

Letter to the Editor

Water vapor adsorption on meta lithium–zirconate ceramic breeding surfaces

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Received 5 May 1997; accepted 24 July 1997

Abstract

Water vapor adsorption on Li_2ZrO_3 surfaces in He and He + 0.1% H_2 purging gases was measured at temperatures from 100 to 500°C and H_2O partial pressure from 1 to 20 Pa. The data sets, the best fitting empirical water adsorption isotherms and water desorption kinetics are reported and discussed. © 1997 Elsevier Science B.V.

1. Background

Low tritium inventory [1] and high radiation resistance to damage [2] make lithium meta-zirconate, both in the form of pellets [1,2] and of pebbles [3], one of the most interesting candidates for tritium breeding in fusion reactor power plants. It is presently considered for the solid water cooled ITER breeding blanket modules [4].

Helium containing H_2 (0.1%) is the ‘reference’ (R) purge gas conceived to remove the tritium generated by the ${}^6\text{Li}(n, \alpha)\text{T}$ reaction and implanted in lithium ceramics during blanket operation. Since the presence of H_2O cannot be avoided in environments containing large amounts of solid oxides, the chemical interaction of H_2 and H_2O (which undergo isotopic exchange with tritium) with Li-ceramic plays a significant role in tritium transport phenomena inside the blanket. Some available data concerning this kind of interaction [6,7] cover a very broad moisture level in the helium purge ranging from tens to thousands volume per million (vpm). In this work the study is approached by ‘temperature programmed desorption/reduction’ (TPD/TPR) techniques imposing a moisture level as close as possible to the one (~ 10 vpm) foreseen in the purging gas at the breeding blanket modules outlet.

2. Materials and measuring techniques

A modified Micromeritics TPD/TPR 2900 apparatus was used for quantitative measurements of H_2 consumption and H_2O production (TPR mode) and water uptake under dynamic and steady state conditions (TPD mode) during Li_2ZrO_3 gas sweeping. Various ceramic specimens (supplied by CEA–France (pellets), by AECL–Canada (pebbles) and by our laboratory (powders)) with quite different surface areas (SA) were found to behave similarly provided TPD measurements were referred to normalized unit surface. We tested Li_2ZrO_3 granules (diam. 200–600 μm) sintered at 1100°C for 2 h in air, with SA = 0.67 m^2/g as measured by the classical BET method. The specimens were annealed at 800°C under dry He purge before each TPD/TPR run. They were then swept by R or helium containing 30 vpm O_2 (a slightly ‘oxidizing’ gas, simply He in the following) at various temperatures (between 100 and 800°C) and moisture levels (from 10 to 250 vpm). Once the equilibrium was reached the water uptake was quantitatively measured by desorbing it under linear temperature scanning from the equilibration temperature up to 800°C and by adding the residual water desorbed at this temperature by a final purging with dry gas.

3. Results

Hydrogen in the R purge was found to react initially with Li_2ZrO_3 generating water vapor due to the total

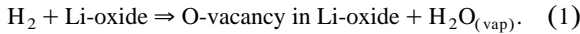
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Table 1

Surface concentration (Γ) of water adsorbed in equilibrium with the ‘reference’ and slightly oxidizing purge gases as a function of temperature and moisture level P (vpm at 1 atm)

