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Letter to the Editors

Li_4SiO_4 pebbles reduction in He + 0.1% H_2 purge gas and effects on tritium release properties

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Abstract

Lithium orthosilicate reduction was examined by Temperature Programmed Reaction (TPR) and Temperature Programmed Desorption (TPD) methods performed in He (or Ar) + H_2 purge gas flowing through pebble bed specimens. The parameters governing the kinetics and the steady-state of the reduction process to Li_4SiO_{4-x} were determined at 800°C. The level x of the O-vacancy concentration at steady-state (of the order of 1.5×10^{-3} mole fraction) was found to be compatible with the impurities content in the specimens. Pebble pre-annealing treatments were found to affect the microstructure and the reduction mechanism. Post-irradiation tritium release by TPD tests were performed on both stoichiometric and reduced pebbles with similar results. Tritium release properties of this breeder system seem to be independent from the material reduction state (x). © 2000 Elsevier Science B.V. All rights reserved.

1. Background

Knowledge of the ⟨Li-ceramics–purge gas⟩ interactions is needed for designing fusion reactor blankets based on solid-state breeding materials. Fabrication processes, impurities and additives in both solid and gas phases of these systems play a significant role in this phenomenology. Among the various Li-ceramics, Li_4SiO_4 is the main candidate for tritium breeding in the Helium Cooled Pebble Bed Blanket (HCPBB). In the past this material was prepared in the form of pellets and pebbles on lab scale, and the effects of adsorbed–chemisorbed H_2O and CO_2 species have been already examined as fabricated specimens by thermal–analytical methods as performed in flowing inert gases or in He + 0.1% H_2 (the actual reference purge gas composition for tritium recovery from solid breeder Li-ceramics in DEMO blanket designs) [1–3] and by Knudsen effusion techniques [4,5]. Ref. [5] reports for the first time about loss of oxygen from Li_4SiO_4 (formation of Li_4SiO_{4-x}) even at 800°C, that was later confirmed by Kawamura et al. [6].

The present work reconsiders the study of such a process for the last (1999–2000) candidate Li_4SiO_4 pebbles for HCPBB, by using Temperature Programmed Desorption (TPD), Reduction (TPR) and Oxidation (TPO) measurements. These specimens were also tested for tritium release by fast TPD methods. Our objective was in fact to verify the influence of the reduction status of the Li_4SiO_4 pebbles on their tritium release properties. Similar measurements had already been performed on the 1997–98 FzK telluria doped pebbles, but unambiguous results could not be obtained since the telluria reduction generated a large amount of H_2O ($2H_2 + TeO_2 = Te + 2H_2O$) masking the amount generated through the reduction to Li_4SiO_{4-x} [3].

2. Experimental

The Li_4SiO_4 pebbles were received from FzK in two different batches (specimens):

Batch 98/2-1: ‘as fabricated’ (by Schott).

Batch OSI-C6/98: the same batch 98/2-1 ‘as stabilized’ by annealing in air at 1000°C for 2 weeks [7]. The main characteristics for both sets of specimens are those concerning chemical composition and geometry (density) that are not significantly changed by the

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Table 1
Some impurity levels in the Li_4SiO_4 pebbles as given by FzK

Element	ppm	Mole fraction
Al	1060 ± 25	0.0041
C	1220 ± 20	0.0136
Ca	92 ± 8	2.7×10^{-4}
Fe	144 ± 7	3.26×10^{-4}
K	74 ± 4	
Mg	25 ± 10	
Na	33 ± 2	
Ti	213 ± 1	5.2×10^{-4}
Zr	50 ± 0.5	

‘stabilization’ stage; these characteristics are reported below (main impurities in Table 1):

Composition:	$Li_4SiO_4 + SiO_2$
Calculated theoretical density:	2.4 g/cc
Effective density:	98% T.D.
Pebble diameter (2*R*):	varying from 0.25 to 0.63 mm
Main components:	Li: 22.4 wt%; Si 23.8 wt% (hence $Li_4SiO_4 = 95.24$ mol% and $SiO_2 = 4.76$ mol%) molecular weight = 117.0

