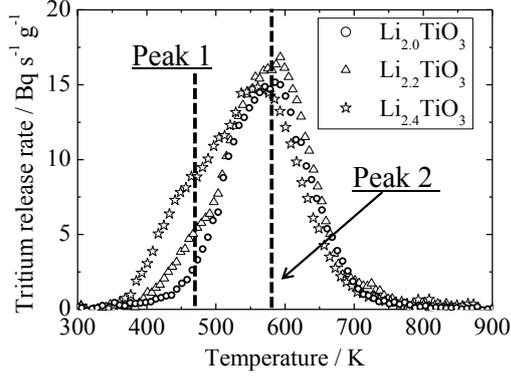


Fig. 2 Tritium-TDS spectra of $\text{Li}_{2+x}\text{TiO}_3$ at the heating rate of 0.5 K/min

study. In this method, $\ln(\beta/T_p^2)$ are plotted against $1/T_p$ for the determination of activation energy, where β is the heating rate and T_p is the peak temperature, based on following equation,

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{RA}{E_a g(\alpha)}\right) - \frac{E_a}{RT_p} \quad (1)$$

where R is gas constant, A is pre-exponential factor, E_a is activation energy of reaction. The term of $g(\alpha)$ is a model-function determined by rate limiting process of reaction. The linear relation between $\ln(\beta/T_p^2)$ and $1/T_p$ was deduced as Eq. 1, and the slope of which is representing $-E_a/R$. The peak separation analysis was done for TDS spectra of $\text{Li}_{2.2}\text{TiO}_3$ and $\text{Li}_{2.4}\text{TiO}_3$ under various heating rates, then peak temperatures for Peaks 1 and 2 in each spectrum were estimated. Table 1 summarizes the peak temperatures of Peaks 1 and 2 for $\text{Li}_{2.4}\text{TiO}_3$ at various heating rates. The peak temperatures were shifted toward higher temperature region with increasing heating rate. Fig. 3 shows the $\ln(\beta/T_p^2)$ vs $1/T_p$ plot for Peaks 1 and 2 for $\text{Li}_{2.4}\text{TiO}_3$. Linear relations between $\ln(\beta/T_p^2)$ and $1/T_p$ were found for each peak. The obtained activation energies of these release peaks were evaluated to be 0.37 eV and 0.63 eV for Peaks 1 and 2, respectively. The similar activation energies were also obtained for $\text{Li}_{2.2}\text{TiO}_3$. Especially, the activation energy of Peak 2 was consistent with that of tritium diffusion for Li_2TiO_3 obtained in our previous study and other works [7, 8]. The activation energy around 0.4 eV has not been reported for Li_2TiO_3 with neutron irradiation [8-10]. In addition, the activation energy for desorption of hydrogen isotopes adsorbed on the surface of Li_2TiO_3 was reported as about

Table 1 Peak temperatures of each peak for $\text{Li}_{2.4}\text{TiO}_3$ at various heating rates

Heating rate (K/min)	T_p for Peak 1 (K)	T_p for Peak 2 (K)
0.5	453	591
1	515	603
5	580	705
10	601	718

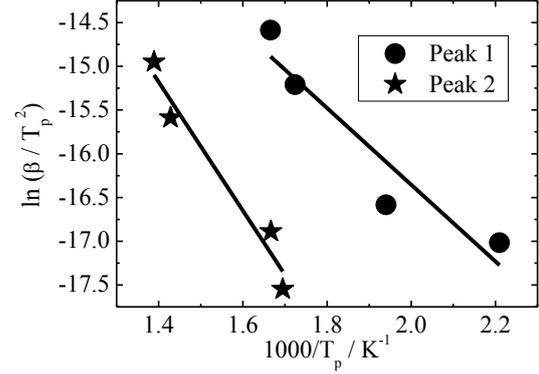


Fig. 3 Analytical results of release kinetics for Peaks 1 and 2 in $\text{Li}_{2.4}\text{TiO}_3$

1.2 eV [11], indicating that Peak 1 would not be associated with Li_2TiO_3 .

