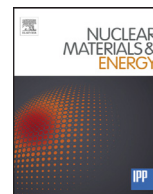




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Dissolution behavior of lithium compounds in ethanol



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ABSTRACT

In order to exchange the components which received irradiation damage during the operation at the International Fusion Materials Irradiation Facility, the adhered lithium, which is partially converted to lithium compounds such as lithium oxide and lithium hydroxide, should be removed from the components. In this study, the dissolution experiments of lithium compounds (lithium nitride, lithium hydroxide, and lithium oxide) were performed in a candidate solvent, allowing the clarification of time and temperature dependence. Based on the results, a cleaning procedure for adhered lithium on the inner surface of the components was proposed.

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1. Introduction

A key step toward the realization of a demonstration fusion reactor is to develop structural materials that can withstand the 14 MeV neutrons generated as a result of the deuterium–tritium fusion reaction [1]. In order to establish an irradiation facility for candidate materials, the International Fusion Materials Irradiation Facility (IFMIF) project is in progress under the Broader Approach Agreement [2,3] to support the materials development programs by providing a fusion-relevant neutron source in which candidate material irradiation performance can be fully assessed. Because the IFMIF is an accelerator-based neutron source that utilizes the deuteron–lithium stripping reaction, the target assembly (T/A), which is the main component, undergoes significant irradiation damage. Therefore, the exchange of the T/A must occur during the in-service inspection [4].

Here, the structure of the T/A is described briefly. The T/A of the IFMIF will be made from ferritic-martensitic steel such as EUROFER and F82H steel. In the T/A, liquid lithium screen flowing at a speed of 15 m/s and a temperature of 250 °C will be formed for the stripping reaction. Since liquid lithium is used as the target material, it exists in the inner surface after operation as the contamination.

Cleaning of the adhered lithium on the inner surface of the removed T/A is required prior to long-term storage. In a previous study [5], we performed dissolution experiments of pure lithium in candidate solvents such as ethanol, pure water, and an ethanol–

water mixture, allowing the clarification of temperature and time dependence.

However, lithium adhering to the T/A is able to react with the atmosphere during the exchange and long-term storage. Therefore, we investigated the chemical reaction of pure lithium at room temperature in air, oxygen, nitrogen, and argon atmospheres under varying humidity to estimate the chemical reaction that occurs during the exchange [6].

Based on these results, we herein describe the dissolution behavior in a candidate solvent of lithium compounds formed upon reaction with the atmosphere during the exchange.

2. Experimental procedure

2.1. Reagents

For the experiments, lithium nitride (Li_3N), lithium hydroxide (LiOH), and lithium oxide (Li_2O) were prepared as the reagents. These shape before the experiments are shown in Fig. 1.

Li_3N and LiOH were synthesized from the pure lithium of the sphere with a diameter of 10 mm through reaction with moisture-containing nitrogen or argon at 80 °C for 7 days and 80 °C for 12 days, respectively. Each shape after the synthesis was upholding the original sphere shape. Although we tried the same synthesis technique also to Li_2O , it was brittle and the cracks were generated during synthesis. Then, we used Li_2O powder of the commercial reagents produced by Soekawa Chemical Co. Ltd. and the reagent for the experiments was manufactured by compression molding using a hydraulic pressure system, resulting in a cylindrical shape with a diameter of 12 mm and a height of 10 mm.

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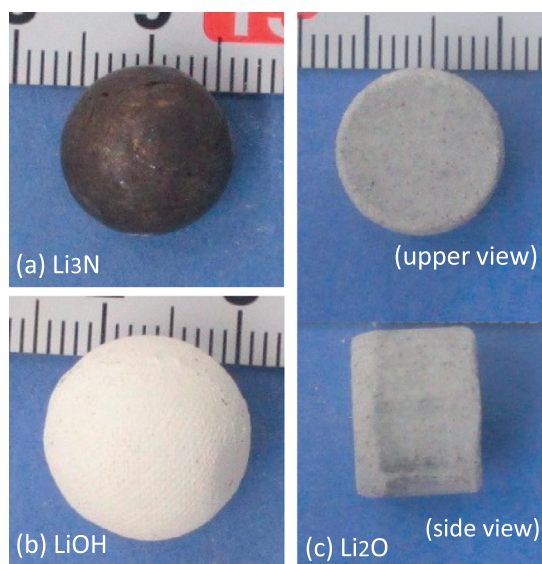


Fig. 1. Shape of the synthesized reagents (before immersion into ethanol).

