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Thermodynamic Performance of Ceramic Tritium

Breeding Blanket Material

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ABSTRACT

Thermodynamic calculations have been made to compare the thermochemical performance of three candidate breeder blanket materials, Li_2O , LiAlO_2 , and Li_4SiO_4 . These calculations were done for the temperature range of 900-1300 K and the oxygen activity range of 10^{-25} to 10^{-5} . Oxygen activity is an influential variable for these materials and must be considered in the diffusion of tritiated species, determining the chemical form of the released tritium, and retention of tritium in the condensed phase. Surface adsorption may also act as a strong contributor to tritium inventory. In general, LiAlO_2 appears better than Li_2O and Li_2O , in turn, appears better than Li_4SiO_4 .

INTRODUCTION

An essential component in every D-T fusion design is the tritium-producing blanket. This tritium breeding blanket not only produces the tritium necessary for maintaining a plasma fuel supply but also provides a medium for converting fusion neutron energy into useful thermal power. The development of an operational blanket is one of the necessary steps in demonstrating the technological feasibility of controlled thermonuclear fusion (D-T).

Currently, emphasis is being directed to evaluation of the lithium-containing oxides, e.g., Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , and Li_2ZrO_3 . The prime candidate material must satisfy many requirements, including desirable neutronic and irradiation characteristics, chemical and morphological stability including resistance to sintering at operating temperatures, compatibility with structural and other blanket materials, and rapid tritium release coupled with low retention.

The tritium inventory of an operating solid breeder blanket may be its single most important performance parameter and is essentially intrinsic to a specific material under specific condi-

tions. The tritium inventory is thought to be partitioned into several distinct phenomena; solubility, bulk diffusion, irradiation effects and gaseous diffusion within the pores. While selection of an inventory limit--be it 10 wppm or 1%--is controversial, candidate materials exhibiting low inventory are clearly more desirable. Tritium inventory is predicted to possess a strong dependence on temperature and an uncertain dependence on burnup. The tritium inventory causes an extra burden on breeding ratios for solid breeder designs.

The solubility contribution to the tritium inventory was originally thought to be the dominant factor. Currently, only Li_2O has received considerable attention in laboratory studies.¹⁻⁴ Even though hygroscopic at room temperature, Li_2O has been shown to have extremely low moisture solubility under blanket operating conditions as shown in Fig. 1. However, increases in T_2O partial pressure in the gas phase over the sample will cause a separate LiOT phase to form with an incremental increase in tritium inventory.

At the present time, suitable thermodynamic data for the oxidic breeders are available in the form of free energies of formation for most of the condensed phases and for the gaseous species. These data permit ideal solution calculations to be performed for all species. However, studies on the solubility of LiOH in Li_2O have given experimental data for the activity coefficient of LiOH in the solid phase. A supportive study by Norman and Hightower⁵ also shows the existence of significant nonideality in this system. In the cases of Li_2O , therefore, extensive calculations based on a nonideal solution of LiOH in Li_2O are possible.

These laboratory studies were complemented by recent in-situ recovery experiments on Li_2O ⁶ which indicated only 0.5 wppm tritium retained at 750°C. In addition, the recent TRIO-01 experiment in ORR⁶ demonstrated in-situ tritium

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Fig. 1. Plot of concentration of LiOH in Li₂O at 850 °C as a function of partial pressure of water vapor in helium carrier gas

recovery from Y-LiAlO₂ while under fission neutron irradiation. These experiments were conducted in part with He-H₂ purge stream which significantly enhances tritium release in comparison to less reducing atmospheres. The chemical form of tritium being released, i.e., condensible (T₂O, HTO) or noncondensable (HT, T₂), continues to be a topic of interest and conjecture since it directly impacts containment and processing systems.

Irradiation effects, including restructuring, trapping and defect generation, can also contribute to the tritium inventory. Although the degree of irradiation-induced trapping is still uncertain, fast reactor closed-capsule irradiation experiments have served to demonstrate that irradiation effects will be limited to a few percent (1 to 9%) of the tritium generated in Li₂O.⁷ Restructuring, in particular grain growth, was once thought to provide an upper temperature limit, but data now indicate that the effect of temperature on diffusion is more dominant than any decrease resulting from larger grain sizes. Interestingly, LiAlO₂ and Li₄SiO₄ retained more tritium in this fast reactor environment and at lower temperatures which indicates mechanisms other than solubility to be rate controlling, for example, surface or diffusional phenomena.

