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Crystal structure change of $Li_{2+x}TiO_{3+y}$ tritium breeder under moist air

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ABSTRACT

To investigate the aging behavior of $Li_{2+x}TiO_{3+y}$, the materials $Li_{2.0}TiO_{3+y}$, $Li_{2.2}TiO_{3+y}$ and $Li_{2.4}TiO_{3+y}$ were stored under moist air at ambient temperature. Under these conditions the weight of $Li_{2.0}TiO_{3+y}$ increased by only 1% in 100 days, which provides evidence for the high chemical stability of Li_2TiO_3. In comparison, under the same storage conditions the weights of $Li_{2.2}TiO_{3+y}$ and $Li_{2.4}TiO_{3+y}$ increased by 14% and 18%, respectively. The observed weight gain is attributed to the uptake of water, and to the reaction of a by-product of $Li_{2+x}TiO_{3+y}$ with water and carbon dioxide. The weight gain curves were evaluated by the Jander equation. From the analysis, it was possible to obtain the diffusion coefficient of water through Li_2TiO_3 particles at ambient temperature. The determined value was 2×10^{-17} m^2/s.

1. Introduction

Lithium ceramics like Li_2TiO_3 are promising candidate materials for the breeding of tritium in fusion reactors [1]. Lithium yields tritium upon capture of the neutrons liberated in the D–T fusion reaction. Because tritium breeding is associated with lithium-depletion the efficiency of the breeding material decreases with progressing time. It follows that lithium-depleted material will require periodical replacement to maintain the tritium-breeding ratio at high values. To improve the life expectancy of the breeding material, Hoshino et al. [2] proposed a modified Li_2TiO_3, i.e. $Li_{2+x}TiO_{3+y}$.

The breeder material $Li_{2+x}TiO_{3+y}$ consists of a mixture of Li_2TiO_3 and Li_4TiO_4 [2]. Excess Li actually generates Li_4TiO_4 during the manufacturing process of $Li_{2+x}TiO_{3+y}$. As well known, Li_4TiO_4 reacts with CO_2 at temperatures above 573 K yielding Li_2TiO_3 and Li_2CO_3 [3]. It is generally valid that almost all of lithium ceramics absorb water and carbon dioxide from air or present in other process gases, giving rise to $LiOH(H_2O)$ and/or Li_2CO_3. On the other hand, $LiOH(H_2O)$ decomposes to Li_2O by heating under a dry conditions [4,5]. In other words, under practical conditions lithium ceramics phases evolve into other lithium compounds with progressing time. It is therefore important to investigate the aging behavior of lithium ceramics in moist air at close to ambient temperatures.

To understand the aging behavior of $Li_{2+x}TiO_{3+y}$ weight changes were followed under moist air at ambient temperature and the occurring phase transformations identified by X-ray diffraction. Weight gain curves were subsequently analyzed by a reaction model for solid-state reactions.

2. Experimental

2.1. Sample characterizations

$Li_{2.0}TiO_{3+y}$, $Li_{2.2}TiO_{3+y}$ and $Li_{2.4}TiO_{3+y}$ were purchased from Kaken Co., Ltd., Japan. For simplicity, these materials are from here on identified as $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$, respectively. Table 1 provides a detailed characterization of the three samples. The supplier guaranteed the lithium content of each of these materials. The particle size of the various samples was determined with a digital microscope. The $Li_{2.0}TiO_3$ particles were of spherical polyhedron form, the mean particle diameter being 8×10^{-5} m. Some large particles had size exceeding 2×10^{-4} m. The $Li_{2.2}TiO_3$ material consisted of 7×10^{-5} m particles with some fine particles attached to the surface. The mean diameter of the $Li_{2.4}TiO_3$ particles was found to be 6×10^{-5} m, their surface also being covered by a very fine powder of less than 1×10^{-5} m.

Fig. 1 shows X-ray diffraction patterns obtained with the Cu Kα line. Silicon powder was added to the samples as internal standard for the determination of lattice constants. The pattern of the $Li_{2.0}TiO_3$ sample consists of the typical Li_2TiO_3 peaks [6–8]. The patterns of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ showed by-products from the manufacturing process (denoted by ∗). Hoshino et al. [2] assigned this by-product to Li_4TiO_4 [9]. However, some of the diffraction peaks characteristic to $LiOH(H_2O)$ [10] also show up under the by-product peaks. Consequently, from the diffraction patterns the by-product phase consists of Li_4TiO_4 and/or $LiOH(H_2O)$. The lattice constants of the Li_2TiO_3 compound were refined with the POWDER CELL package [11,12]. The crystal structure of Li_2TiO_3 reported belongs to the monoclinic system with an appropriate space group of C2/c [8]. The refinement of the lattice constants was initiated from

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Table 1
Characterizations of samples.