Table 1
Results of X-ray analysis of the synthesized reagents.

Reagent	Sampling position	Compounds (ICDD no.)	Traces
Li ₃ N	Surface	Li ₃ N (76-0821)	–
	Inside	Li ₃ N (76-0821)	Li ₂ O, LiOH, Li ₂ NH
LiOH	Surface	LiOH (85-0736)	–
	Inside	LiOH (85-0736)	–
Li ₂ O	–	Li ₂ O (12-0254)	LiOH

After the manufacturing process, the samples were removed and the synthesized reagents and crystal structures were analyzed by X-ray diffraction (XRD), as summarized in Table 1.

2.2. Apparatus

A schematic representation of the experimental apparatus is shown in Fig. 2.

These devices, which comprise an exposure pot, a micro balance, and a vacuum chamber, were installed in the argon

Table 2
Experimental conditions.

Reagent	Solvent	Temperature (°C)	Exposure time (h)
Li ₃ N	Ethanol	10, 30, 50, 70	~7
LiOH			~17
Li ₂ O			~30

glove box. The Pyrex glass exposure pot was connected to a constant temperature water bath system, allowing the temperature of the ethanol to be controlled with the combined use of a stirrer. The reagent was set in a stainless steel mesh container and temporarily removed during weight change measurements using a microbalance. The vacuum chamber was also used for the evaporation of ethanol in the sample prior to the measurement.

2.3. Experimental procedure

The experimental conditions and procedures are summarized in Table 2 and Fig. 3, respectively.

Lithium compounds (Li₃N, LiOH, and Li₂O) were immersed in ethanol (99.5% purity) at 10 °C, 30 °C, 50 °C, and 70 °C, with maximum exposure times of 7, 17, and 30 h, respectively. As described above, the reagents were extracted from the exposure pot during the experiment and the weight and size of the samples were measured after the evaporation of ethanol. The sampling step for weight measurement was approximately 1 h.

The dissolution progress of the samples in ethanol was measured using the weight and outer diameter.

3. Results and discussion

3.1. Dissolution behavior of lithium compounds in ethanol

A photograph of the lithium compounds immersed in ethanol at 30 °C is shown in Fig. 4 as an example.

Although Li₃N was dark brown prior to the examination, the surface became partially white after the immersion. The surfaces of LiOH and Li₂O did not change from their original colors of white and gray, respectively, upon immersion. All reagents were reduced to similar figures with time at each temperature. No exfoliation was observed for any of the reagents upon ethanol immersion.

