Enhanced Tritium Transport and Release by Solids Modification

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CONF-891204--18

ABSTRACT

DE90 005636

To improve the tritium release characteristics of lithium ceramics, we are investigating the affects of dopants on tritium transport and release. Prior work has suggested a correlation between tritium and lithium diffusion in lithium-containing ceramics. This correlation has led us to propose a mechanism for tritium diffusion in which the tritium diffuses in the form of a lithium vacancy-triton complex. If this is the case, one should be able to increase the tritium diffusivity by increasing the number of lithium vacancies and thereby increasing the number of vacancy-triton complexes. The size of the increase in the diffusivity, however, will be dependent upon several parameters, including the binding energy of the vacancy-triton complex. Our calculations indicate that, under conditions comparable to those in some in-pile irradiation experiments, a binding energy of around 84 kJ/mol should increase the diffusivity and lead to a decrease in the steady-state tritium inventory by about a factor of six.

Work supported by the U.S. Department of Energy, Office of Fusion Energy under Contract W-31-109-Eng-38.

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INTRODUCTION

Current trends in fusion reactor designs, e.g. the International Thermonuclear Experimental Reactor (ITER), indicate some preference for lowering the operating temperature of the tritium breeding blanket to $<300^{\circ}\text{C}$. This could lead to a substantial increase in the tritium inventory in a ceramic breeder blanket, because the candidate materials presently exhibit poor tritium release characteristics at these low temperatures. However, we may be able to improve the tritium release characteristics at low temperature by solids modification through doping with heterovalent ions. Studies on ceramic materials have shown that diffusivity can be increased by orders of magnitude when doping the material with heterovalent ions. Defect diffusion in Al_2O_3 was increased six orders of magnitude by addition of MgO .¹ Diffusion of tritium in silicon carbide was increased four orders of magnitude by doping with aluminum, while diffusion of tritium in Al_2O_3 was increased four orders of magnitude by doping with MgO .²

The presence of dopants in these materials may lead to 1) an increase in the carrier concentration and 2) a change in the local electronic environment. These can lead to higher diffusivity because of changes in the diffusion frequency factor and the activation energy. In addition, there is evidence that the presence of impurities on the surface can lead to a substantial increase in the desorption rate constant.³

The work covered herein uses lithium aluminate (LiAlO_2) as an example for discussion. Lithium aluminate exhibits excellent mechanical and irradiation properties for breeder blanket application, comparing favorably with the other solid breeder candidates. However, at low temperatures ($300\text{--}500^{\circ}\text{C}$), tritium transport and release from the aluminate are slow. If the tritium transport and release characteristics could be improved, lithium aluminate would be more

attractive as a candidate tritium breeding material. In this paper we will report on our theoretical investigation of the potential for increasing the tritium diffusivity in lithium aluminate by doping with MgO to create lithium vacancies.

THEORY

A random walk model for self-diffusion in a solid gives the diffusivity as

$$D = ga^2 \nu N \exp(-\Delta G_m / RT) \quad (1)$$

where g =geometric factor, a =jump distance, ν =jump frequency, N =number of carriers, and ΔG_m = the free energy of migration.⁴ This equation indicates that one can increase the diffusivity by increasing the number of carriers. For tritium diffusion in a lithium-containing ceramic, the carriers are believed to be lithium vacancies. Therefore, one should be able to increase the tritium diffusivity by increasing the number of lithium vacancies in the material.

In a pure material, the number of lithium vacancies present will be determined by the thermal equilibrium between the perfectly ordered structure and any defects which contain a lithium vacancy (such as a Frenkel defect composed of a lithium vacancy and a lithium interstitial, or a Schottky defect composed of an oxide vacancy and two lithium vacancies). In lithium aluminate, the most abundant defects should be Frenkel defects. The lithium vacancy concentration in the pure material will be determined by the energy required to form these defects and the temperature of the lithium aluminate. As the temperature increases, the number of lithium vacancies will increase, thereby increasing the potential for higher tritium diffusivity. The

effective tritium diffusion activation energy will include the free energy of migration plus the formation energy of the lithium vacancy.

In impure materials, there will be additional vacancies caused by the impurities. For example, substitution of a Li_2O unit in the crystal with an MgO unit would result in a lithium vacancy. Over a given temperature range, the number of vacancies due to these impurities may be much larger than those due to thermal equilibrium. The number of lithium vacancies will be independent of the temperature over this range, and the tritium diffusion activation energy will be equal to the free energy of migration. As the temperature is increased above this range, the number of vacancies due to thermal equilibrium will increase, and the number of vacancies due to defects may no longer dominate. If the impurity concentration is low enough, a point will be reached where the vacancies due to thermal equilibrium dominate. At temperatures above this point the tritium diffusion activation energy will once again be equal to the free energy of migration plus the energy of formation of a Frenkel defect.