Sample	Composition [Li]/[Ti]	Mean size of particle	Compound	Lattice parameter of Li_2TiO_3
$Li_{2.0}TiO_3$	1.96	8×10^{-5} m Large particles were included up to 2×10^{-4} m	Li_2TiO_3	Monoclinic $a = 5.0695 \times 10^{-10}$ m $b = 8.7858 \times 10^{-10}$ m $c = 9.8372 \times 10^{-10}$ m $\beta = 99.028°$
$Li_{2.2}TiO_3$	2.19	7×10^{-5} m The sample was consisted of homogeneous particles	Main Li_2TiO_3 by-product Li_4TiO_4 and/or $LiOH(H_2O)$	Monoclinic $a = 5.0741 \times 10^{-10}$ m $b = 8.7866 \times 10^{-10}$ m $c = 9.8565 \times 10^{-10}$ m $\beta = 98.512°$
$Li_{2.4}TiO_3$	2.39	6×10^{-5} m The sample was included several fine particles (below 1×10^{-5} m)	Main Li_2TiO_3 by-product Li_4TiO_4 and/or $LiOH(H_2O)$	Monoclinic $a = 5.0695 \times 10^{-10}$ m $b = 8.7995 \times 10^{-10}$ m $c = 9.8293 \times 10^{-10}$ m $\beta = 98.404°$

the reported crystal structure [8]. Table 1 gives the values of the determined lattice constants. These values agree well with the ones reported by Kataoka et al. [8].

2.2. Experimental procedures

To investigate the aging behavior of $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ known amounts (of the order of 1 g) of these materials were stored under moist air in a closed vessel. Each sample was placed separately in a glass pan and all of them introduced into a glass vessel of $15 \times 10^{-3}\,m^3$ equipped with a water reservoir, which contained pure water. A cover on the glass vessel served to achieve a closed system. The closed vessel, located at all times in a dim room, showed temperature variations within the range 299–303 K and a constant humidity at about 95%. Periodical removal of each sample from the closed vessel and weighing provided information on eventual changes in weight.

3. Results

Fig. 2 shows the evolution of the weight gain of the investigated samples. The ordinate gives the weight gain normalized to the original weight (w_0) and the abscissa the time of exposure to moist air. As evident, the weight of $Li_{2.0}TiO_3$ remained unchanged to within 1%. The weight of the other two samples instead increased significantly by exposure to moist air. The change in the weight of $Li_{2.2}TiO_3$ shows three distinct regions. The first region manifests during the initial 30 days, the second within the period 30–70 days, and the third beyond 70 days. During the first 30 days, the weight gain evolution increases exponentially. Subsequently, the weight increases almost linearly until 70 aging days and then, finally, the weight approaches a constant value. The weight gain of $Li_{2.2}TiO_3$ after 100 days had elapsed was 14%. The weight gain evolution patterns of $Li_{2.4}TiO_3$ was similar to that of $Li_{2.2}TiO_3$, but in this case, the final weight gain reached 18% after 100 days. It appears that the mechanisms and kinetics of the weight gains by $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ are essentially the same. The results also indicate that the weight gain takes place by multistep process.