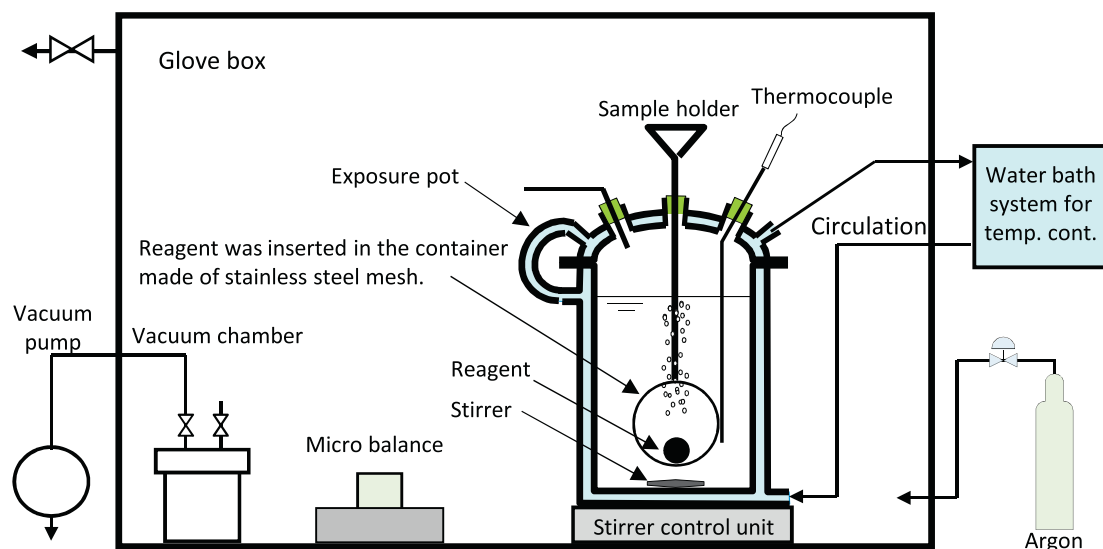


Fig. 2. A schematic representation of the experimental apparatus.

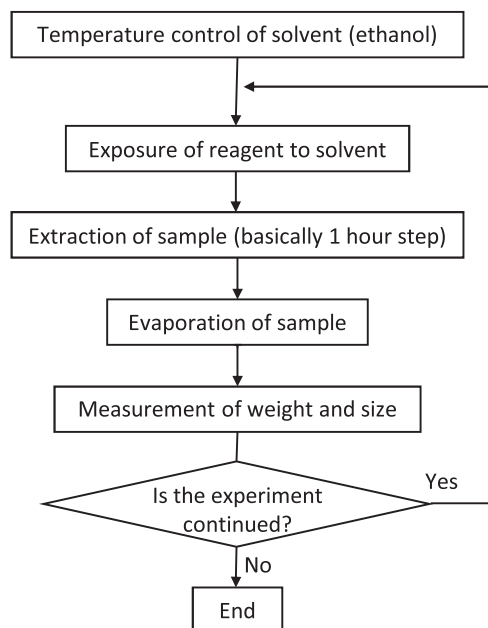
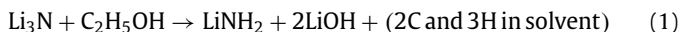


Fig. 3. Experimental procedure.

Based on these observations, the dissolution thickness and rate were calculated from the weight loss and density of the sample.

The progress of dissolution thickness for each reagent during exposure is shown in Fig. 5.

It was confirmed that the dissolution of Li_3N at each temperature progressed linearly with exposure time (Fig. 5 (a)). It seemed as the dissolution approximately increased with increasing test temperature; however, the progress at 50°C was equivalent to that at 30°C . The XRD pattern of the sample surface exposed at 50°C for 7 h is shown in Fig. 6. Lithium amide (LiNH_2 , the card number of the International Centre for Diffraction Data [hereinafter referred to as the "ICDD #"]: 71-1616) and LiOH (ICDD #32-0564) were detected in small quantities in the original compound (Li_3N , ICDD #76-0820).



At this case, both dissolution of the reaction products (LiNH_2 and LiOH) were progressed with parallel (i.e. 3 mol of lithium are dissolved into ethanol). So, the dissolution rate of Li_3N became to be much higher than that of LiOH as described in later.

The dissolution of LiOH at each temperature also progressed linearly with exposure time (Fig. 5(b)). However, unique