From the previous discussion, it is clear that the effects of impurities on the number of lithium vacancies depend on the purity of the starting material, the temperature, and the defect formation energy. The effects of impurities on the tritium diffusivity will depend on these three parameters, as well as the efficiency of the lithium vacancy as a carrier for the tritium and on the tritium concentration. We calculated the effects of the tritium concentration (i.e., the tritium generation rate), the lithium vacancy/tritium binding energy, and the dopant level on the tritium diffusivity of lithium aluminate doped with MgO .

MODEL

Our calculations of the effect of impurities on tritium diffusion in LiAlO_2 are based on the following model. Tritium is produced within a spherical grain at a constant generation rate G . The tritium diffuses slowly as tritium bound to oxygen, i.e., OT^- with a diffusivity equal to the oxygen diffusivity in LiAlO_2 . The tritium also reacts with lithium vacancies to form a lithium-vacancy/tritium complex ($\text{V}_{\text{Li}}\text{T}$), which has a diffusivity given by the lithium vacancy diffusivity.

The rate of reaction to form the lithium vacancy/tritium complex is determined by the law of mass action to be

$$R_{\text{form}} = K_f [\text{T}] [\text{V}_{\text{Li}}] = g D_V / a^2 [\text{V}_{\text{Li}}] [\text{T}] \quad (2)$$

where $[\text{V}_{\text{Li}}]$ is the lithium vacancy concentration, K_f is the formation rate constant of complex, D_V is the vacancy diffusion coefficient, and $[\text{T}]$ is the uncomplexed tritium concentration. Because the complex should readily form once the vacancy and tritium atom are in adjacent positions, we have assumed that the rate of reaction is controlled by the migration of a lithium vacancy to a site adjacent to the tritium atom. The rate constant for dissociation of the complex is given by

$$R_{\text{diss}} = 4 \nu \exp(-G_b/RT) [\text{complex}] \quad (3)$$

where G_b = binding energy of the complex. To focus on the effects of the impurities on diffusion, we will use the following diffusion boundary conditions for the T and V_{Li} species:

$$[\text{T}] = 0 \text{ at } r=a \quad (4)$$

$$[\text{V}_{\text{Li}}\text{T}] = 0 \text{ at } r=a \quad (5)$$

For LiAlO_2 , the values for the energy of migration of the lithium atom and the formation energy for a Frenkel defect are not well known. There is some dispute over the activation energies for lithium migration and over the temperature regime where the break from extrinsic to intrinsic diffusion

occurs. However, simple calculations and comparisons to similar materials can act as a guide in choosing representative values.

Lithium conductivity data and lithium nuclear magnetic resonance data indicate an activation energy for lithium diffusion in LiAlO_2 in the extrinsic region of about 75.3 kJ/mol.^{5,6} This is in good agreement with data for lithium diffusion in Li_2SiO_3 and Li_2O .^{5,6} An activation energy of 121.8 kJ/mol has been reported for the lithium ion conductivity in LiAlO_2 in the intrinsic region.⁵ A quick calculation reveals that if this number is correct, then near the melting point of LiAlO_2 , there would be a defect concentration of 0.07 defects per Li site. This value is much too high. A defect concentration on the order of about 1×10^{-4} per site is expected for a stoichiometric oxide.⁷ An activation energy of 121.8 kJ/mol in the intrinsic region also seems too small when compared to the values for cation diffusion in Li_2O and Al_2O_3 . Activation energies for diffusion of the cation in the intrinsic region in Li_2O and Al_2O_3 of 243 and 364 kJ/mol, respectively, have been reported.^{8,9} Reported tritium diffusion activation energies in LiAlO_2 provide further support for the position that the activation energy for lithium migration in the intrinsic region of 121.8 kJ/mol is too low. Activation energies of tritium diffusion of 80.8 and 90.4 kJ/mol have been reported for LiAlO_2 samples doped with 1300 ppm Mo and 650 ppm Na, respectively.^{10,11} The large number of vacancies due to the Mo dopant suggests that the diffusion is extrinsic in both cases. For the diffusion to be extrinsic for the second case, the number of intrinsic defects must be less than the extrinsic number of defects. If the intrinsic activation energy is 121.8 kJ/mol, leading to a defect formation energy of 92 kJ/mol, then the transition from intrinsic to extrinsic diffusion would occur at a temperature

of about 488°C (761 K) for the Na-doped sample. No change in diffusion activation energy was observed over the temperature range 357-657°C (630-930 K) for this sample.¹¹

Based on these data and the expected similarity in lithium diffusion for Li_2O and LiAlO_2 , we have chosen a value of 243 kJ/mol as an estimate of the lithium diffusion activation energy in LiAlO_2 in the extrinsic region.