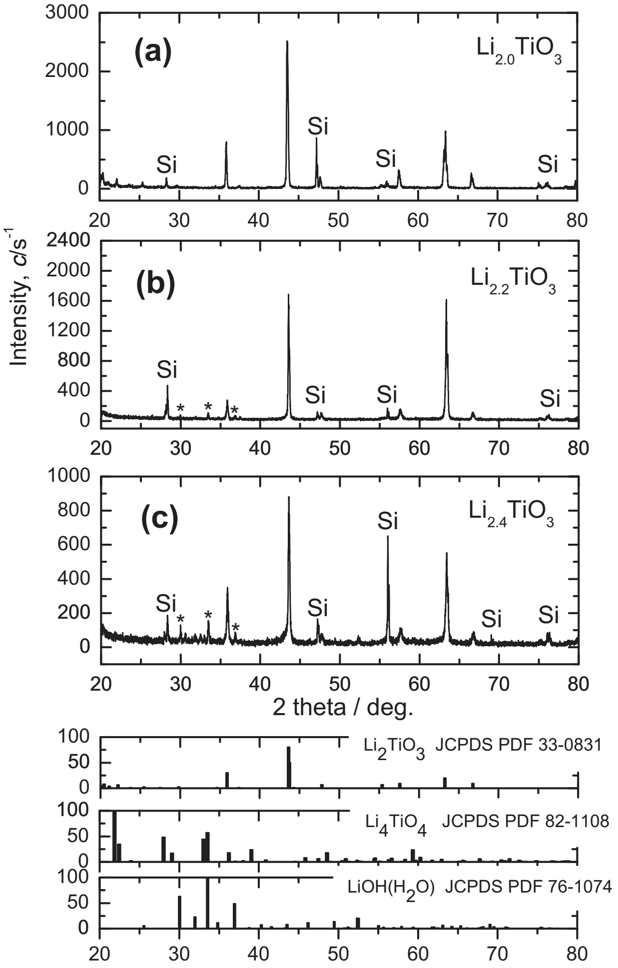

Fig. 1. X-ray diffraction patterns of $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$. The Cu Kα line served for the determination of patterns. Internal standard for the evaluation of lattice constants was pure silicon powder. * identifies by-product peaks.

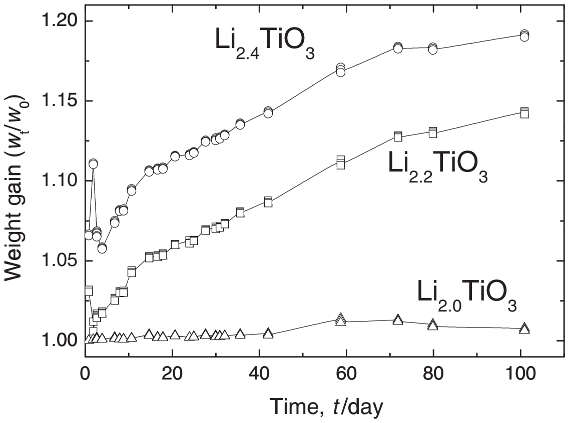

Fig. 2. Time-evolution of weight changes during exposure to moist air. The weight gain has been normalized to the original weight of the samples.

Fig. 3 shows X-ray diffraction patterns of $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ after exposure to moist air. As apparent, the diffraction pattern of $Li_{2.0}TiO_3$ agrees with the one before exposure to humid-

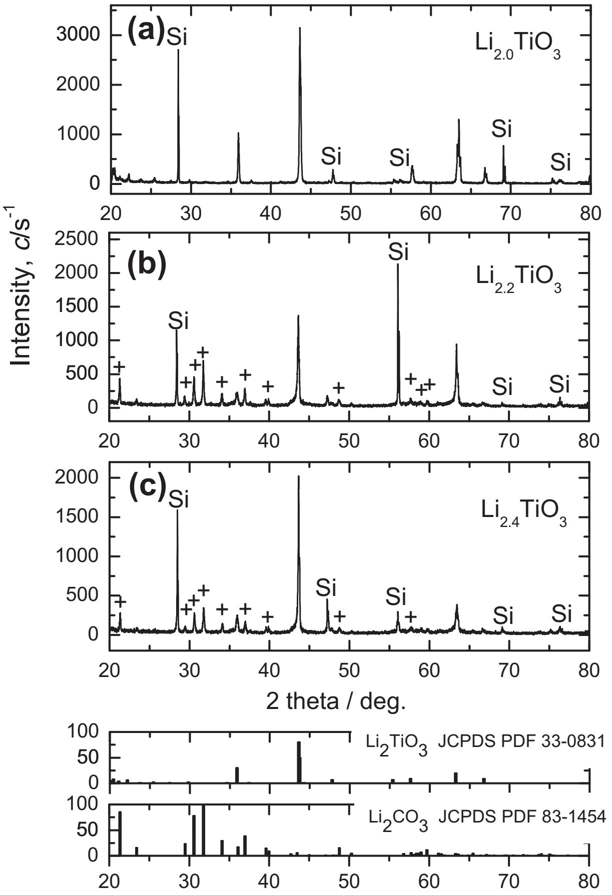

Fig. 3. X-ray diffraction patterns of samples after exposure to moist air for 100 days. Internal standard for the evaluation of lattice constants was pure silicon powder. + identifies Li_2CO_3 peaks.

