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Abstract

This paper reports on the experimental investigation of tritium permeation in flibe (2LiF-BeF$_2$) at the Safety and Tritium Applied Research facility of the Idaho National Laboratory. A stainless steel cell formed by two independent volumes separated by a 2mm thick nickel membrane is maintained at temperatures between 500 and 700 degrees Celsius. A controlled amount of T$_2$ gas is flown in excess of argon in the source volume in contact with the bottom side of the nickel membrane, while a layer of molten salt is in contact with the top side. The tritium permeating above the liquid surface is carried by an argon flow to a diagnostic system comprised of a quadrupole mass spectrometer, a gas chromatographer and a proportional counter. Tritium permeability in flibe as a function of temperature is determined by the measured permeation flow rates reached in steady-state conditions, while the diffusivity is determined by fitting the transient process with the analytical solution for the diffusion process. As a result, the solubility of tritium in flibe as a function of temperature is also determined.

Keywords: fusion, tritium, molten salt, diffusivity, solubility

1. Introduction

The work presented in this paper was performed at the Idaho National Laboratory (INL) Safety and Tritium Applied Research (STAR) facility as part of the molten salt research within the framework of the second Japan/US Program on Irradiation Test for Fusion Research (JUPITER-II), which began in 2001 [1]. The material investigated is the lithium fluoride (LiF) and beryllium difluoride (BeF$_2$) eutectic, usually referred to as flibe, which has a reference composition of 2LiF+1BeF$_2$ moles. This paper reports on results of tests aimed at the investigation of tritium transport properties in flibe. In fusion systems hydrogen containing species in the molten fluoride salts include H$_2$, HT, T$_2$, HF, and TF. Tritium is generated by neutron capture in lithium, while hydrogen and fluorine are present for active chemistry control or as a residual product of salt purification. In general, the transport processes are dependent on the following properties: solubility and diffusivity in the molten salt, dissociation at the surface and diffusion in contacting materials, mass transport and possibly recombination at gas-melt interfaces. The experiments here described are primarily designed to measure the overall tritium permeation through a layer of salt of known thickness, which is the integrated phenomena resulting as a combination of the processes previously named. However, careful design of the experiments based on the carrier-gas method allows the separate measurement of the dominant fundamental transport properties (diffusivity and solubility) [2].

The interaction of hydrogen isotopes with flibe is complicated by the peculiar structure of ionic liquids, for which electrochemical processes play an important role in determining transport properties [3]. In the case of flibe the chemical behavior is determined to a great extent by the fluorine potential in the molten salt (redox condition), which is in turn affected by the radiation environment and nuclear transmutation reactions, by reactivity with container or other contacting materials, by reactivity with the gaseous environment over the salt and by interaction with impurities [4, 1]. In the work here presented the salt and all the gas lines exposed to its vapors are carefully maintained in the same chemical condition, mainly characterized by a low level of impurities (Table 1) and constant hydrogen saturation. The former is ensured by following handling, purification and sampling procedures established at STAR [1], while the consequences of the latter will be discussed later in the paper. The effect of variable redox condition on tritium transport (for example by contact with metallic beryllium) is not discussed.

2. Experimental

The permeation experiment is part of a complex system necessary to handle the hazard related to tritium radioactivity and beryllium toxicity, many components of which are shared by other experiments in STAR. In relation to the experiments here described the system can be divided in four parts with different functions: a stainless steel glove box capable of tritium and beryllium handling, within which is housed the heating system and the permeation cell; the tritium delivery and collection system; the diagnostics system; the auxiliary gas lines. A description of the system and procedures related to tritium handling is beyond the scope of this paper as they are common to most experiments in STAR [1, 5]. For the purpose of this work the system is responsible to deliver a uniform flow with rates between 1 and 20 sccm of a mixture of research grade argon gas and T_2 with variable concentration determined by pre-mixing in the gas source, as well as handling all the gas outflows that are contaminated by tritium during operations. The heater configuration has been used for all molten salt related activities in STAR [1]. The heater is responsible to maintain the permeation cell at a uniform temperature between 550 C and 700 C, with a temperature gradient across the molten salt layer below 2 C both in the axial and radial direction. The diagnostic system is designed to measure the concentration of tritium above the molten salt surface in a wide range of concentration ranging from 0.1 ppm to 10vol%. The gas mixture is first sampled through a bleeding valve by a quadrupole mass spectrometer (Dycor model Ametek M200), then enters the switch system of a gas chromatographer (Shimadzu model GC-14B coupled with chromatopac C-R8A data processor). The gas exiting the GC flows then into a proportional counter were the tritium activity is measured (Aloka model GC-2003BU with Canberra power supply, signal amplifier and timer). The auxiliary components are mostly gas delivery systems necessary for the operation of the experiments such as pressurized gas bottles (UHP argon and hydrogen), regulators, purifiers, mass flow controllers and pressure instruments. A deuterium source is used as alternative input gas for tritium during calibration and initial testing.