RESULTS AND DISCUSSION

Our simulations of tritium diffusion in lithium aluminate indicated that it may be possible to increase the tritium diffusivity in this material by doping it with heterovalent ions. The binding energy of the lithium-vacancy/tritium complex in MgO-doped LiAlO_2 was found to have a large impact on the effectiveness of doping at increasing the apparent tritium diffusivity. Calculations were performed with binding energies ranging from 63 to 92 kJ/mol. The calculated amount of tritium in the form of the mobile vacancy-tritium complex for three different binding energies and two levels of lithium vacancy concentrations is shown in Table I. At the tritium generation rate investigated, the most effective binding energy was 84 kJ/mol.

Table I

Percent of Total Tritium as a -Vacancy/Tritium Complex for Different Binding Energies and Lithium Vacancy Concentrations
[Tritium Generation Rate = 1×10^{-10} T/(mol $\text{LiAlO}_2 \cdot \text{sec}$)]

Binding Energy (kJ/mol)	63	84	92
Lithium Vacancy Concentration= 1×10^{-6}	0.6%	33%	74%
Lithium Vacancy Concentration= 1×10^{-4}	38%	99%	>99%

With a binding energy of 84 kJ/mol, Table I shows that there is a large difference in the percentage of tritium in the more mobile form (lithium-vacancy/tritium complex) when the lithium vacancy concentration is changed from 1 ppm to 100 ppm. At a vacancy concentration of 1 ppm, only 33% of the tritium is in the form of the complex, while for a vacancy concentration of 100 ppm (obtained by doping) the percentage of tritium in the mobile form increases to 99%.

The increase in mobile tritium with increasing vacancy concentration should result in a substantial decrease in the tritium inventory. For a binding energy of 84 kJ/mol and a lithium vacancy concentration of 1 ppm, the steady-state tritium inventory is calculated to be 1.68×10^{-14} mol T/grain LiAlO_2 (103 ppm), with 33% of the tritium in the form of immobile T^+ . When the lithium vacancy concentration is increased to 100 ppm, the tritium inventory decreases dramatically to 0.28×10^{-14} mol T/grain LiAlO_2 (17 ppm), with 99% of the tritium in the form of a vacancy-triton complex. These calculations suggest that doping can lead to a decrease in inventory by a factor of six.

For larger binding energies, even at low vacancy concentrations, the majority of the tritium exists as a lithium-vacancy/tritium complex. For example, for a binding energy of 92 kJ/mol, the lithium-vacancy/tritium complex is the dominant form for tritium, even with a vacancy concentration as low as 1 ppm. Changing the vacancy level from 1 ppm to 100 ppm for the tritium generation rate given in the table only results in the vacancy-tritium complex increasing from 74% to 99.7% of the total tritium. The vacancy concentration in the undoped case (1 ppm) is still large enough to effectively bind most of the tritium due to the large equilibrium constant favoring the formation of

the complex. In this case doping still improves the diffusivity and decreases the inventory. However, the decrease in inventory is not as dramatic as that seen for a binding energy of 84 kJ/mol.

For lower binding energies, the majority of the tritium exists in the less mobile T^+ form, even when the level of lithium vacancies is raised to 100 ppm by doping. For example, at the tritium generation rate used for the calculations with a binding energy of 63 kJ/mol, the vacancy-tritium complex accounts for only 38% of the tritium inventory for a 100 ppm lithium vacancy concentration, while the complex accounts for only about 1% of the tritium inventory for a 1 ppm lithium vacancy concentration. Here, the equilibrium constant for formation of the complex is too small, even when the vacancy concentration is high. However, even with only 38% of the tritium in the complexed form, the inventory is reduced by about 30%. In addition, if the dopant level is increased to 1000 ppm, then the proportion of tritium in the complexed form is increased to 99%, and the inventory is decreased by a factor of 10.

Table II

Percent of Total Tritium as a -Vacancy/Tritium Complex
for Different Lithium Vacancy Concentrations
(Binding Energy = 63 kJ/mol)

Vacancy Concentration	Percent Tritium as Vacancy-Tritium Complex
1×10^{-6}	0.6
1×10^{-4}	38
2×10^{-4}	55
5×10^{-4}	75
1×10^{-3}	99

We have also calculated that the dependence of the effectiveness of doping on the tritium generation rate will be small. Increasing the generation rate by four orders of magnitude had only a minor effect on the tritium distribution. For a binding energy of 92 kJ/mol, increasing the generation rate from 1×10^{-10} mol T/(mol $\text{LiAlO}_2 \cdot \text{sec}$) (similar to the generation rate for some in-pile tritium extraction experiments) to 1×10^{-6} mol T/(mol $\text{LiAlO}_2 \cdot \text{sec}$) only increased the amount of complexed tritium from 74 to 76% when the vacancy concentration was 1 ppm, while for a vacancy concentration of 100 ppm, the percentage of tritium in the complexed form was greater than 99% for both generation rates. A similar pattern was observed for a binding energy of 63 kJ/mol. Increasing the generation rate by a factor of 4 resulted in no noticeable change in the percentage of tritium in the form of the lithium-vacancy/tritium complex when the vacancy concentration was 100 ppm, and only a change of less than one percent when the vacancy concentration was 1 ppm.