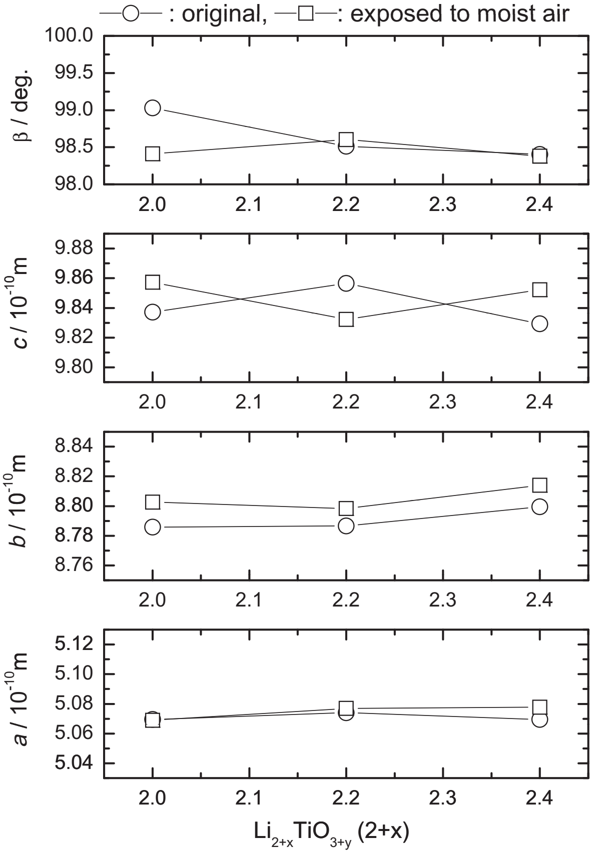

Fig. 4. Lattice constant change of $Li_{2+x}TiO_{3+y}$ compounds caused by exposure to moist air. The constants were refined using the POWDER CELL package.

ity. Thus, it is possible to conclude that from the weight change measurements and the diffraction pattern assignments, $Li_{2.0}TiO_3$ has scarcely reacted. On the other hand, many new diffraction peaks (denoted by +) appeared in the patterns of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ after storage under moist air (see Fig. 3), these peaks were assigned to Li_2CO_3 [13]. Actually, $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ have evolved into a mixture of Li_2TiO_3 and Li_2CO_3. The lattice constants of the Li_2TiO_3 compound present in each sample were refined. They are plotted in Fig. 4. Since the lattice constants of Li_2TiO_3 after the exposure are essentially the same as before the exposure, it is evident that Li_2TiO_3 is chemically rather stable. The weight gain is probably due to water adsorption/absorption and possibly to reactions of some by-products in $Li_{2.2}TiO_3$ and in $Li_{2.4}TiO_4$ with moist air.

4. Discussion

As indicated by the X-ray diffraction pattern Li_4TiO_4 and/or $LiOH(H_2O)$ are by-products present in $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ before the experiment (see Fig. 1). Possible reactions of the by-products with CO_2 are:

$$Li_4TiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2TiO_3 \quad (1)$$

and

$$2LiOH(H_2O) + CO_2 \rightarrow Li_2CO_3 + 3H_2O. \quad (2)$$

Li_4TiO_4 can also react with moisture according to

$$Li_4TiO_4 + 3H_2O \rightarrow 2LiOH(H_2O) + Li_2TiO_3 \quad (3)$$

and the produced $LiOH(H_2O)$ undergo further reaction with CO_2 as shown above. According to Togashi et al. [3], however, Li_4TiO_4 will not react with CO_2 at temperatures below 573 K. Consequently, under the present experimental conditions, reaction (1) probably does not play a role. On the other hand, Li_4TiO_4 reacts with H_2O to give $LiOH(H_2O)$ via reaction (3). $LiOH(H_2O)$ will react with absorbed CO_2 according to reaction (2) [14]. The fact that the weight gain profiles show the multistep process as shown in Fig. 2. Therefore, Li_4TiO_4 changed to Li_2CO_3 via $LiOH(H_2O)$ after storage under moist air.

To quantify the change in weight, analysis method for solid-state reactions proposed by Sharpe et al. [15] was applied. Weight gain curves typical for the 0–30 day period could be reproduced well with a diffusion controlled reaction mechanism in a sphere model using the well known Jander equation [15,16].