Fig. 4 shows the tritium-TDS spectrum for Li_4TiO_4 irradiated with thermal neutron measured at the heating rate of 0.5 K/min. This spectrum was measured by PC1 and no tritium release was found by PC2, indicating that almost all of tritium was released as water form. The tritium-TDS spectrum of Li_4TiO_4 can be separated into two release stages at 450 K and 600 K, and named as Peak A and Peak B, respectively. Especially, FWHM of Peak B was quite narrow compared to the other spectra as shown in Fig. 2. The peak temperature of Peak A was almost consistent with that of Peak 1.

Isothermal heating experiments were done for Li_4TiO_4 exposed to tritium-deuterium mixture gas to determine the tritium release kinetics for Li_4TiO_4 . Because of the exposure temperature of 673 K, which is higher than the release temperature of Peak A, the release kinetics of Peak B was examined in these experiments especially. Two probable processes which control the tritium release in Li_4TiO_4 are considered as diffusion and de-trapping processes. In the diffusion limited release process, tritium would diffuse slowly toward the surface and release on the surface quickly. In the de-trapping limited one, tritium would be initially trapped strongly by the trapping sites. Tritium release would be initiated by de-trapping from the

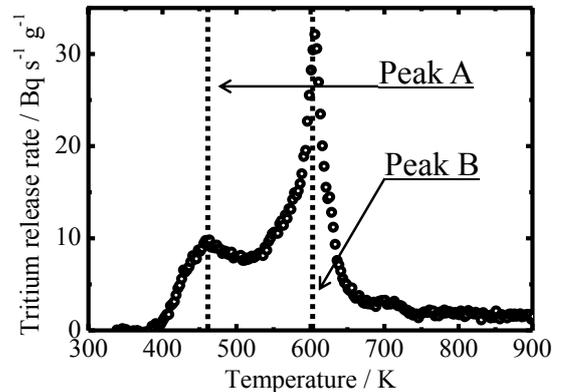


Fig. 4 Tritium-TDS spectrum of Li_4TiO_4 with thermal neutron irradiation

trapping sites. The other processes are quite faster than the de-trapping process, so these processes are not apparent on tritium release kinetics. The tritium release controlled by diffusion process is expressed by Fick's diffusion equation [12]. In particular for tritium release via diffusion in spherical media, tritium release with respect to elapsed time, t can be expressed in the following equation,

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{a^2}\right) \quad (2)$$

where α is fraction of released tritium to total amount, a is the radius of media, namely grain radius and D is diffusivity. On the other hand, the rate of de-trapping limited release should be controlled only by the concentration of trapped tritium in the material, indicating that de-trapping limited release is the first-order reaction, which is expressed as follows,

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (3)$$

where k is the rate constant of reaction [13]. Comparing the theoretical curve derived from Eqs. 1 and 2 with tritium release by isothermal heating, the rate limiting process on tritium release was determined. Fig. 5 shows the isothermal tritium release behavior at various temperatures for Li_4TiO_4 exposed to tritium-deuterium mixture gas. The theoretical curves by de-trapping limited release model and diffusion limited release model were also shown in this figure. As shown in Fig. 5, theoretical curves based on diffusion limited release model could hardly reproduce isothermal tritium release for Li_4TiO_4 . The theoretical curves by de-trapping limited release model could reproduce tritium release curve in the temperature region around 600-700 K, as shown in Fig. 6, indicating that tritium release for Li_4TiO_4 was controlled by de-trapping process.