The stabilization treatment by long-term annealing was found to induce deep recrystallization of the dendritic structure characterizing the ‘as fabricated’ pebbles (an amorphous-like structure showing no grain formation). The details of the process and extended SEM analysis are reported in [7]. It has to be remarked that the stabilized form presents well-defined grain boundaries, grain size ranging from 1 to 5 μm, and that a layer of lithium metasilicate (Li_2SiO_3, <10 μm thick) diffuses to the pebbles surface.

The instruments and procedures used in this work for testing solid–gas chemical interactions and post-irradiation tritium release measurements are reported elsewhere [3,8].

It is worth recalling that, depending on the type of experiment, we measured on line during the runs: the H_2 consumed by the reaction of the specimen with $Ar + H_2$ (0.1%) purge (TPR tests); the H_2O generated by the reaction of the specimen with $He + H_2$ (0.1%) purge (TPD–TPR); the O_2 consumed and H_2O generated by the reaction of the specimen with $He + O_2$ (TPO–TPD).

3. Li_4SiO_4 pebbles reduction tests

A ‘standard’ overnight (16 h) pre-treatment of the Li_4SiO_4 pebbles at 800°C in air was initially employed in order to remove the moisture and carbonates impurities generally present in this kind of material after exposure to normal room environment.

After such a pre-treatment, about 3 g of pebbles were soon inserted in the TPD/TPR capsules and rapidly connected to the inert gas lines in order to keep as clean as possible the pebbles surface. For each run, the pebbles were then heated using the following selected temperature programmed schedule, while swept with the process gas at 20 cm^3/min:

(i) heating up by linear temperature scanning at the rate $\beta = 10$ K/min up to 800°C followed by
(ii) isothermal annealing at 800°C for about 1000 min (a typical overnight time),
(iii) re-oxidation of the specimen by the standard pre-treatment step (800°C in air overnight).

However, such re-oxidation in air at 800°C was found to produce impurities influencing the H_2O generation above 600°C under annealing ramp by $He + 0.1\%$ H_2 purge gas sweeping. This contribution to the whole reduction process was eliminated by using pure oxygen in dry He for the re-oxidation step at 800°C. This last re-oxidation procedure avoided any interaction of the material with environmental CO_2, which probably takes place at high temperatures to give strongly chemisorbed carbonates resulting in generation of volatile species (for example CO or CH_4 and H_2O) during decomposition–reduction by H_2.

The effect of such an improved pebble ‘cleaning’ is clearly shown in Fig. 1: comparing the initial heating

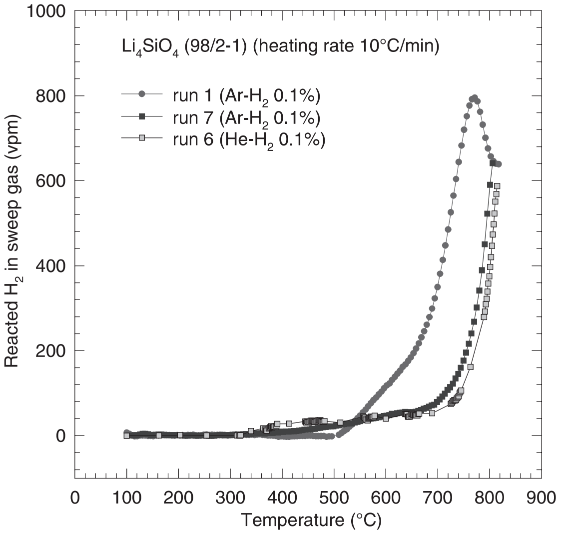

Fig. 1. Initial TPR signals during the heating ramps performed on ‘as fabricated’ pebbles; run 1 refers to reduction of pebbles previously annealed as re-oxidized in air at 800°C; runs 6 and 7 refer to H_2 consumed and H_2O generated during the heating ramp of pebbles previously re-oxidized by pure O_2 in dry He at 800°C.

