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Fabrication, Properties, and Tritium Recovery
from Solid Breeder Materials

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ABSTRACT

The breeding blanket is a key component of the fusion reactor because it directly involves tritium breeding and energy extraction, both of which are critical to development of fusion power. The lithium ceramics continue to show promise as candidate breeder materials. This promise was recognized by the International Thermonuclear Experimental Reactor (ITER) design team in its selection of ceramics as the first option for the ITER breeder material. Blanket design studies have indicated properties in the candidate materials data base that need further investigation. Current studies are focusing on tritium release behavior at high burnup, changes in thermophysical properties with burnup, compatibility between the ceramic breeder and beryllium multiplier, and phase changes with burnup. Laboratory and in-reactor tests, some as part of an international collaboration for development of ceramic breeder materials, are underway.

1. Introduction

The development of ceramic breeder materials has progressed systematically in laboratory experiments, in-reactor testing, and tritium transport and release modeling. These efforts have resulted in development of a broad properties data base for several materials in differing configurations (i.e., sintered pellets, pebbles, single crystals)[1-5]. The lithium-containing ceramics (Li_2O , Li_2ZrO_3 , $\gamma\text{-LiAlO}_2$, and Li_4SiO_4) are considered to have excellent potential as tritium breeders because of the ease of tritium recovery, excellent thermal performance, and good irradiation behavior. Also, these efforts have indicated that optimum information on materials performance is obtained when a candidate material is tested in a fashion that results in multiple effects taking place (gas production, atomic recoil, and tritium production, release, and recovery).

Current experimental research is addressing issues identified in ITER blanket design studies, for example, compatibility of the breeder with the beryllium multiplier, tritium release behavior at high burnup, effects of breeder burnup on thermophysical properties, and operation at lower temperatures (i.e., <623 K). At present, the design studies place a great emphasis on neutron irradiation effects, and the experimental effort reflects interest in multiple effects. However, complementary separate-effects laboratory experiments are still required to ensure correct interpretation of a material's irradiation behavior. This paper will focus on recent research concerning candidate materials properties, fabrication methodology, irradiation behavior, and tritium transport, as well as computer modeling of tritium transport and release.

2. Materials Preparation and Fabrication

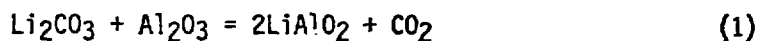
In this section the varied processes used to prepare the candidate ceramic breeder material are identified. The powder preparation, fabrication of shapes, and industrial scale production will be discussed.

2.1 Materials Preparation

Preparation methods for the ceramic breeders fall into one of three classes, namely: a) solid state reactions, b) solution processes (aqueous or alcohol), and c) sol-gel methods. Each method, when done properly, yields high purity materials.

2.1.1 Lithium aluminate LiAlO_2

The standard technique for the synthesis of LiAlO_2 is the solid state reaction:



This reaction, introduced by Hummel[6], is widely used at a temperature of about 700°C[7-9]. The time allowed for reaction is between 3 hours[8] and

96 hours[7]. The reaction product is crushed, milled, and shaped. By selecting proper conditions for pressing and sintering, it is possible to adjust the grain size of the final product. LiAlO_2 powder can also be prepared by suspending a stoichiometric amount of LiOH and $\text{Al}(\text{OH})_3$ in methanol and boiling this suspension under reflux conditions[6]. A finely divided powder with good flowability is obtained after spray drying. Pure $\beta\text{-LiAlO}_2$ was formed after annealing in air for several hours at 125°C ; pure $\gamma\text{-LiAlO}_2$ can be obtained by calcination above 850°C [10].

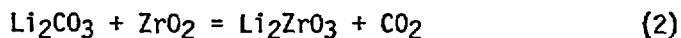
Lileev et al.[11] described a reaction in which metallic aluminum is dissolved in an aqueous solution of LiOH , and $\text{Li}(\text{Al}_2[\text{OH}]_7)\cdot n\text{H}_2\text{O}$ precipitation occurs immediately after formation. If the Li/Al ratio is set similar to that of LiAlO_2 , the hydrate of the hydroxoaluminate is also precipitated[12,13]. At low temperature, the precipitate is very fine and can easily be spray dried. After calcination at 900°C , $\gamma\text{-LiAlO}_2$ is formed.

The preparation of lithium aluminate powder by sol-gel processes seems to be difficult[14-15].

Dopants are added to improve the materials properties: the dopant elements were introduced either as the oxide (Ga_2O_3 or SiO_2), which was mechanically blended with the Al_2O_3 powder, or as the acetate (Mg , Zn , Cu), which was dissolved in an aqueous solution. In both cases the resulting mixture was blended with Li_2CO_3 and processed as described above[16]. It is important to note that additions of Mg , Zn , Ga , and Y enhance sinterability, whereas Si addition decreases it[16].

2.1.2. Lithium metazirconate Li_2ZrO_3

The technique used to prepare Li_2ZrO_3 is based on the reaction:[17]



This reaction can be performed at temperatures between 550° and 900°C [17,18]. Instead of the carbonate, it is possible to use Li_2O [19] or

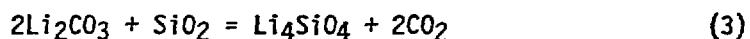
Li_2O_2 [18]. The reaction product can be milled and pressed into the desired shapes. Lithium metazirconate can also be prepared by precipitation from solution. Suiter et al.[20] dissolved Li_2CO_3 in a warm water solution of citric acid and ethylene glycol. The solution was cooled to room temperature and mixed with a solution of $\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$. The mixture was hydrolyzed at 50°C for 8-16 hours and dried at 115°C for 6 hours. Calcination in air at 600 - 850°C yielded a fine grain, workable powder.