The weight gain until 30 days (see Fig. 2) is ascribed to the uptake of water and the reaction of Li_4TiO_4 with H_2O to yield $LiOH(H_2O)$. Subsequently, $LiOH(H_2O)$ absorbs CO_2. This plausible reaction mechanism is shown schematically in Fig. 5. Basis of the mechanism are the following assumptions:

(1) The dispersion of Li_4TiO_4 grains in the $Li_{2+x}TiO_{3+y}$ particles is essentially uniform.
(2) The diffusion of H_2O in $Li_{2+x}TiO_{3+y}$ is slow. Because the weight gain curves until 30 day were explained by a diffusion controlled reaction.
(3) The rate of reaction (3) is considerably faster than that of the diffusion process of water.

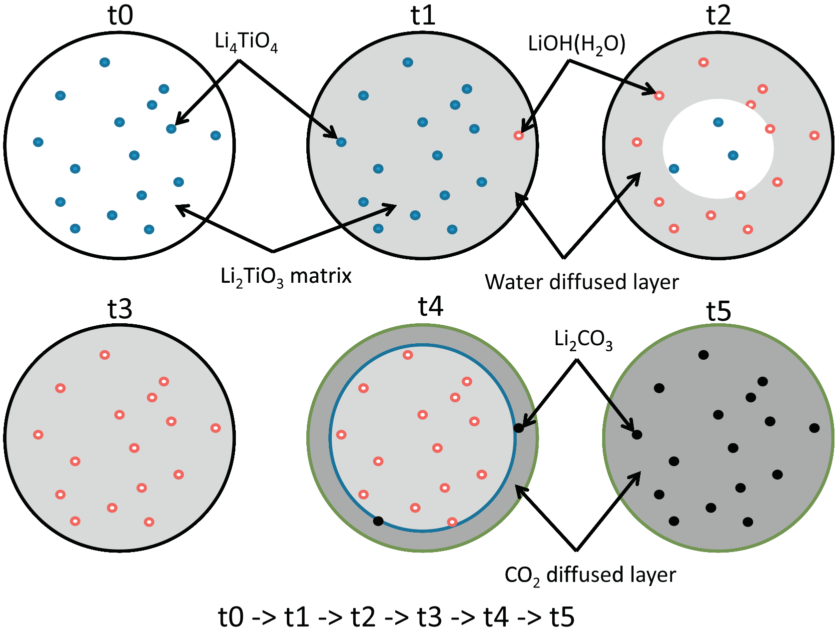

Fig. 5. Visualization of the reaction mechanism resulting in the formation of lithium carbonate when $Li_{2+x}TiO_{3+y}$ is exposed to moist air.

(4) The diffusion of CO_2 in $Li_{2+x}TiO_{3+y}$ is slower than that of H_2O. Since the weight gain curves were subdivided into three regions (see Fig. 2), the curves resulted from some reaction sequence. Li_2CO_3 is the end product.
(5) The rate of reaction (2) is moderate.

The t_0 in Fig. 5 illustrates the starting condition. $Li_{2+x}TiO_{3+y}$ particles can be considered to consist of Li_4TiO_4 grains in a Li_2TiO_3 matrix. At times t_1–t_3, H_2O slowly penetrates into the bulk of the $Li_{2+x}TiO_{3+y}$ particles and reacts with Li_4TiO_4 grains to yield $LiOH(H_2O)$. $LiOH(H_2O)$ on the surface layer further reacts with CO_2 to produce Li_2CO_3. At times t_4 and t_5 CO_2 has diffused into the bulk converting $LiOH(H_2O)$ into Li_2CO_3. It should be mentioned that the Li_2TiO_3 matrix does not react with H_2O and CO_2. Only the product phases are responsible for the uptake of water.