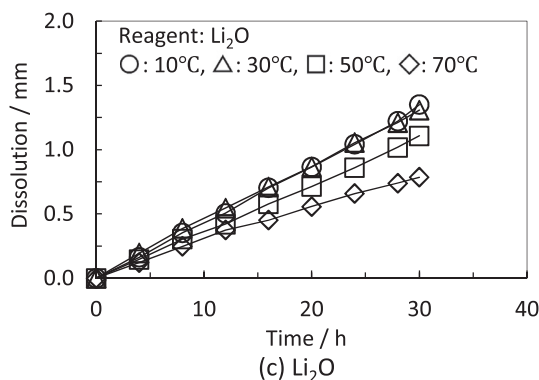
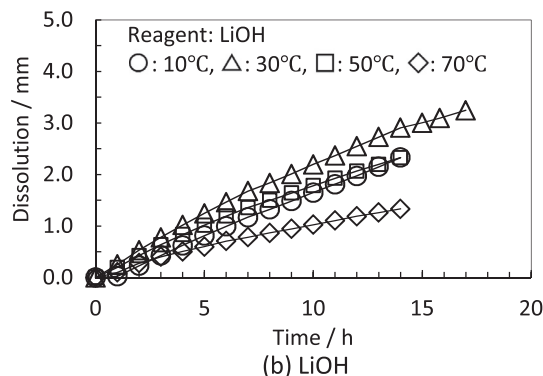
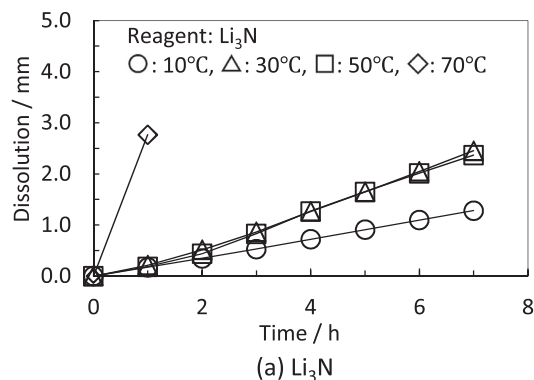
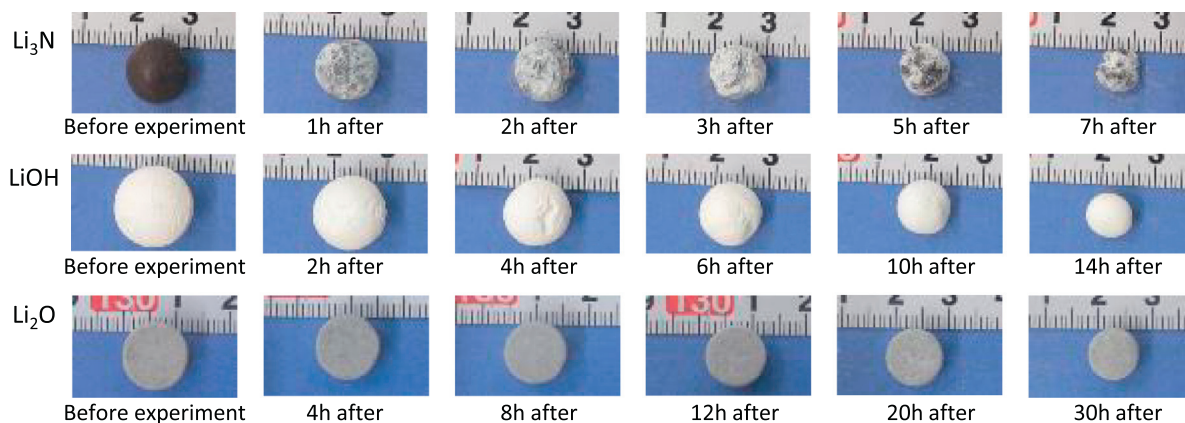


Fig. 5. Dissolution behavior of lithium compounds in ethanol.

Fig. 4. Change in lithium compounds in ethanol at 30°C .