Alcoholic suspensions may also be used[21]. Methanol is preferred, as the problems associated with the contamination of the final product by carbon are minimal. The mixture is hydrolyzed with water and the alcohol is distilled off. This yields a very fine milky suspension, which is spray dried in a centrifugal atomizer. Lithium metazirconate is obtained by calcination for two hours in air at 650°C .

Lithium zirconate powder can also be obtained from a gel[22] prepared by adding an aqueous solution of LiOH to a solution of zirconylchloride. Chlorine is removed before the lithium hydroxide addition by washing with water. The final gel can be dried at temperatures between 200° and 600°C . Sinterable powder is obtained by ball milling the dried product.

2.1.3. Lithium orthosilicate Li_4SiO_4

Kracek[23]-prepared lithium orthosilicate by the reaction:



This reaction can be performed at temperatures between 600 and 1100°C . To improve the mixture of the starting powders, it is possible to mill the lithium carbonate, together with amorphous silicate in isopropanol[24]. After calcination for 72 h at 650°C the desired product is obtained.

Suiter[25] recognized that it is difficult to obtain a high quality product by this procedure. However, high purity Li_4SiO_4 can be prepared by an organo-metallic route[20] from a mixture of Li_2CO_3 , acetic acid, and

tetraethylorthosilicate ($(C_2H_5O)_4Si$ (TEOS) in isopropyl alcohol. The solution is stirred, heated to dryness, and slowly calcined at 700° - $800^{\circ}C$. Reaction times range from 4 to 24 hours, depending upon the sample size. The reaction product had to be milled to obtain a sinterable product.

Sinterable lithium orthosilicate powder can be obtained by reacting SiO_2 and LiOH in methanol[26,27]. After wetting the SiO_2 with methanol, anhydrous LiOH is added. During reflux, LiOH is dissolved and an insoluble organic intermediate is formed with an Li/Si ratio similar to that of lithium orthosilicate. The reaction is terminated when a homogeneous milky suspension has been formed. Water is added and the aqueous suspension can be spray-dried. After calcination for 2 to 4 hours at $500^{\circ}C$, the powder is ready for pressing and sintering.

In a purely organic process[28], an ethanolic solution of TEOS is hydrolyzed by slow addition of a nitric acid solution at pH 2.5. The water/TEOS and ethanol/TEOS molar ratios are fixed at 10. After 30 min of hydrolysis at room temperature, the solution is mixed into a second solution containing lithium butoxide in cyclohexane (0.75 mol/l) held at $60^{\circ}C$. A yellow gel is obtained, which can be oven dried for 3 hours at $150^{\circ}C$ in a CO_2 free atmosphere. Dried powders can be isostatically cold-pressed into pellets. The pellets are then heated at 400° and $600^{\circ}C$ (5 hours) and sintered (7 hours) at a temperature of about $900^{\circ}C$.

To improve tritium recovery, modification of this material by Al, Mg, and P addition was tested. The material was produced as a suspension in methanol[10,29]. The doping elements were added as $Al(OH)_3$ or $Al(OC_2H_5)_3$, $Mg(OH)_2$, and P_2O_5 .

2.1.4 Lithium oxide Li_2O

Lithium oxide can be prepared by decomposition of the carbonate[30,31]:



This reaction leads to a high quality product after annealing for 1-4 hours in vacuum at 1000°C. If the decomposition is performed at 700-750°C in a high vacuum, a sinterable powder is obtained[32]. Lithium oxide can also be obtained by precipitation of Li_2O_2 from a solution of LiOH in a dilute mixture of hydrogen peroxide in ethanol. Li_2O is obtained by heating this precipitate at 300°C in a vacuum[33]. The resulting powder was free flowing and sinterable, but not completely decomposed. A complete decomposition could be obtained at temperatures above 800°C.

2.2 Fabrication of shapes

For the different blanket concepts, the breeder material may be in the form of pellets, discs, or small size granules. Irradiation experiments characteristically use pellets or discs that are fabricated by uniaxial cold pressing; in some cases cold-isostatic pressing is applied[9,28]. B. Rasneur[8] (for lithium aluminate) and M. Smahi et al.[28] (for lithium orthosilicate) have demonstrated that it is possible to obtain desired densities by proper selection of pressing force and sintering temperature. In this case sintering below $0.7 T_M$ leads to products with specified densities and small grain sizes.

One may overcome the need for high sintering temperatures by the use of sintering aids. Doping with Mg, Zn, Cu, Ga, and/or Y increases sinterability of the aluminate[16,34]. Traces of LiOH can act as a liquid sintering aid to improve sintering of Li_2O at relatively low temperatures[28,29]. Even "high purity" Li_2O , where the last traces of LiOH and Li_2CO_3 are removed during a vacuum annealing step, sinters well at 1000°C[7].