The permeation cell used for the experiment is shown in Fig. 1. In its standard operation mode it can be described as formed by two internal volumes (light and dark shade) and one external (white background). The external volume can be purged to measure the amount of tritium leaking from the inside, but during standard operation it is maintained undisturbed in order to allow the build-up of a small tritium concentration and minimize leaks. The source volume (dark shade) is part of the input line and contains the

gas mixture flowing directly from the tritium source. All internal surfaces along the lines are composed of stainless steel except the plate between the source volume and the sample volume (light shade) that is made of Nickel 200 and acts as a window for tritium permeation. The concentration of tritium in contact with the nickel plate is kept constant by a slow moving flow (typically 4 sccm). The sample volume contains the molten salt and is part of a gas line that flows into the diagnostic system. A sweep flow composed of a mixture of argon and hydrogen is flown through the sample line. The sweep gas flow rate is an important parameter for carrier-gas method experiments [2], and its choice is a trade off between a shorter time lag for diffusivity measurements (favored by higher flow rates) and higher accumulated concentrations of permeating gases resulting from lower flow rates, which enhances detection. Ultimately the limit is imposed by the sensitivity of the diagnostic system. From an extensive calibration of the system with deuterium and to allow comparison with similar experiments with other fluoride salts we set the reference sweep flow rate at 20 sccm [6]. The sample volume internal surfaces are made of nickel in order to avoid the dissolution of metal impurities from contact between the molten salt and stainless steel. The amount of tritium leaking from the sample volume is relatively low because of its lower concentration on the downstream side of the salt layer. The sample volume upper cap as well as the remaining gas lines is composed of stainless steel. In steady-state conditions traces amounts of hydrogen fluoride are present above the salt surface, and carried by the sweep gas would react with steel surfaces unless balanced by the presence of hydrogen in the flowing mixture [1,4,7]. Hydrogen is also necessary to reduce tritium fluoride by isotopic exchange in order to correctly account for the total amount of permeating tritium, unless a system to condense and recover tritium fluoride is present [8, 9]. We decided to rely on isotopic exchange and not to use a TF condenser because the latter would not allow time dependent measurements of concentration that are necessary to determine the material diffusivity with the gas-carrier method. The concentration of hydrogen needed in the sweep gas is then determined by the completion of the tritium fluoride reduction. A hydrogen concentration of 5%vol was found to be enough in the conditions tested and adopted during standard operations. The effect of hydrogen-saturated conditions in the salt on the transport of deuterium and tritium is not known, as further discussed in Section 3. However, high traces of hydrogen are likely to be always present when flibe is purified through hydro-fluorination as well as the need for HF

reactivity control, therefore the conditions adopted for this studies are relevant to flibe-cooled fusion blanket systems.

3. Results and discussion

The physical process considered in this work can be described by the one dimensional diffusion equation:

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where c is the molar concentration of tritium, D the diffusivity of tritium in flibe, x the direction perpendicular to the flibe layer surface and t is time. It is assumed that: i) the ratio of the layer thickness vs its radius is sufficiently small to neglect diffusion in the radial direction as well as the effect of natural convection in the liquid; ii) the permeation resistance of the nickel plate is negligible compared to that of the liquid layer so that the process is dominated by bulk diffusion in flibe. The assumptions have been verified by previous experiments with hydrogen using the same permeation cell design and similar input concentrations [6]. The dependence of the permeating flux on the square root of the input partial pressure of T_2 (Fig. 2) confirms that tritium diffuses in the salt in the ionic form T^+ bonded to negative ions available in the ionic liquid structure [7,8,9,10,11] and recombines at the salt surface with excess hydrogen present in the sweeping gas to form HT, contrary to what observed in flinak [6]. The transport mechanism in the salt depends on the fluoride potential, which is determined by the experimental conditions already described. It has been suggested that the characteristic behavior of beryllium fluoride to retain its solid tetrahedral structure in the liquid form may dominate tritium transport, and molecular dynamics simulation showed how BeF_4^- ions would account for the described mechanism [12]. Diffusion in the ionic form would also account for the high values of measured solubility, closer to HF reference values rather than H_2 [13,14,15]. The presence of hydrogen may affect the diffusion process, accelerating tritium molecular recombination at the interfaces. However in the conditions of this study it has been experimentally verified that D_2 permeation in nickel alone is not affected by the presence of H_2 [16]. Regardless of which mechanism is responsible for diffusion of atomic tritium, in steady state conditions the solution of (1) for the molar flux of T at the liquid surface can be written in the well-known form:

$$j_T = \frac{D_{flibe,T} \cdot K_{flibe,T}}{L_{flibe}} \cdot \sqrt{p_{T_2,input}} \qquad (2)$$

where D is the diffusion coefficient of tritium in flibe, K the solubility of tritium in flibe, L is the flibe layer thickness and p is the partial pressure of T_2 on the input side of the nickel plate. The molar flux is directly calculated from the HT concentration in the sweep flow measured by the instruments described in Section 2. The results plotted against the input partial pressure are shown in Fig.2. The solid marks have been obtained with the initial flibe layer thickness of 8.1 mm and in the input partial pressure range for which the experiment was initially designed. The results confirm the square root of pressure dependence of the flux (plotted solid lines with 1/2 slope). In these conditions the absolute steady state concentration of all combined hydrogen isotopes is measured with very good accuracy by the GC, while the qms allows to distinguish the contribution of the various molecular combinations (typically H_2 and HT). The proportional counter is used to confirm the results with a second independent measurement of the HT concentration, in particular for the time dependant diffusion process because of its good time resolution. The empty marks have been obtained with an increased flibe layer thickness of 13.7 mm and with input partial pressures below 100 Pa, resulting in detected concentrations below 1 ppm in the sweep flow. The molar flux plotted in Fig.2 has been adjusted to account for the thickness increase, therefore the results confirm the assumptions of the model. In other words, the permeability Q (the product of diffusivity and solubility):

$$Q = \frac{j \cdot L}{\sqrt{p}} \qquad (3)$$

is indeed a function of temperature only and not dependent on the layer thickness nor on the input pressure. In this concentration range the qms cannot detect the HT concentration above the H_2 signal and the data are based on the proportional counter response only. While the time dependent data needed to measure the diffusivity still have good accuracy, the uncertainty of the counter response in terms of absolute concentration is reflected in the relative higher scattering of the steady state flux values at low pressure.

For the one-dimensional process here described the time dependant diffusion equation (1) has the analytical solution:

$$\frac{Q(\tau) - Q(0)}{Q(\infty) - Q(0)} = 1 + \sum_{n=1}^{\infty} A_n \cdot \exp(-\alpha_n^2 \tau) \qquad (4)$$

where Q is the permeability as defined in (3) and:

$$\tau = \frac{D \cdot t}{L^2} \tag{5}$$

is a non dimensional parameter that normalizes the solution through a variable transformation in the time domain. The first three coefficients of the series expansion are reported in Table 2. The normalized expression on the right hand side of (3) is often referred to as the diffusion master curve. When the experimental data are plotted as permeability against the master curve in logarithmic scale τ can be simply evaluated as the time shift between the data and the master curve, and from τ the diffusion coefficient can be estimated if the layer thickness is known [2]. The measured tritium diffusivity in flibe between 550 C and 700 C is plotted in conventional form in Fig.3. The most recent results of hydrogen diffusivity in flinak and deuterium diffusivity in flibe are also included for verification [6, 7]. The data are well fitted by the correlation:

$$D_{flibe,T} = 9.3 \times 10^{-7} \cdot \exp\left(-\frac{42154}{R_g \cdot T}\right) \tag{5}$$

where D is expressed in [m^2/s], T in [K] and the universal gas constant R_g is 8.3144 J/mol. The measured activation energy of tritium in flibe of 42.154 kJ/mol is compares well to that reported in previous experiments (44 kJ/mol [9]) as well as that for hydrogen in flinak [6].

Once the diffusivity has been determined the solubility can be derived from the measured steady state molar flux as expressed in (2). The measured tritium solubility is plotted in Fig.4 and fitted by the correlation:

$$K_{flibe,T} = 7.892 \times 10^{-2} \cdot \exp\left(-\frac{35403}{R_g \cdot T}\right) \tag{6}$$

where K is expressed in [mol/m^3 Pa] and other variables as in (5). The measured solubility is similar to that reported for deuterium in flibe [7], several order of magnitude higher than that reported for other inert gases in fluoride salts [15] and closer to that reported for HF [13,14]. However the slope of the solubility correlation suggests an endothermic process typical of inert gases as opposed to what reported for hydrogen in flinak [6].