Temp. (°C)	P (vpm) in He + 0.1% H_2	Γ ($\mu\text{mol}/\text{m}^2$)	P (vpm) in He + 30 vpm O_2	Γ ($\mu\text{mol}/\text{m}^2$)
100 ± 2	–	–	10 ± 1	2.4 ± 0.1
100 ± 2	50 ± 3	4.2 ± 0.2	40 ± 2	3.2 ± 0.2
100 ± 2	90 ± 5	4.4 ± 0.2	90 ± 5	3.5 ± 0.2
100 ± 2	150 ± 8	4.7 ± 0.2	150 ± 8	3.7 ± 0.2
100 ± 2	–	–	200 ± 10	4.0 ± 0.2
200 ± 2	–	–	10 ± 1	1.00 ± 0.05
200 ± 2	60 ± 3	2.0 ± 0.1	40 ± 2	1.30 ± 0.07
200 ± 2	90 ± 5	2.2 ± 0.1	90 ± 6	1.45 ± 0.07
200 ± 2	150 ± 8	2.6 ± 0.1	150 ± 8	1.75 ± 0.07
300 ± 2	–	–	10 ± 1	0.40 ± 0.05
300 ± 2	60 ± 3	1.10 ± 0.05	40 ± 2	0.65 ± 0.05
300 ± 2	–	–	90 ± 5	0.80 ± 0.05
300 ± 2	100 ± 5	1.20 ± 0.06	125 ± 7	0.90 ± 0.05
300 ± 2	200 ± 10	1.40 ± 0.07	150 ± 8	0.95 ± 0.05
400 ± 2	–	–	10 ± 1	0.15 ± 0.05
400 ± 2	60 ± 3	0.60 ± 0.03	40 ± 2	0.35 ± 0.05
400 ± 2	–	–	80 ± 4	0.45 ± 0.05
400 ± 2	100 ± 5	0.70 ± 0.04	90 ± 5	0.50 ± 0.05
400 ± 2	200 ± 10	0.75 ± 0.04	150 ± 8	0.50 ± 0.05
400 ± 2	–	–	250 ± 13	0.75 ± 0.05
500 ± 2	60 ± 3	0.28 ± 0.02	–	–
500 ± 2	100 ± 5	0.40 ± 0.02	–	–
500 ± 2	225 ± 11	0.45 ± 0.02	–	–

reduction of unavoidable oxidized defects present as a consequence of the calcining and sintering steps in air, according to the rough scheme of



Some tests characterizing this reaction were reported elsewhere [5]. Once the oxidized defects were completely reduced by R purge, the pre-conditioning of the specimens was considered completed. It is to be noticed that SA was not changed although the specimens darkened: Afterward the equilibration and TPD runs were performed in R environment to obtain the equilibrium constants of reaction (2) and the kinetic parameters of the water desorption step:



The results (the surface concentrations (Γ) as a function of the environmental conditions) are reported in Table 1 together with the data set obtained in He (on ‘oxidized’ surfaces).

4. Discussion and conclusion

With the exception of the 100°C data set of Table 1, Γ was found to be related to the water content (P , expressed in volumes per million in He at 1 atm) in the purging

gases, by the empirical relation

$$\Gamma = (a + b/T(^{\circ}\text{C}))\log(1 + P(\text{vpm})), \quad (3)$$

where $a = -0.30 \pm 0.04$, $b = 218 \pm 12$ for He environment; and $a = -0.48 \pm 0.02$, $b = 326 \pm 5$ for R-purging gas.

These data also follow the Freundlich–Hasley law (Eq. (4)) (Fig. 1)

$$\theta = (a_0 P)^{RT/(q_m(1-rT))}, \quad (4)$$

where the surface coverage $\theta = \Gamma/\Gamma_m$, $\Gamma_m = 15.6 \mu\text{mol}/\text{m}^2$ is the surface concentration at full water coverage, the adsorption heat is defined as $q = -q_m \ln \theta$; P is here expressed in Pa and the temperature in K; r (K^{-1}) is adjusting parameter. The best fitting parameters with the experimental data (for 200, 300 and 400°C) are reported in Table 2. These results show how in R purge water and energy adsorption are higher with respects to the ones found in He due to the modification of surface defect types and concentrations (reaction (1)).

Although there are differences in slopes, the present data trends and the equations reported by Kawamura et al. [6,7] are in fair agreement with the exception of the 400°C case. For low water vapor pressures ($P \rightarrow 0$) a linear correlation between θ and \sqrt{P} (adsorption with dissociation) Henry’s law

$$\theta = \sqrt{P/b} \quad (\text{where } b = b_0 \exp(E_{\text{diss}}/RT)) \quad (5)$$

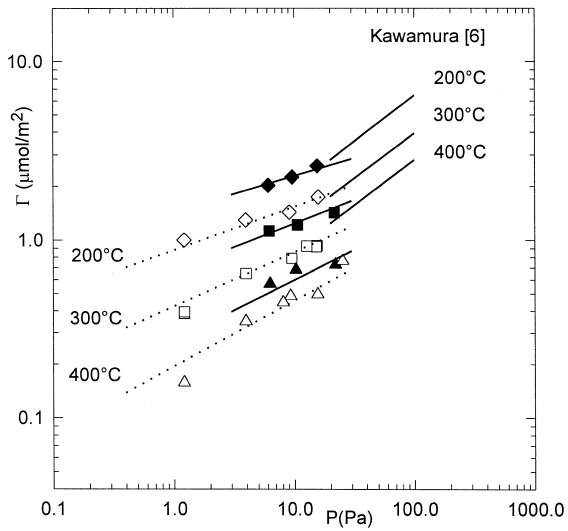


Fig. 1. H₂O adsorption on Li₂ZrO₃ at 200°C (diamonds); 300°C (squares) and 400°C (triangles) in He (open points) and R (full points) purging gases. Freundlich fits and Kawamura's equations [6] are also plotted.