In this paper, comparisons are made of the results from a series of ideal solution calculations for all species of Li₂O (except LiOH in

Li₂O), LiAlO₂, and Li₄SiO₄. The SOLGASMIX code^{8,9} was used for calculating the equilibria of multielement-multispecies gas and condensed phases, based on the minimization of system free energy. In these calculations, the ceramic breeder systems are treated on an equal volume basis and are normalized on this to 1 mol Li₂O. The gas phase is taken to be 15 vol % and to contain inert gas at one atmosphere pressure for the system. It is assumed that 10⁻⁴ g atoms lithium has been transmuted to 10⁻⁴ g atoms tritium. The oxygen content of the system is established by the requirements of various oxygen activities.

THERMODYNAMIC RELATIONSHIPS IN CERAMIC BREEDERS

Thermodynamic calculations have been made to predict the thermochemical performance of the candidate materials for the 900-1300 K temperature range and oxygen activity range of 10⁻²⁵ to 10⁻⁵. For Li₂O the gas phase species considered include H₂, T₂, HT, O₂, H₂O, T₂O, HTO, LiOH, (LiOH)₂, LiOT (LiOT)₂, Li₂O, Li, LiH, and LiT. The condensed phase Li₂O was considered to contain the solutes LiOH, LiOT, LiH, LiT, and Li. A second condensed phase of LiOH(l) was not present in the 900-1300 K temperature range.

Although the Li₂O calculations correspond more closely to actual conditions because of the use of measured activity coefficients, the results from ideal solution calculations on LiAlO₂ and Li₄SiO₄ allow comparisons of these systems to be made on the basis of the best available data. Such comparisons are useful for the technological evaluation of tritium management in a breeder blanket.

In the LiAlO₂ calculations, the gaseous species were T₂, O₂, T₂O, LiOT, (LiOT)₂, LiO, Li₂O, AlO₂T, AlOT, and Al. Two condensed phases must be considered for this system: the major phase, LiAlO₂, and the minor phase, LiAl₅O₈. The amount of this minor phase is small because we consider the effects of only 10⁻⁴ g atom burnup of the lithium. LiOT was taken to be a solute in both of these phases. Elemental lithium and lithium tritide were included as additional solutes in the LiAlO₂ phase.

For the Li₄SiO₄ system, the gas phase species were the same as those for the Li₂O system except for the addition of SiO(g) and SiO₂(g). The condensed phases considered for this system were the major phase, Li₄SiO₄, and the minor phase, Li₂SiO₃. Calculations showed a phase of LiOT would not form under the given conditions. The solutes LiOT, LiT, and Li were considered to be present in both of the condensed silicate phases.

A comparison of the molar quantities of the gas phase species that are of concern in tritium recovery, T₂ and T₂O, is presented in Figs. 2 and 3 for the temperatures 900 and 1300 K. The

Fig. 2. Molar quantities of gas phase species at 900 K over Li_2O , LiAlO_2 and Li_4SiO_4

molar quantities are plotted as a function of oxygen activity in order to emphasize the importance of this variable. At 900 K, both the T_2 and the T_2O species have a higher partial pressure over LiAlO_2 than over Li_2O or Li_4SiO_4 through the whole oxygen activity range. At 1300 K, the same relationship among the breeders holds over the oxygen activity range of 10^{-20} to 10^{-15} . However, below an oxygen activity of 10^{-20} , these gaseous components are stronger over Li_4SiO_4 than over Li_2O , but LiAlO_2 still shows the greatest ability to release them.

The sharp reduction in the T_2 and T_2O quantities shown in several of the curves at oxygen activities below 10^{-20} is a consequence of the reducing conditions represented by these low oxygen activities. At high temperature and low oxygen activity there is an increase in the activity of elemental lithium. This increase activity provides a driving force for conversion of tritium to tritide and for the corresponding reduction of tritium as T_2 and T_2O .