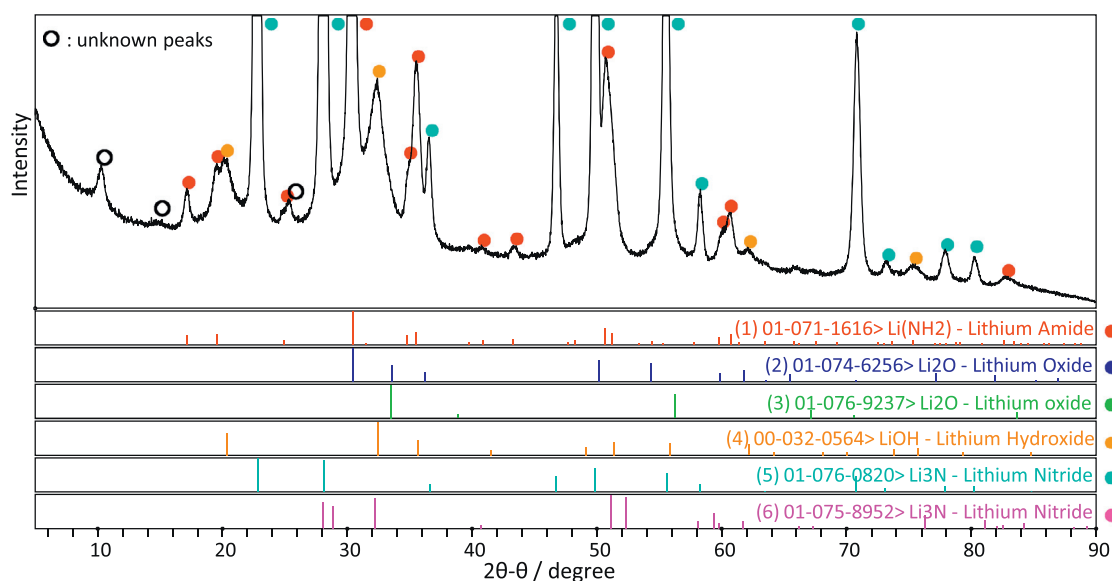


Fig. 6. XRD results of Li_3N exposed in ethanol.

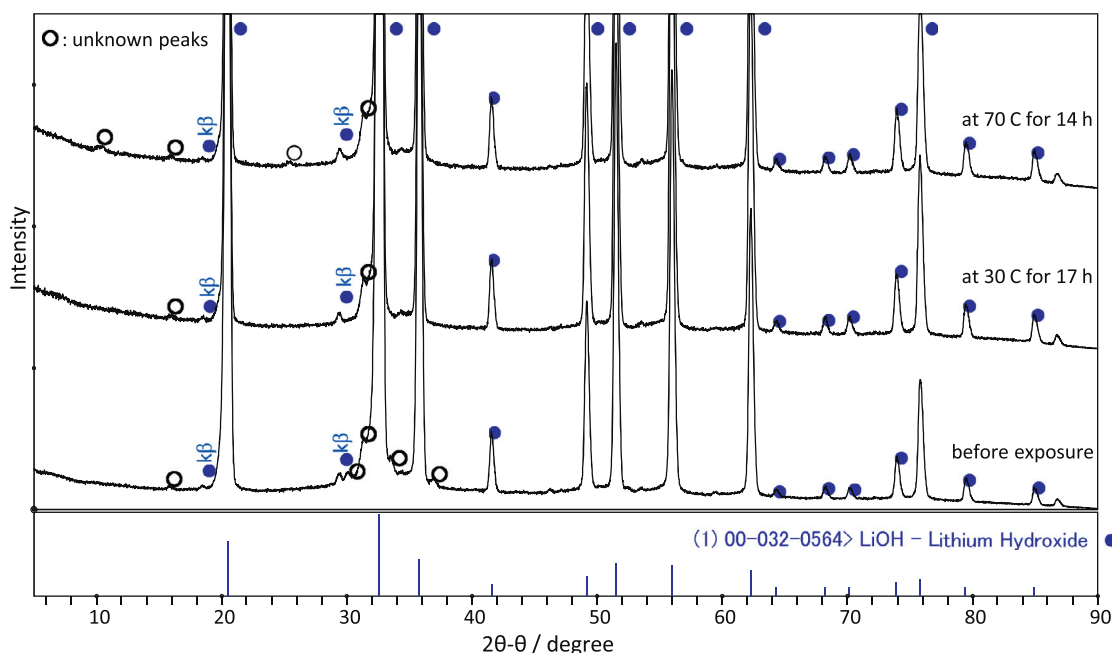
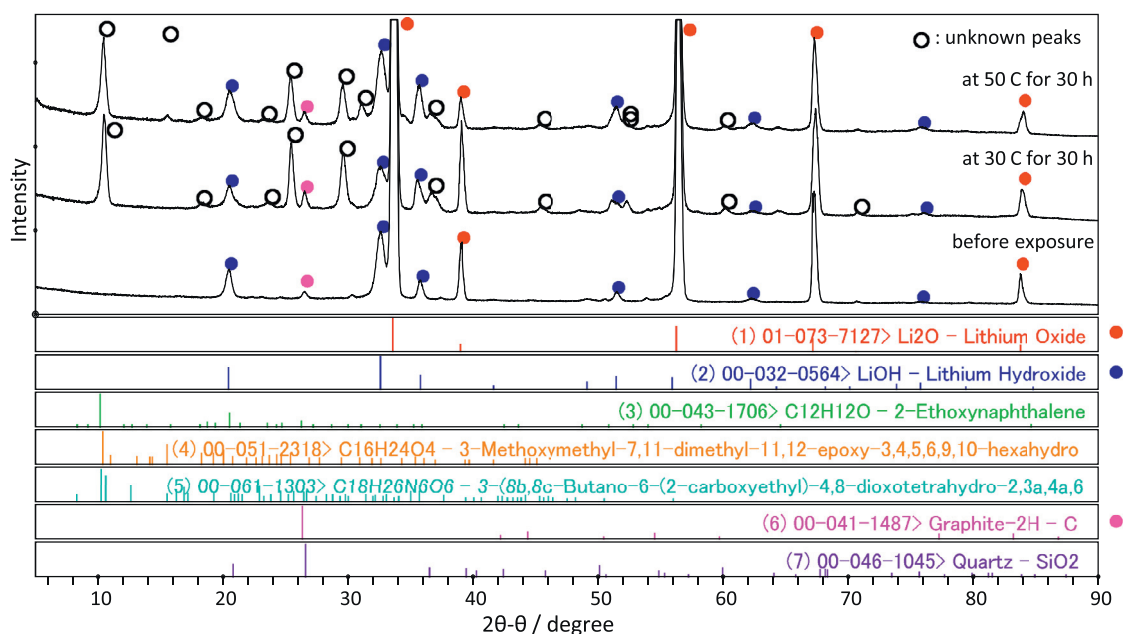