was found to hold; the corresponding parameters best fitting the data are reported in Table 2. Note how the data fit is still acceptable with the non-dissociative water adsorption case (Fig. 2). However $E_{\text{diss}} = 47$ kJ/mol is consistent with the heat of adsorption as evaluated at low coverage (q^* in Table 2). Hence the water adsorbed must be considered as completely dissociated according to Kawamura [6,7].

Water desorption rate from Li₂ZrO₃ surface undergoing linear temperature at various rates (β , from 5 to 20°C/min) after water saturation at 150°C in He gave complex TPD patterns involving several desorption sites. Similar behavior was observed in He purge. Three main peaks (with temperatures at peak maxima, $T_{m,i}$) were

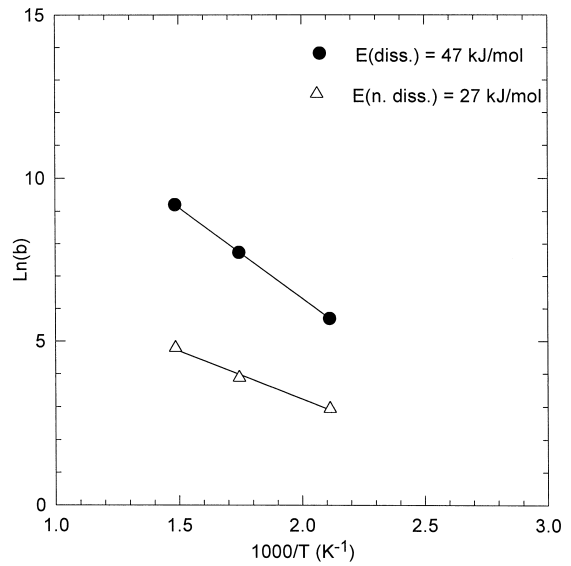


Fig. 2. Arrhenius plot of Henry's coefficients for the water adsorption by dissociative and non-dissociative cases.

considered in the TPD analysis by using [8]

$$2 \ln T_{m,i} - \ln \beta = E_{d,i}/RT_{m,i} + \ln(E_{d,i}/A_i R) \quad (6)$$

involving the activation energies ($E_{d,i}$) and the preexponential factors (A_i) following the classical desorption rate constant Eq. (7)

$$K_{d,i} = A_i \exp(E_{d,i}/RT) \quad (7)$$

for each i th site. The resulting values were

$$E_{d,1} = 61, \quad E_{d,2} = 78 \text{ and } E_{d,3} = 63 \text{ (kJ/mol)}.$$

The present data are useful to obtain the adsorbed water inventory on a Li₂ZrO₃ breeding bed once the surface area, the temperature and the moisture level in the purge are known. The consequent tritium inventory may also be evaluated by properly taking into account the isotopic exchange phenomena in the envisaged conditions of a solid breeding blanket during reactor operation.

Table 2

Best fitting parameters for Eqs. (4) and (5) with experimental data

Freundlich–Halsey law parameters (Eq. (4))	He purge	R purge
q_m (kJ/mol)	18.7 ± 1.5	27 ± 4
a_0 (Pa ⁻¹)	$(7.3 \pm 5.4) \times 10^{-6}$	$(7.1 \pm 10.9) \times 10^{-6}$
r (K ⁻¹)	$(2.9 \pm 0.6) \times 10^{-4}$	$(5.8 \pm 0.5) \times 10^{-4}$
θ^* (for $T = 773$ K; $P = 10$ Pa)	0.031	0.04
$q^* = -q_m \ln \theta^*$ (kJ/mol)	65	87
Henry's law parameters (Eq. (5))	He purge	R purge
b_0 (Pa)	$(4.25 \pm 0.13) \times 10^7$	–
E_{diss} (kJ/mol)	46.8 ± 0.2	–

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