Tritium held in the condensed phase represents a significant part of the tritium inventory. Figure 4 provides a comparison of the breeder materials with respect to this factor. At 900 K, the tritoxide concentration is not very sensitive to oxygen activity. However, in

Fig. 3. Molar quantities of gas phase species at 1300 K over Li_2O , LiAlO_2 and Li_4SiO_4

LiAlO_2 a significant decline in the concentration begins as oxygen activities drop below 10^{-20} . Across the oxygen activity range, the concentration of tritoxide is lowest in LiAlO_2 ; different behavior appears at 1300 K. At oxygen activities below 10^{-15} , the tritoxide concentration drops for Li_2O and LiAlO_2 , but the decline starts for Li_4SiO_4 only when the oxygen activity drops below 10^{-20} . For oxygen activities approximately between 10^{-15} and 10^{-23} , the tritoxide concentration in Li_2O is greater than in LiAlO_2 . At lower oxygen activities, the concentration is greater in LiAlO_2 . Of these three breeder materials, Li_4SiO_4 presents the least favorable prospect overall in respect to tritoxide concentration.

For these conditions of temperature and oxygen activity, another species must be considered, namely, tritide, T^- . This species is unstable in high oxygen activity environments. However, in a low oxygen activity environment, it is more stable and its concentration rises as the temperature rises. At 1200–1300 K, both tritoxide and tritide must be considered as contributors to the tritium inventory.

Gas phase transport of lithium-containing species to cooler zones presents at least two potential effects of significance in breeder

Fig. 4. Comparison of tritoxide concentration in solid solution in Li_2O , LiAlO_2 and Li_4SiO_4

design: plugging or constricting of purge gas channels and neutronic changes. The most important species participating in this plugging process in the breeder blanket are LiOT(g) and Li(g) . Figure 5 shows the activities of LiOT(g) as a function of oxygen activity. At 900 K, there is little dependence on oxygen activity, and the absolute values of the LiOT activity are notably small for the LiAlO_2 system--about 3.5 orders of magnitude less than for the Li_2O system. In addition, Li_4SiO_4 is nearly as good as LiAlO_2 . At 1300 K, the LiOT vapor concentration over LiAlO_2 is still nearly two orders of magnitude less than that over Li_2O through most of the oxygen activity range; however, the two curves approach each other at lower oxygen activities. At the lowest oxygen activity shown, Li_4SiO_4 performs least desirably; at higher oxygen activities, Li_2O is the poorest performer. (Earlier experience from fission reactor fuel technology suggested that, at least for a stagnant gas phase, a vapor pressure of about 10^{-7} MPa was a critical level above which vapor phase transport was significant.)

Elemental lithium vapor, at 1300 K, over Li_2O and Li_4SiO_4 is shown in Fig. 6 to be essentially the same for these materials (the curves are nearly superimposed) and to be a prominent

Fig. 5. Vapor pressure of tritoxide over Li_2O , LiAlO_2 and Li_4SiO_4

gaseous component over them at low oxygen activity. Moreover, at low oxygen activity, the Li(g) vapor pressure exceeds that of LiOT(g) (compare with Fig. 5) and is nearly three orders of magnitude greater than that over LiAlO_2 . At low oxygen activity and high temperature, therefore, LiAlO_2 appears significantly freer of potential problems from lithium vapor transport.

SUMMARY

These comparisons suggest that on most counts the thermochemical performance of LiAlO_2 is better than that of Li_2O , and that it is better generally than that of Li_4SiO_4 . More specifically:

(1) Under given conditions, both the T_2 and $T_2\text{O}$ concentrations in the gas phase are greater for LiAlO_2 than for Li_2O or Li_4SiO_4 .

(2) The amount of LiOT in solid solution is less for LiAlO_2 than for the other two breeders at low temperature and also at high temperature and intermediate oxygen activities, but this advantage goes to Li_2O at low oxygen activity and high temperature.

Fig. 6. Comparison of elemental lithium vapor pressure over Li_2O , LiAlO_2 and Li_4SiO_4

(3) The amount of lithium-containing species in the vapor is less for LiAlO_2 at all temperatures and oxygen activities.

Recognition of the substantial surface area on the particles of breeder material has raised the question of the extent of the contribution to tritium recovery by surface adsorption of tritium as T and/or OT^- . This issue has been explored by the calculational techniques for LiAlO_2 and this, too, has been shown to be dependent on oxygen activity, and, of course, on temperature. Under some conditions, the tritium tied up on the surface can be a significant fraction of the total inventory.

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