The most common route to obtain small sized spheres from lithium ceramics is granulation[15]. Granulation is usually performed in a rotating drum or plate. To obtain higher density, spheres are fabricated by extrusion of plasticized powder followed by cutting and rounding[27]. Plasticization is achieved by addition of 2-5 % "Avicel" and water to the powder. Sintering of granules is usually performed in rotary kilns. Experience has shown that, in the case of sintering Li_4SiO_4 in a rotary kiln above 1000°C, both

agglomeration and adherence of particles to the sample vessel have been observed. To overcome this problem, sintering in a fluidized bed is recommended[27]. Fluidized bed sintering has the additional advantage of smoothing the surfaces of the particles. For lithium orthosilicates it is possible to obtain high quality spheres by melting Li_4SiO_4 powder and producing droplets by spraying the melt[35]. Annealing the product for 2 hours at 1000°C yields a high quality product.

2.3 Industrial scale production

For industrial scale production of ceramic breeder materials, emphasis must be placed on using high quality starting materials and consideration must be given to the impurity content of the final product. In addition, attention must be given to the stoichiometry and the Li^6 isotopic content as both greatly determine the irradiation behavior of the fabricated material. The microstructure of the solid determines tritium transport and mechanical strength. In this context the grain size and shape are important because they relate to the transport and release of tritium.

Some 20 to 30 tons of ceramic is likely to be needed for an operating nuclear reactor. Fabrication of a ceramic, even to strict specifications in quantities of that magnitude, should not be a serious problem once the laboratories have decided on a process. It should be recalled that 30,000 tons of ceramics was required for the gaseous diffusion barriers of the Eurodif plant and was fabricated in three years. The erection and start-up of two different facilities using different fabrication routes required two years[3].

Recently, 70 kg of Li_4SiO_4 [27] was produced in a laboratory process. As this test was made using large machines that can accommodate larger quantities of material, one can assume that scale-up of this production test is possible. The starting liquid mixture was spray dried followed by calcination in a "Convex"-dryer[36]. A high quality product was obtained.

For LiAlO_2 two methods will fulfill the requirements for large scale production: the precipitation process in an aqueous solution [12] and the reaction of the hydroxides in methanol[10]. Another method for mass production of lithium aluminate is the sol-gel process. Even though the current experience is not very promising[14,15], one may be able to develop a mature process. From the broad experience in production of nuclear fission fuel, a variety of shapes (e.g., pellets, discs) should easily be achieved.

Large scale production of lithium metazirconate can be done by processes employing organic suspensions[19,20]. The processes described in section 2.1.2 appear to be suited for scale-up to larger quantities. Also the sol-gel process may be applied for the production of small spheres for sphere-pac blanket concepts[22].

For large scale production of lithium oxide, the precipitation of Li_2O_2 as a precursor from a LiOH solution[10] looks to be most promising. The low temperature decomposition of Li_2CO_3 [29], which gives a highly active powder, takes too much time (1 to 80) to be technically feasible.

3. Materials Properties

Within the framework of the ITER project, the status of the ceramic breeder materials properties data base was recently examined[5]. The data base was reviewed and assessed, correlations were recommended, and areas where more work is needed were identified. In this section we will focus on thermochemical, thermophysical, thermomechanical, and compatibility properties of candidate ceramic breeder materials. Along with tritium retention and release and irradiation behavior, materials properties are essential for configuring ceramic breeder blankets, establishing operating temperatures, minimizing chemical corrosion and mechanical interaction of the various materials in contact, and assessing the blanket lifetime. Emphasis is placed on the most recent data and on ongoing experiments; discussion of other data is found in several references[25,37,38].

Based on the high melting points which were reassessed in recent investigations of the $\text{Li}_2\text{O-SiO}_2$, $\text{Li}_2\text{O-Al}_2\text{O}_3$, and $\text{Li}_2\text{O-ZrO}_2$ phase diagrams[39,40] and on vapor pressure data and thermodynamic calculations, there is indication of good thermal stability of the four ceramics and of good thermochemical behavior for LiAlO_2 and Li_2ZrO_3 . However, depending on the environmental atmosphere, there is potential for lithium mass transfer for Li_2O and, to a lesser extent, for Li_4SiO_4 .

Thermophysical properties of major relevance are thermal conductivity and thermal expansion. Thermal conductivity is rather low for the lithium-containing ceramics, varies with porosity and temperature, and is sensitive to the presence of impurities and other defects. Recent measurements[41] indicate that thermal conductivity is higher for LiAlO_2 and lower for Li_4SiO_4 than previously expected. Correlations have been established as a function of porosity and temperature. For 80% T.D. solid and 600°C temperature, the values are 3.54, 2.83, 1.42, 0.82 $\text{W/m}^{\circ}\text{K}$, respectively, for Li_2O , LiAlO_2 , Li_2ZrO_3 , and Li_4SiO_4 [5]. The effective thermal conductivity of pebble beds depends on the size and density of pebbles, surface conditions, packing fraction, gas composition, gas pressure, and purge gas flow rate. The thermal conductivity of Li_2O pebble beds (5 mm pebbles) was investigated at JAERI[42], and that of Li_4SiO_4 pebble beds (0.5 mm pebbles) at KfK[43] under different helium flow conditions.