4. Conclusions

Tritium diffusivity and solubility in the molten salt flibe (2LiF-BeF$_2$) have been measured in the temperature range between 500 C and 700 C. Tritium flows from the source in molecular form T$_2$, but is absorbed in the nickel plate in atomic form and does not recombine at the nickel/flibe interface but instead diffuses in the salt in the atomic form, either bonded as T$^+$ to BeF4$^-$ ions or as HT, or both. The transport properties have been correlated by the following expressions respectively:

$$D_{flibe,T} = 9.3 \times 10^{-7} \cdot \exp\left(-\frac{42154}{R_g \cdot T}\right)$$

$$K_{flibe,T} = 7.892 \times 10^{-2} \cdot \exp\left(-\frac{35403}{R_g \cdot T}\right)$$

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Fig.1. Permeation cell scheme with relevant dimensions

Fig.2. Measured T molar flux versus T2 input partial pressure.

Fig.3. Measured T diffusivity in flibe.

Fig.4. Measured T solubility in flibe.

Table 1. Composition and impurities concentration [ppm] in first layer salt (S1) and addition (S2)

Table 2. First three coefficients of diffusion master curve expansion

Fig.1
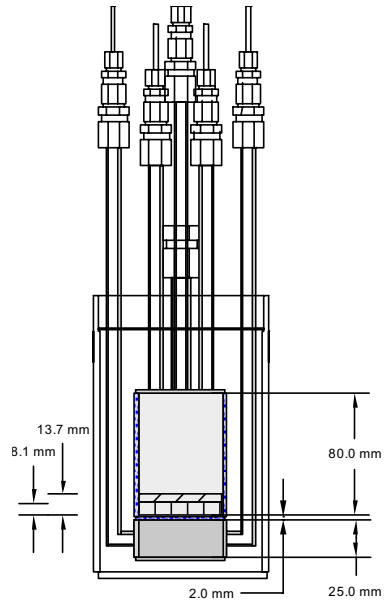Size: full column

Fig.2
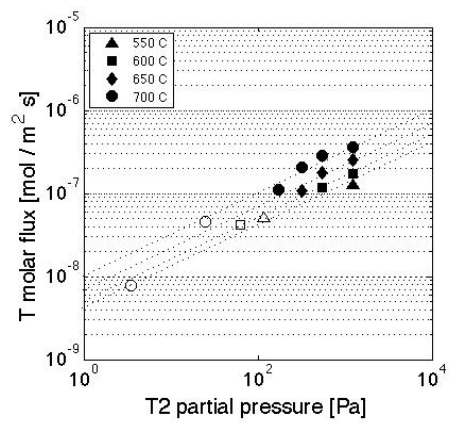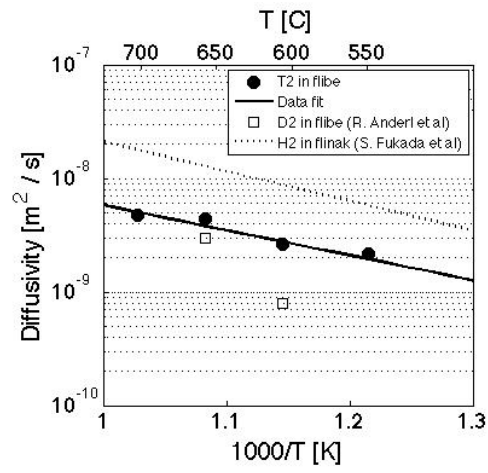Size: full column

Fig.3
Size: full column
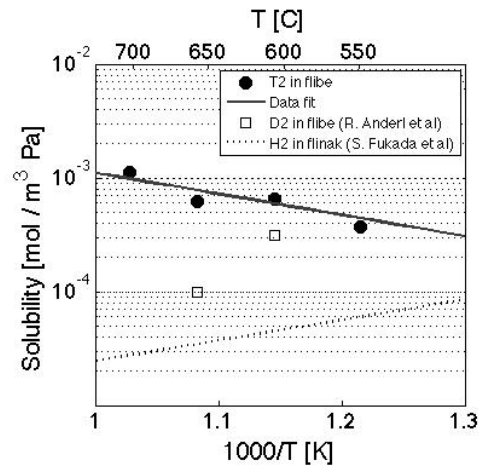
Fig.4
Size: full column

	Li/Be	W	Fe	Ni	Cr	Al
S 1	1.50	51.11	43.37	42.68	20.47	32.73
S 2	1.50	40.98	39.27	70.27	15.46	22.84

Table 1.
Size: full column

A1	α1	A2	α2	A3	α3
-2	9.87	2	38.48	-2	157.9

Table 2.
Size: full column