It may be assumed that the weight gain until 30 days reflects reaction stages t_0–t_3 (see Fig. 5), where the weight gain curves are caused by the diffusion of water into Li_2TiO_3 matrix. It should be noted that according to the model the weight gain is governed by the diffusion rate of water. To obtain the weight gain curve until 30 days, the Jander equation was modified according to

$$\frac{w_t}{w_0} = s(1-(1-\sqrt{kt})^3) \tag{4}$$

and

$$k = \frac{2D}{r_0^2}, \tag{5}$$

where w_t is the sample weight at time t, w_0 is the initial weight, k is a rate constant and s is a scale factor. The rate constant (k) is given by the diffusion constant (D) and the radius (r_0) of the $Li_{2+x}TiO_{3+y}$ particles. The scale factor (s) and the rate constant (k) are fitting parameters to generate the curves. Fig. 6 shows the results of the analysis by the modified Jander equations. The calculated curves are the solid lines. As apparent, the weight gain data for $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ can be simulated well by the calculated curves. Table 2 summarizes the obtained kinetic parameters. The scale factor, s, is an index for the amount of water uptake by $Li_{2+x}TiO_{3+y}$. The absolute amount could not be evaluated from the present results, because $Li_{2+x}TiO_{3+y}$ was not completely dry when it was introduced into the vessel. The diffusion coefficient, however, could be determined from the rate constant and the particle radius. The diffusion coefficient corresponds to the diffusion rate of water through the Li_2TiO_3 matrix as shown in Fig. 5. Particle radiuses were obtained using a digital microscope. The diffusion coefficients of water through $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ were found to be 2.0×10^{-17} m^2/s and 2.6×10^{-17} m^2/s, respectively. The diffusion coefficient through $Li_{2.2}TiO_3$ was found to be close to that of $Li_{2.4}TiO_3$. From these

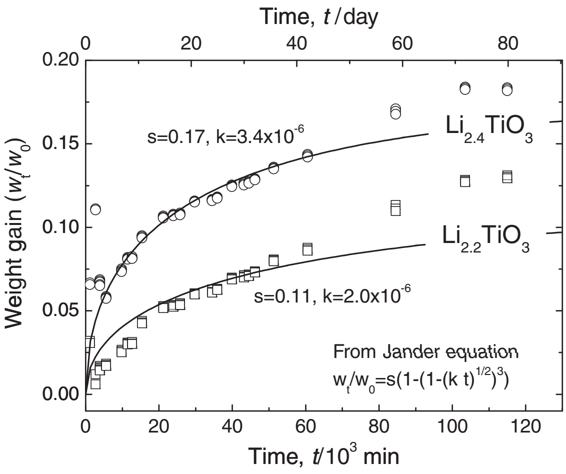

Fig. 6. Simulation of the weight increase experienced by $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ when exposed to moist air using a modified Jander equation.

Table 2
Kinetics parameters obtained by Jander equation.

	Rate constant, k (min^{-1})	Scale factor, s	Initial radius, r_0 (10^{-6} m)	Diffusion coefficient, D (m^2/s)
$Li_{2.2}TiO_3$	2.0×10^{-6}	0.11	35	2.0×10^{-17}
$Li_{2.4}TiO_3$	3.4×10^{-6}	0.17	30	2.6×10^{-17}

results it is estimated that a water molecule can penetrate about 1.3×10^{-6} m per day into a Li_2TiO_3 particle.

5. Conclusions

To shed light on the aging behavior of $Li_{2+x}TiO_{3+y}$ its constituents $Li_{2.0}TiO_3$, $Li_{2.2}TiO_3$, and $Li_{2.4}TiO_3$ were exposed to moist air at ambient temperature. While the weight of $Li_{2.0}TiO_3$ increased by approx. 1% during after 100 days of exposure, the weight gains of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ under the same exposure conditions were found to be 14% and 18%, respectively. This constitutes evidence of the comparatively high chemical stability of Li_2TiO_3. X-ray diffraction patterns showed that pristine $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$ contained Li_4TiO_4. However, after the exposure to moist air the X-ray diffraction peaks of Li_4TiO_4 disappeared and those typical of Li_2CO_3 showed up. Thus, it appears that during the exposure to moist air Li_4TiO_4 is transformed Li_2CO_3 via intermediate $LiOH(H_2O)$. Consequently, $LiOH(H_2O)$ and Li_2CO_3 cause the uptake of water.

The solid-state reaction model proposed by Jander successfully simulated the weight gain curves of $Li_{2.2}TiO_3$ and $Li_{2.4}TiO_3$. The analyses indicated that the diffusion coefficient of water in Li_2TiO_3 particle has a value of about 2×10^{-17} m^2/s at ambient temperature.

Another conclusion of the present work is that the by-products purposely added to $Li_{2+x}TiO_{3+y}$ significantly influence the rate of $Li_{2+x}TiO_{3+y}$ aging in the presence of moist air.

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