Differences in thermal expansion between ceramic breeders and steel structures can give rise to mechanical interactions. Differential thermal expansion stresses, like differential swelling, offer potential for cracking of ceramic breeders; therefore, low thermal expansion is desired. Li_2O and Li_4SiO_4 have the largest and LiAlO_2 and Li_2ZrO_3 have the smallest thermal expansion: 1.5%, 1.41%, 0.62%, and 0.57% at 600°C, respectively.

Although ceramic breeder materials have no structural role, their fracture resistance and deformation behavior are of particular importance in the engineering design of breeder blankets. Fragmentation of the ceramic breeder should be avoided or minimized in order to prevent plugging of purge circuits and diminished heat transfer. The pebble bed configuration is

envisaged for ceramics which exhibit poor resistance to fragmentation. Mechanical characteristics of interest are elastic moduli; Poisson's ratio; compressive, bending, tensile strengths; and thermal creep. These properties are used to predict the response of materials to thermal loads and to calculate the lower bound on the thermal gradient which may contribute to material fragmentation.

Except for LiAlO_2 , the mechanical properties data base is still rather sparse. However, properties correlations can be developed as functions of grain size, porosity, temperature, and stress (thermal creep)[5,44]. The data base needs to be completed, particularly at higher temperatures. Recent LiAlO_2 data for ultimate compressive strength and ultimate bending strength at room temperature and at 600°C do not corroborate the decrease with temperature previously observed[45]. Except for Li_2ZrO_3 , thermal creep data are available above 700°C . Thermal creep can alleviate the breeder/structure mechanical interaction and accommodate swelling. The highest creep rate is observed for Li_2O , which also exhibits the greatest tendency to swelling.

Similar to other materials characteristics, mechanical properties are influenced by the presence of impurities and defects, and the use of additives can be attempted to enhance the mechanical strength of ceramic breeders. Such work is in progress at CEA with LiAlO_2 [46]. As pulsed operation is anticipated in some fusion devices, the thermal cycling behavior of ceramic breeders should be investigated. Thermal cycling tests, simulating mechanical and thermal stresses in a pebble bed during reactor operation, helped optimize the composition and annealing conditions of Li_4SiO_4 pebbles and improved mechanical properties, as judged from the small amount of broken pebbles after test[47].

The compatibility of ceramic breeders with structural materials has been widely investigated both in vacuum and in flowing atmospheres with or without moisture added. Reaction rates for LiAlO_2 , Li_2ZrO_3 , and Li_4SiO_4 were found to be much lower than the reaction rate for Li_2O in the temperature range of interest. Reaction rates increase with increasing temperature and moisture concentration. Recent studies[48,49] of the interaction of Li_2SiO_3 , Li_4SiO_4 ,

and Li_2O with 316L steel at constant H_2O partial pressure (100 and 1000 vppm) in flowing argon at 700°C and 800°C have shown that Li_2O has excellent compatibility behavior. Further, gas flow experiments are planned at 600°C and 900°C to clarify the difference with the Li_2O behavior in closed capsule systems. For all the breeder ceramics, correlations of penetration depth in steels versus temperature were established. Compatibility of Li_2O with beryllium was recently tested in the blank test of SIBELIUS; examinations are underway[50]. Some work has also been initiated in Japan. Compatibility of the ternary ceramics with beryllium was reported[48,51]. In the latter work three types of beryllium were tested; namely, high oxygen content (1000-5000 ppm), low oxygen content (50-100 ppm), and Be-0.4% Ca (<200 ppm). As far as ternary ceramics are concerned, and contrary to expectations based on thermodynamic considerations, the interaction of ceramic with beryllium is negligible up to 650°C for Li_4SiO_4 and up to 700°C for LiAlO_2 and Li_2ZrO_3 for durations of 3000 hours. Additional tests of LiAlO_2 , Li_4SiO_4 , and Li_2ZrO_3 with beryllium and Be-Ca alloy at 600°C during 3000 hours a) in dynamic vacuum, b) in dry helium purge flow, c) in helium + 90 ppm H_2O + 25 ppm H_2 purge flow confirmed a very limited interaction, whatever the environmental atmosphere[51].

It is assumed that a BeO layer forms on the metal surface and protects it from further oxidation. The impact that neutron irradiation may have on the protective BeO layer was studied in the SIBELIUS experiment[52]. In this experiment, ceramics (Li_2O , LiAlO_2 , Li_4SiO_4 , and Li_2ZrO_3), beryllium, and steels (316 L, 1.4914) were placed together in stacks and were irradiated in the mixed spectrum neutron flux in the core of the SILOE reactor at 550°C for 2000 hours in a helium + 0.1% H_2 purge flow. Observations of the couples Be/ Li_2O , Be/ LiAlO_2 , Be/ Li_4SiO_4 , and Be/ Li_2ZrO_3 as well as Be/316 L and Be/1.4914 steels are underway. Comparison with the SIBELIUS blank test, performed in identical conditions (specimens, arrangement, contact pressure, environmental atmosphere, temperature, and time) can identify any irradiation effect.

Because neutron irradiation continuously changes the composition of the ternary ceramics and induces damage in all ceramic breeders, their properties

and behavior can be affected. The irradiation behavior of the ceramic breeders was investigated in both thermal[53] and fast reactors[54].