Fig. 7. XRD results of LiOH exposed in ethanol.

temperature dependence was observed as follows. The maximum progress was obtained at 30°C , whereas the minimum was at 70°C . The data at 10°C and 50°C were nearly identical and were plotted between 70°C and 10°C . XRD results of the exposed samples, which were exposed in ethanol at 70°C for 14 h and 30°C for 17 h, are shown in Fig. 7 along with the results before exposure. No difference was observed before and after exposure, with only LiOH (ICDD #32-0564) being detected. Unfortunately, information regarding the unique temperature dependence was not obtained.

As shown in Fig. 5(c), the dissolution of Li_2O at each temperature also progressed linearly with exposure time. However, the progress of Li_2O was slower than that of Li_3N and LiOH . The dissolution at 10°C and 30°C were approximately the same, decreasing slightly upon increase in temperature. XRD results of the exposed samples, which were immersed in ethanol at 50°C for 30 h and 30°C for 30 h, are shown in Fig. 8 along with the results before

exposure. The diffraction pattern of both exposed samples were approximately the same, with the LiOH peaks and undetermined peaks being observed in the original sample (Li_2O). In order to establish the chemical constitution of the undetermined peaks, X-ray fluorescence analysis was performed for the Li_2O sample. The results before and after exposure are shown in Fig. 9. The major impurity was carbon (C), with aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), calcium (Ca), iron (Fe), and zinc (Zn) also being detected in small quantities. Since all elements except carbon were observed on the sample before exposure, it could be concluded that these were mixed during ethanol exposure, while the increase in carbon intensity might be caused by ethanol immersion. As such, the undetermined peaks are most likely $\text{C}_{12}\text{H}_{12}\text{O}$ (ICDD #43-1706), $\text{C}_{16}\text{H}_{24}\text{O}_4$ (#51-2318), and $\text{C}_{18}\text{H}_{26}\text{N}_6\text{O}_6$ (#61-1303), as shown in Fig. 5(c).



4. Conclusions

Dissolution experiments of lithium compounds (Li_3N , LiOH , and Li_2O) in ethanol were performed in the temperature range from 10 °C to 70 °C. The dissolution progressed linearly with the exposure time in all experiments. However, the temperature dependence differed among the compounds, and the dissolution rate of LiOH and Li_2O was a constant in the temperature range.

During the handling of the T/A replacement of the IFMIF, adhered lithium on the inner surface will involve a number of parallel reactions with different kinetics, and lithium compounds such as Li_2O , Li_3N and LiOH will be formed. Based on the experiments, the dissolution rate of the adhered lithium will be estimated to be greater than 0.05 mm/h, since Li_2O which showed the slowest reaction will be the determining one of the full cleaning process.

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