ramp TPR signals obtained during the reduction step following a re-oxidation step in air (run 1) and the ones obtained during reductions following a re-oxidation in He + O_2 (runs 6 and 7). Once the pebbles were reduced and re-oxidized in helium at 800°C, the reaction sketched in a formal way by

$$H_2 + Li_4SiO_4 \rightarrow xH_2O + Li_4SiO_{4-x} + (1-x)H_2 \qquad (1)$$

could thus be studied without any interference due to reducible *volatile* species formed by impurities absorbable from the environment. However, it was not possible to eliminate the interference due to other impurities forming non-volatile reduced forms.

In Fig. 2, the evolution of H_2 consumed and of H_2O produced (obtained in two different sets of experiments for each of the two specimens) are plotted in a semi-log diagram. The recovery of the original status by O_2 titration at different reduction degrees (x) was found to be quantitative and to follow the reaction scheme (2)

$$O_2 + Li_4SiO_{4-x} \rightarrow Li_4SiO_4 + (1-x/2)O_2. \qquad (2)$$

During recovery from the reduced steady-state by annealing in dry helium containing O_2, the oxidation of the previously reduced defects (oxygen vacancies) allowed Li_4SiO_{4-x} to recover in few hours the original stoichiometry (x/2 moles of O_2 for each H_2O mole generated in the reduction stage). The x/2 value was determined by step-wise quantitative analysis of the O_2 needed to reach the steady-state for (2). The subsequent reproducibility of the reduction evolution following the scheme (1) demonstrates the full reversibility of the redox processes (1) and (2) and its effectiveness in the pebbles cleaning at 800°C. Finally, inside the 'reduced' Li_4SiO_{4-x} phase by process (1) no formation of any kind of hydrides could be observed because no H_2O generation and release was observed during the re-oxidation stage (2).

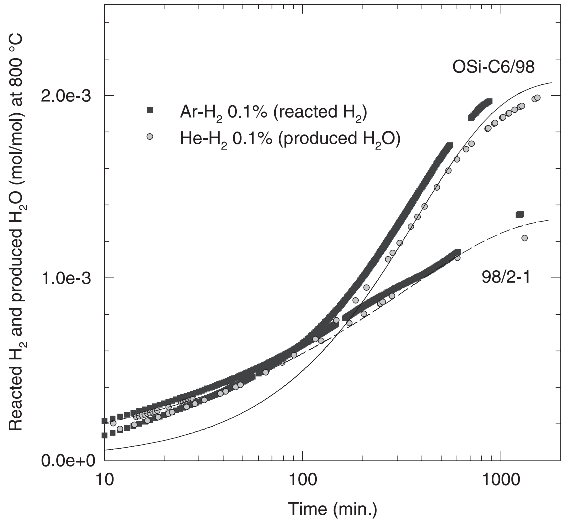

Fig. 2. Evolution of O-vacancy concentration in the pebble bed specimens during annealing at 800°C as resulting from H_2 consumed (full squares) and H_2O generated (circles), respectively, measured in Argon and Helium H_2 doped purging gases. The continuous line is calculated by Eq. (4) by using average values of the best fitting parameters (τ^* and x_{eq}) reported in Table 2 (4th and 5th columns). The dashed line is calculated by Eq. (6) by using average values of the best fitting parameters (τ and x_{eq}) reported in Table 2 (2nd and 3rd columns).