Irradiations were conducted in mixed neutron spectra reactors for relatively short times, typically a few reactor cycles (one cycle is ~25 days) and at temperatures up to ~750°C. These experiments include the ALICE, DELICE, ORDALIA, and EXOTIC series. These irradiations correspond to low dpa values and low lithium burnups and, in general, have shown no significant changes in microstructure, dimensions, phase composition, and mechanical strength for the ternary ceramics. Fragmentation has occurred in some cases. In addition, the COMPLIMENT irradiation experiment[55] is designed to: 1) compare the irradiation damage caused by fast neutron scattering with the damage caused by the $\alpha + T$ particles from the ${}^6\text{Li}(n,\alpha)T$ reaction in a ceramic breeder, and 2) compare the irradiation behavior of various ceramic breeders under identical irradiation conditions. To this end, specimens of LiAlO_2 , Li_2SiO_3 , Li_4SiO_4 , Li_2ZrO_3 , and Li_2O supplied by five European organizations were irradiated in HFR-Petten cadmium-screened neutron flux for 178 FPD and in the OSIRIS Saclay thermal flux for 77 FPD at 400-450°C and 650-750°C. In both cases the total damage amounted to 1.8 dpa.

The FUBR tests indicate that tritium retention is lowest for Li_2ZrO_3 and highest for LiAlO_2 , and that helium retention follows a similar order. However, Li_2O has a high retention of helium at high burnup and low temperature (<773K). In the FUBR tests, Li_4SiO_4 showed a tendency for fragmentation as compared with LiAlO_2 and Li_2O , while Li_2ZrO_3 remained relatively crack free during irradiation. Fragmentation was not burnup dependent and was thought to result from thermal stresses arising from thermal gradients and thermal expansion[56]. Swelling was observed to be very low for LiAlO_2 (85% T.D.) and Li_2ZrO_3 at 973 K and 1173 K, slightly lower for Li_4SiO_4 , and rather high for Li_2O . Swelling was thought to arise from the retained helium in the material.

The thermal conductivity of irradiated Li_2O and LiAlO_2 has been investigated by Ethridge[57] in the temperature range 373-1173 K. Samples were irradiated at 773-1173 K to lithium burnup of 11.5×10^{20} captures/cm³.

In general, the measured conductivity of the irradiated material was quite similar to that for non-irradiated material. Reductions in thermal conductivity at temperatures < 573 K were observed from lithium oxide samples as a result of irradiation-induced lattice damage, whereas at temperatures > 573 K the thermal conductivities approached values well within the error band of non-irradiated lithium oxide. This is consistent with the general expectation that at higher temperatures the annealing of irradiation-induced defects would improve thermal conductivity. The thermal conductivity of irradiated lithium aluminate samples remained relatively constant with temperature for all irradiation times and temperatures and was only slightly lower than that of non-irradiated LiAlO_2 at low temperatures.

4. Tritium Recovery

Tritium release rate and the chemical form of the released tritium species are important factors controlling tritium recovery from a ceramic breeder in a blanket fuel cycle. Tritium recovery from the sweep gas and tritium permeation are sensitive to the tritium species form. Tritium migration in ceramic breeders is comprised of many processes, such as bulk diffusion, grain boundary diffusion, surface desorption, percolation through the interconnected porosity, and transport at the breeder/sweep gas interface. Moreover, it is important to clarify their mutual interaction. Surface desorption, which is affected by the chemical composition of the sweep gas and the oxygen potential of the system, often becomes the rate determining step. However, the exact details of this process remain to be elucidated.

Tritium recovery studies have been conducted by combination of laboratory studies, in-reactor tritium release experiments, and modeling activities. Review papers[1-3] and evaluation studies on ceramic breeders[4,58,59] are useful. Trends of recent studies on tritium release are summarized in this section.

4.1 Laboratory Studies

Thermal anneal tritium release tests and laboratory studies on adsorption and exchange reactions provide information on the release process. Out-of-pile tritium release experiments were performed for Li_2O [60,62], Li_2SiO_3 [61-65], Li_4SiO_4 [28,61-65], LiAlO_2 [62,66,67], Li_2ZrO_3 [62,68], Li_8ZrO_6 [62], and doped lithium ceramics[16,67,69-70]. From many experiments, tritium diffusivities in the grain were calculated and compared, and a correlation between tritium diffusivities (and activation energies) and the lithium/oxygen density ratio was developed[71]. The lithium/oxygen density ratio reflects a degree of the $\text{Li}^+-\text{O}^{2-}$ interionic interaction. The data for Li_2O show a strong shift in mechanism over a very narrow temperature range ($\sim 30^\circ\text{C}$), suggesting large differences in the activation energies for diffusion and desorption. In order to explain many results, surface desorption must be included[63-65,73]. Breitung et al.[64,65] constructed a surface recombination model after considering two surface sites for chemisorption of OT or OH.

The tritium chemical form on the surface and in the bulk is considered to be determined by the oxygen potential in the system[73]. Adsorption and absorption of water vapor on lithium ceramics were measured[74-76]. For Li_2O , adsorption is dominant at low temperature, while at higher temperature larger amounts of absorption were observed. O'Hira et al. studied interaction of T_2 and H_2 with Li_2O [77,78]. The amount dissolved was found to be proportional to the square root of the equilibrium pressure. The interaction of hydrogen with Li_2O surface was studied theoretically via quantum chemical cluster methods[79].