The activation energy of tritium de-trapping was derived to be about 1.2 eV from the de-trapping rate constants at various temperatures, which was close to the

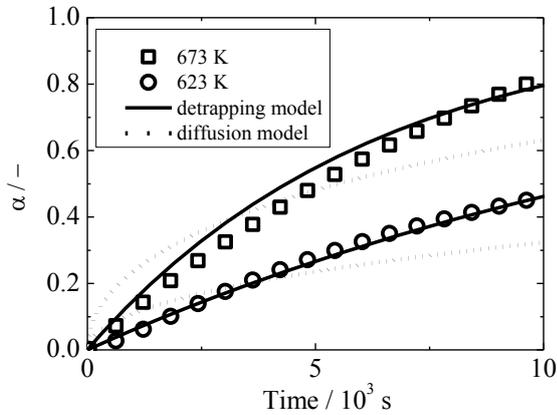


Fig. 5 Comparison of isothermal tritium release to theoretical curves derived from de-trapping and diffusion processes

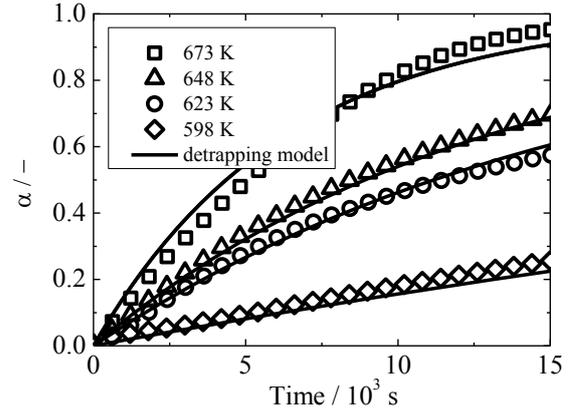


Fig. 6 Isothermal tritium release for Li_4TiO_4 exposed to tritium-deuterium mixture gas

decomposition energy of hydrogen from O-H bonds [14]. A FT-IR spectrum for Li_4TiO_4 exposed to pure D_2 gas showed the IR absorption in the wavenumber range of 2450-2750 cm^{-1} (not shown here). It was reported that O-D bonds in lithium ceramics showed IR absorption in this wavenumber region[15], indicating that O-D bonds were formed in Li_4TiO_4 by D_2 gas exposure. Therefore, it was considered that tritium trapped as O-T bonds were de-trapped by the decomposition of O-T bonds and released as Peak B for Li_4TiO_4 .

However, the activation energy of Peak 2 in $\text{Li}_{2+x}\text{TiO}_3$ was different from that of the decomposition of O-T bonds in Li_4TiO_4 . In addition, the tritium retentions as Peak 2 in $\text{Li}_{2+x}\text{TiO}_3$ were almost similar to that of Li_2TiO_3 , although more than half of tritium was retained as O-T bonds in Li_4TiO_4 with neutron irradiation. These facts would indicate that the tritium releases derived from O-T bonds should be small in $\text{Li}_{2+x}\text{TiO}_3$.

The crystal structure of Li_4TiO_4 before and after D_2 gas exposure were compared by XRD method as shown in Fig. 7. In the measurements, silicon was used for reference. The diffraction patterns of Li_4TiO_4 exposed to D_2 gas were quite similar to that without D_2 gas exposure, indicating that the crystal structure was not changed by D_2 gas exposure. These results indicated that LiOD structure (crystal) was not formed in Li_4TiO_4 . It was reported that Li_4TiO_4 is reactive with water vapor and forms O-H bonds on the surface [4], considering that water vapor as impurity was adsorbed on the surface of Li_4TiO_4 during air exposure or TDS measurements, which would induce the formation of O-H bonds. Similar results have been obtained in Li_2O [13]. The rate limiting process of tritium release for Li_2O was changed by heating temperature: i.e. in a lower temperature region, tritium release was controlled by decomposition of surface O-T bonds. In a higher temperature region, tritium release was governed by diffusion process. The rate limiting process was changed at 570 K, and this temperature was closed to Peak B appearing in this study, indicating that O-T bonds was mainly formed on the surface of Li_4TiO_4 and decomposed