CONCLUSIONS

Our calculations indicate that, with a binding energy of the lithium-vacancy/tritium complex ranging from 84 kJ/mol to 63 kJ/mol in LiAlO_2 , one could greatly reduce the tritium inventory by doping. This is supported by recent experimental data, suggesting that tritium is released at lower temperatures in MgO-doped LiAlO_2 release than in undoped LiAlO_2 .²¹ These constant rate heating experiments on sintered pellets of pure LiAlO_2 and LiAlO_2 doped with MgO indicated an improvement in tritium release for the doped material. The tritium release was observed at significantly lower temperatures for the doped material (release peaks at temperatures of 300-

425°C) than for the undoped material (release peaks at 550-850°C).²¹ No hypothesis as to the mechanism responsible for improving the tritium release was reported.

The energies used in our calculations are in the range of those expected for a vacancy-triton complex. Binding energies for complexes of hydrogen or hydroxide moieties with divalent magnesium vacancies have been calculated to be in the range of 275 to 310 kJ/mol.²⁰ Since the binding energy is believed to be due to mainly coulombic interactions, which are proportional to the product of the charges, one would expect the binding energy for a lithium-vacancy/hydrogen complex to be about one-half this amount (137 to 155 kJ/mol). This is not too far from the binding energy of 84 kJ/mol which we found to be most effective in reducing the tritium inventory. This suggests that one should be able to enhance tritium release and reduce inventory at low temperatures in LiAlO₂ by doping the material to create lithium vacancies.

REFERENCES

- 1) J.D. Fowley, R.A. Causey, D. Chandra, and T.S. Elleman "Radiation Effects and Tritium Technology for Fusion Reactors," Proceedings International Conf., Gatlinburg, TN, 1975.
- 2) K. Kitazawa and R.L. Coble, J. Amer. Cer. Soc. 57 (1974)250.
- 3) J. L. Mitchell, D. Lazarus, Phys. Rev. B. 12 (1975)734.
- 4) J. L. Mitchell and D. Lazarus, Phys. Rev. B. 8 (1973)1715.
- 5) J. W. DeFord and O. W. Johnson, J. Applied Physics 46 (1975)1013.
- 6) P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26 (1965)1067.
- 7) T. Matsuo, H. Ohno, K. Noda, S. Konishi, H. Yoshida, H. Watanabe, J. Chem. Soc. Faraday Trans. (1983)79.
- 8) R. M. Biefeld, R. T. Johnson, Jr., J. Electrochem. Soc. 126 (1979)1.
- 9) Y. Oishi, Y. Kamei, M. Akiyama, T. Yanagi, J. Nucl. Mater. 98 (1979)341.

- 10) D. Guggi, H. R. Ihle, D. Bruning, U. Kurz, S. Nasu, K. Noda, T. Tanifuji, J. Nucl. Mater. 118 (1983)100.
- 11) Y. S. Oei and H. Richtering Ber Bunsenges. Phys. Chem. 80 (1976)1007.
- 12) R. J. D. Tilley, "Defect Crystal Chemistry and its Applications" Chapman and Hall, New York, 1987.
- 13) S. Konishi and H. Ohno, J. Amer. Cer. Soc. 67 (1984)418.
- 14) H. Ohno, S. Konishi, T. Nagasaki, T. Kurasawa, H. Katsuta, and H. Watanabe, J. Nucl. Mater. 133-134 (1985)79.
- 15) H. J. Matzke, Advances in Ceramics 17 (1986)1.
- 16) A. V. Chadwick, K. W. Flack, J. H. Strange, and J. Harding, Solid State Ionics, 28-30 (1988)185.
- 17) W. C. Mackrodt Advances in Ceramics 10 (1984)62.
- 18) D. Bruning, D. Guggi, and H. R. Ihle, Fusion Technology 1 (1982)543.
- 19) K. Okuno and H. Kudo, J. Nucl. Mater. 138 (1986)210.
- 20) A. N. Cormack, P. Saul, and C. R. A. Catlow, Physica 131B (1985)139.
- 21) F. Botter, D. Cherquitte, M. Gautier, and P. Maire, Fusion Technology 1988 Elsevier Science Publishers, 1989.