Desorption experiments of adsorbed water or hydrogen on lithium ceramics were also conducted in order to study the mechanism of the surface reaction. Kopasz et al.[80] observed multiple activation energies for water desorption from LiAlO_2 and Li_4SiO_4 , suggesting multiple types of desorption sites. Fischer[81,82] measured H_2O release from LiAlO_2 treated with H_2O and H_2 by temperature programmed desorption method, and also explained experimental results by different surface sites for desorption. Exchange reactions at the surface were also studied using hydrogen isotopes[83-85]. When HTO adsorbed on Li_2O was released by the purge gas containing H_2 , HT and HTO were released[84]. The release rate was found to be proportional to the square

root of the hydrogen pressure. Release of adsorbed HTO on Li_2O was also studied by purge gas containing H_2O [85]. It can be concluded from these studies that many useful kinetic data on the surface reaction were obtained, although the mechanisms remain to be clarified.

Gas permeation experiments through open pores were performed using disks of Li_4SiO_4 [86]. The Permeation rate had a good correlation with open porosity. The permeation rate of interactive gases with the pore surface remains to be studied. Mass transport by vaporization and condensation of LiOH is also an important process not only from integrity of the blanket but also from tritium recovery. More reliable thermodynamic and kinetic data are required for this purpose[88].

4.2 Irradiation Experiments

In-situ tritium release experiments have been conducted for candidate materials: Li_2O [80-100], LiAlO_2 [90,100-104], Li_2ZrO_3 [90,105], Li_6ZrO_7 [102,105], Li_8ZrO_6 [102,105], Li_2SiO_3 [88], and Li_4SiO_4 [102]. While the quantity of breeder material may vary, all these experiments combine effects of neutrons, temperature, and purge gas chemistry in one test. One of the BEATRIX-II experiments used a solid pellet specimen with a large radial temperature gradient to provide some "engineering" integrated performance data. In the SIBELIUS experiments[52], the effects of the beryllium multiplier on compatibility and tritium release were studied. In the future, integrated experiments involving ceramic breeder, neutron multiplier, coolant, purge gas, temperature, and neutrons are required to study the synergistic effects of many parameters such as burnup, temperature gradients, presence of other materials, sweep gas composition, and flow rate under the conditions anticipated in the fusion reactor. Integration with tritium permeation behavior and tritium recovery from the sweep gas is also important to design the blanket fuel cycle.

In in-situ tritium release experiments, tritium residence time was usually less than one day, except for extreme cases such as a high density sample with small open porosity[105]. The chemical form of the released

root of the hydrogen pressure. Release of adsorbed HTO on Li_2O was also studied by purge gas containing H_2O [85]. It can be concluded from these studies that many useful kinetic data on the surface reaction were obtained, although the mechanisms remain to be clarified.

Gas permeation experiments through open pores were performed using disks of Li_4SiO_4 [86]. The Permeation rate had a good correlation with open porosity. The permeation rate of interactive gases with the pore surface remains to be studied. Mass transport by vaporization and condensation of LiOH is also an important process not only from integrity of the blanket but also from tritium recovery. More reliable thermodynamic and kinetic data are required for this purpose[88].

4.2 Irradiation Experiments

In-situ tritium release experiments have been conducted for candidate materials: Li_2O [80-100], LiAlO_2 [90,100-104], Li_2ZrO_3 [90,105], Li_6ZrO_7 [102,105], Li_8ZrO_6 [102,105], Li_2SiO_3 [88], and Li_4SiO_4 [102]. While the quantity of breeder material may vary, all these experiments combine effects of neutrons, temperature, and purge gas chemistry in one test. One of the BEATRIX-II experiments used a solid pellet specimen with a large radial temperature gradient to provide some "engineering" integrated performance data. In the SIBELIUS experiments[52], the effects of the beryllium multiplier on compatibility and tritium release were studied. In the future, integrated experiments involving ceramic breeder, neutron multiplier, coolant, purge gas, temperature, and neutrons are required to study the synergistic effects of many parameters such as burnup, temperature gradients, presence of other materials, sweep gas composition, and flow rate under the conditions anticipated in the fusion reactor. Integration with tritium permeation behavior and tritium recovery from the sweep gas is also important to design the blanket fuel cycle.

In in-situ tritium release experiments, tritium residence time was usually less than one day, except for extreme cases such as a high density sample with small open porosity[105]. The chemical form of the released

tritium was both HT and HTO, the fraction of each depended on the partial pressure of hydrogen and the oxygen potential in the system. Using in-situ tritium release experiments, kinetics data of the tritium release steps were evaluated. Tritium diffusivities in the grain were measured in many tests by temperature change methods. Tritium diffusivity in the grain boundary was also estimated by using different size particles but the same microstructure[98,101]. However, in many experiments, tritium release was not explained only by bulk diffusion; many studies have examined the effects of hydrogen in the sweep gas. Kwast and Briec[96,103] showed that the desorption reaction cannot be explained by the first-order reaction, implying that the activation energy for desorption depends on surface coverage. Hydrogen pressure dependence on surface reaction was also studied by varying H₂ partial pressure. Kurasawa[93] showed 0.5th power dependence for single crystal and 1.0 for the sintered pellet. Tanaka[100,101] showed 0.5th power dependence for sintered particles of Li₂O and LiAlO₂. However, for lower oxygen-potential sample of Li₂O, surface reaction was faster and H₂ pressure dependence was the power of 1.0[99]. This shows that surface reaction is affected by the surface condition. The possibility of direct HT release from the surface was also presented[92,99]. Temperature was changed from 550 to 600°C under the sweep gas of He + 0.1%H₂. Two peaks were observed, and the second peak had a good correlation with the moisture. The mechanism was considered to be affected by the surface reaction but is not yet fully elucidated.