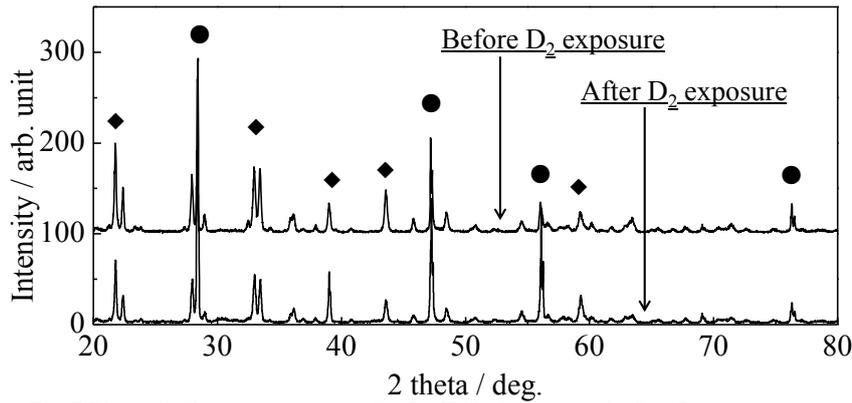


Fig.7 X-ray diffraction patterns for Li_4TiO_4 before and after D_2 gas exposure
 ◆ indicates Li_4TiO_4 structure and ● indicates reference silicon [5]

as observed as Peak B. The small tritium retention as O-T bonds in $\text{Li}_{2+x}\text{TiO}_3$ would imply that the amount of water on the surface of Li_4TiO_4 in $\text{Li}_{2+x}\text{TiO}_3$ was small. Because the $\text{Li}_{2+x}\text{TiO}_3$ was the mixtures of Li_2TiO_3 and Li_4TiO_4 , the effective surface area of Li_4TiO_4 in $\text{Li}_{2+x}\text{TiO}_3$ should be small, resulting in the small retention of tritium as O-T bonds.

Peak B appearing in the TDS spectrum of Li_4TiO_4 could be assigned to the release of tritium as O-T bonds in this study. However, the assignment for Peak A was not completed although this peak also appeared in TDS spectra of $\text{Li}_{2+x}\text{TiO}_3$. The water vapor on the surface of Li_4TiO_4 may provide trapping sites for tritium as O-T bonds. A part of tritium migrated from bulk region of Li_4TiO_4 at lower temperatures, corresponding to tritium release as Peak A, would be trapped on the surface at lower temperature region. Li_4TiO_4 would easily react with water vapor in air, therefore, the experiments for Li_4TiO_4 without any air exposure are required to elucidate the tritium retention and release as Peak A, and consequently the relations of tritium retention as Peak 1 and the amount of excess lithium in $\text{Li}_{2+x}\text{TiO}_3$. The experiments in vacuum system would be a promising way to exclude the effects of surface O-T bonds. Therefore, it was considered that hydrogen isotope gas exposure and subsequent TDS experiments in the same vacuum system would reveal the tritium release mechanisms from Li_4TiO_4 in detail.

4. Conclusions

The release kinetics of tritium for $\text{Li}_{2+x}\text{TiO}_3$ and Li_4TiO_4 were studied by means of TDS. Tritium-TDS spectrum with the heating rate of 0.5 K / min for $\text{Li}_{2+x}\text{TiO}_3$ irradiated with thermal neutron consisted of two release stages at 480 K and 580 K, namely Peaks 1 and 2, respectively. The activation energy of Peak 1 was estimated to be around 0.37 eV, while that of Peak 2 was about 0.63 eV. The latter one corresponded to the activation energy of tritium diffusion in Li_2TiO_3 . For Li_4TiO_4 irradiated with thermal neutron, two tritium

release stages named as Peaks A and B were also observed at 450 K and 600 K, respectively, in tritium-TDS spectrum at the heating rate of 0.5 K / min. As the release temperature regions of Peak 1 and Peak A were almost the same, tritium releases of these peaks were considered to be originated from the same process. The O-T bonds were easily formed on the surface of Li_4TiO_4 , appearing as Peak B in TDS spectrum.

Acknowledgements

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