Addition of H₂O to the sweep gas also showed effectiveness in enhancing tritium desorption[99,100,104]. The mechanism for this is considered to be surface swamping by water or creation of a larger surface recombination rate with larger concentration of surface water. Tritium release behavior was also affected by impurities in lithium ceramics, as shown in CRITIC-I experiments[94-97]. Carbonate and free oxygen generated by burning were considered important. BEATRIX-II experiments also showed the importance of sweep gas flow rate[92].

4.3 Computer Model Development

Computer modeling is an important tool for clarifying the mechanism of tritium migration and for estimating tritium inventory in a breeder blanket system. Two modeling workshops have been held[106,107] in which tritium release data and the modeling methodology were discussed. Among lithium ceramics many data on Li_2O and LiAlO_2 are available; however, more data are required for other ceramics. Also for Li_2O and LiAlO_2 , data are needed on surface reaction and effects of irradiation, trapping, high burnup, and high fluence.

One segment of the modeling activity has focused on individual processes in tritium migration[108-114]. Typical of these is a surface reaction. In order to explain tritium release behavior observed in in-pile and thermal anneal tritium release experiments, surface desorption models were utilized. In some studies, apparent reaction rate constants were used from the analogy to heat transfer without thorough knowledge of the release mechanism. Surface recombination model is one method. Surface heterogeneity was modeled using multi-surface sites with different activation energies for tritium desorption and was successful for explaining some in-situ results[72]. Terai et al.[111,112] constructed a surface reaction model to estimate HT and HTO release rates assuming simple reaction. Exchange reaction of the released HTO on the surfaces of lithium ceramic and construction material was also studied and modeled. However, until now, a satisfactory model has not been presented to explain the surface reaction rate and the chemical form of the released tritium at the same time. Continuing and intensive efforts to model surface reaction combined with in-pile and postirradiation tests are required.

An integrated model was constructed to estimate tritium inventory and quantitatively to make clear the important process. The model by Billone et al.[109,110] considered inter-granular and grain diffusion, tritium desorption from the surface, and solubility. In the model made by Raffray et al.[114-117], the same processes were considered, but one feature of their model is a better characterization of the processes at the breeder surface and their linking to the bulk and pore regions.

4.4 Solids Modification for Tritium Release Enhancement

Many methods are being considered to enhance tritium release from lithium ceramics. To improve the surface desorption rate, the addition of H₂ or H₂O to the sweep gas is considered, which apparently enhances the surface reaction rate. Characterization of the solid microstructure is also an important scheme. If tritium diffusivity in the grain is slow, such as the case in LiAlO₂, small grain size is required. Interconnected open porosity will shorten the tritium migration path.

Recently, doping has been considered as an effective way to improve the tritium transport process. Lithium aluminate doped by Mg, Ga, Si, Zn, or Cu was prepared and tested by Botter et al. [16,67,118]; Al or Mg doped orthosilicate was tested by Vollath et al. [69-70]. Tritium release behavior studied by post-irradiation tritium release test or electrical conductivity measurement was reported to be improved. In some tests larger tritium trapping at low temperature was observed [67,118]. Basically improvement of transport can be attributed to improved tritium diffusion through enhancement of the lithium-ion diffusion by introduction of lithium-ion vacancies due to doping. Kopasz et al. [119] discussed the tritium-lithium vacancy complex from doping level and thermal equilibrium.

5. Defect and Irradiation Behavior

Ceramic breeder blankets have been selected as the first option in the ITER conceptual design study. A recent review on the status of the properties data base has revealed, however, that there is serious lack of knowledge about irradiation effects, particularly on microstructural changes and the associated breeding performance.

Some fundamental approaches have been taken in studying irradiation-induced defects and transport phenomena, using convenient means such as electron, X-ray, and accelerated ion irradiations. Rather limited studies have been made on those neutrons. Some pioneering attempts with high flux fast neutrons have just begun to open a way for answering some of the long-standing critical questions.

5.1 Fundamental Studies on Irradiation Effects

Earlier studies on the formation and recovery of various types of irradiation-induced defects in Li_2O were made by irradiation with oxygen ions followed by electron spin resonance (ESR) and optical absorption measurements[119]. More recently, similar studies have been carried out using in-situ luminescence for detection of defects[121]. Studies on LiAlO_2 using various instrumental techniques, including transmission electron microscopy, has added further support for the ideas that F^+ centers and impurity centers[122] as well as formation of a second phase, LiAl_5O_8 may be formed[123].

In evaluating the effects of oxygen ion and lithium ion irradiation on lithium ion diffusion and the associated tritium transport, the ionic conductivity was measured with materials such as Li_2O , Li_4SiO_4 , and Al-doped Li_4SiO_4 [124-128]. Measurements were made either during or after irradiation. For measurements after irradiation the dependence on fluence changed with the range of temperature tested, from which types of defects formed were estimated (e.g., Fig. 1). Based on these observations, prediction was made of the effects of irradiation on diffusivity of lithium ions and tritium.

The valence states of tritium in Li_2O irradiated with thermal and 14 MeV neutrons were studied using a radiochemical method[129,130]. The defect state was estimated by observing changes in the amount of T^+ , T^- and T^0 as functions of fluence and temperature.

5.2 Performance Tests and Spectrally Simulated Neutron Environments

The FUBR-1 experiment in EBR-II on large-diameter Li_2O and LiAlO_2 specimens yielded the first test results on dimensional stability after fast neutron irradiation up to 4% burnup[131]. Higher stability of Li_2O relative to LiAlO_2 was recognized. A similar observation was also reported for the CRITIC-1 experiment[95].

The international program of BEATRIX-II completed its Phase 1 experiments at FFTF in March 1991 after 300 EFPD to reach 4% burnup with fast neutrons. Direct observation of the irradiated materials will begin in late 1991. The in-situ results of tritium recovery and temperature measurements for specimens of different geometry-temperature configurations indicated that Li_2O has potential as a breeder material[132,133].

The BEATRIX-II Phase 2 experiment is planned to start in June 1991 for another 300 EFPD operation to attain 8% burnup on an Li_2O ring and Li_2ZrO_3 spheres.

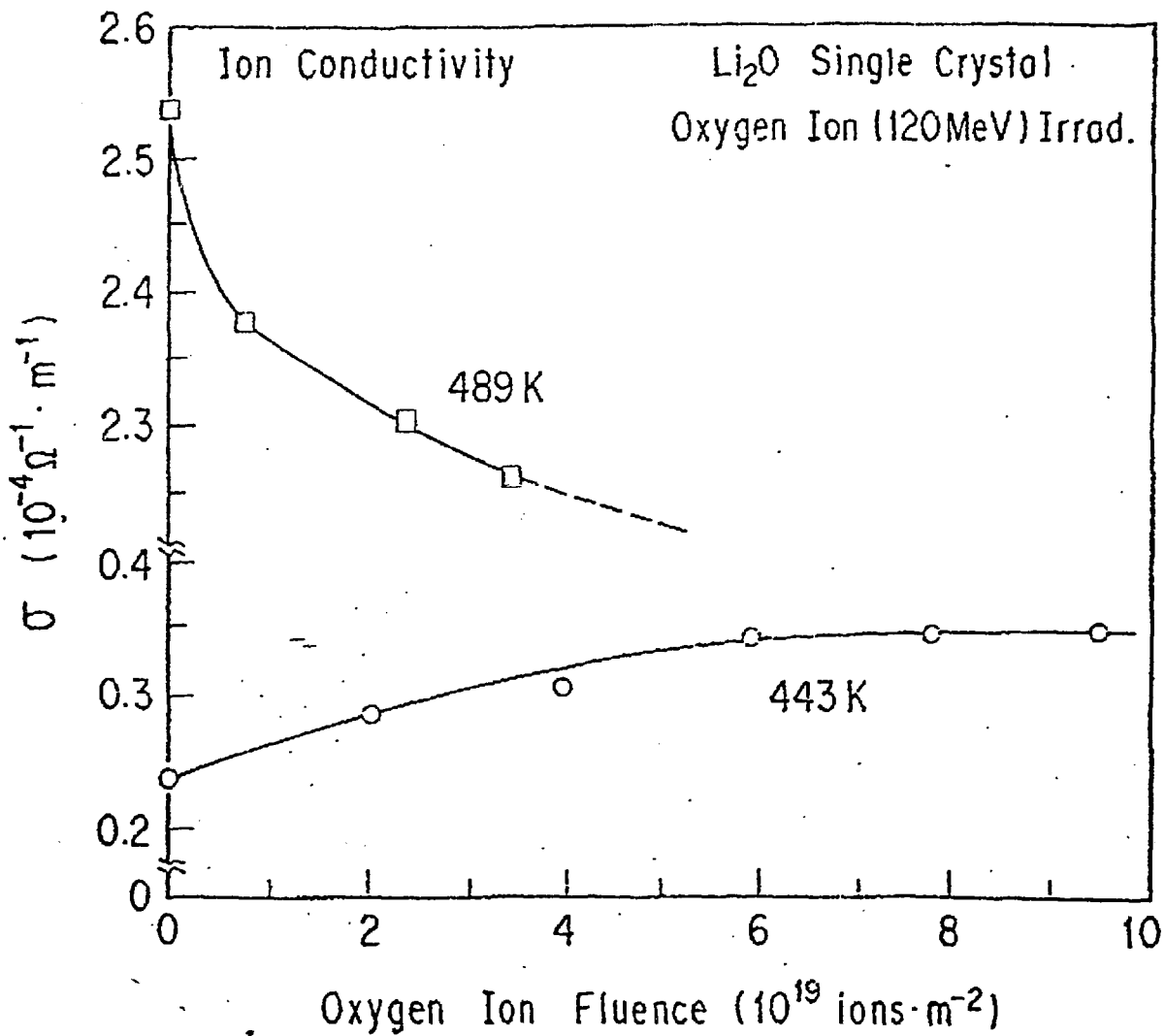


Figure 1. Ionic conductivity in the postirradiation condition for Li_2O irradiated with 120 MeV oxygen ions as a function of the irradiation ion fluence.

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