Analysis of the data reported in Fig. 2 was tried by assuming the reaction (1) always in equilibrium at the pebbles surface (at the distance from the pebble center $r = R$). In this case, the hydrogen gas partial pressure P_{H_2} and the oxygen vacancy concentration x_{eq} are related by an equilibrium constant K' (3)

$$P^n_{H_2} = K'x_{eq} \quad (\text{for } r = R, n \text{ and } K' \text{ constants}). \qquad (3)$$

At a given constant temperature and near constant P_{H_2} it is assumed that x_{eq} remains constant at $r = R$. The rate of change of the average O-vacancies concentration inside the pebbles $x(t)$ is assumed to follow a first-order reaction process (4):

$$\frac{dx(t)}{dt} = h\big(x_{eq} - x(t)\big) \qquad (4)$$

then

$$x(t) = x_{eq}\big(1 - e^{-ht}\big), \qquad (5)$$

where h is the mass transfer coefficient, and $h^{-1} = \tau^*$ is the time constant characterizing the process.

Alternatively, such an $x(t)$ evolution may be assumed to be fully controlled by the O-vacancy diffusion (D = diffusion coefficient) inside the spheres (radius R) whose surface is kept under the constant uniform boundary condition (3). In this case Eq. (6) is assumed to hold

$$x(t) = x_{eq}\left[1 - 6/\pi^2\sum_1^{\infty} n^{-2}\exp(-n^2t/\tau)\right] \qquad (6)$$

with

$$\tau = R^2/(\pi^2 D). \qquad (7)$$

A best fit analysis was performed by the two criteria-equations (5) and (6) applied to the data sets obtained for the two pebble bed specimens. The best fitting parameters x_{eq} (the steady-state x value for $t \rightarrow \infty$) and time constants τ^* and τ are shown in Table 2.

The diffusion mechanism (Eq. (6)) was found to better describe the reduction process of the 'virgin' pebbles 98/2-1, while a desorption like mechanism (Eq. (5)) seems to hold for the reduction of 'stabilized' pebbles. The respective functions, as evaluated by the parameters reported in Table 2, are also plotted in Fig. 2. For the 'as received' specimen D has been evaluated by

Table 2
Best fitting parameters of Eqs. (5) and (6) to the experimental time evolution of the O-vacancy concentration in two Li_4SiO_4 pebble types undergoing reduction by *R* gas purge after their re-oxidation at 800°C

Pebble bed specimen No.	98/2-1 (as fabricated, then reduced and re-oxidized in dry He)		OSI-C6/98 (as annealed at 1000°C × 2 weeks, then reduced and re-oxidized in dry He)	
Purge gas environment	τ (min)	x_{eq} (mole fraction)	τ^* (min)	x_{eq} (mole fraction)
Argon + H_2 (0.1%)	452	1.35×10^{-3}	375	2.0×10^{-3}
Helium + H_2 (0.1%)	450	1.31×10^{-3}	382	1.82×10^{-3}

Eq. (7) (in a purely formal way) using an average value for the pebble radius *R* and results to be $\sim 1 \times 10^{-10}$ m^2/s. It was not possible to consider a microstructure related diffusion path length, such as the grain radius, since this last could not be evaluated [7]. In the early stage (few tens of minutes after the run start) a further minor reduction process seemed to occur, however its contribution to *x* becomes negligible in longer times (Fig. 2).

Thermodynamic calculations (as performed by SOLGASMIX code) seem to give incompatible results with the existence and the stability of oxygen vacancies in pure Li_4SiO_4 lattice in the environmental conditions typical of this work [9]. Impurities within the pebbles may make this reduction possible. Looking at metallic impurities (Table 1) aluminum (Al), titanium (Ti) and iron (Fe), their amounts are not negligible if compared with the value $x_{eq} \sim 1.5 \times 10^{-3}$. Fe^{3+} could easily be reduced to Fe^{2+}at 800°C and could contribute to $x(t)$ in the first stage of the reduction process. Moreover Al^{3+} may occupy Si^{4+} sites in the Si sub-lattice of the Li_4SiO_4 forming -1 negatively charged defects, which makes possible O-vacancies formation and stabilization. Finally well-formed grain boundaries of the stabilized form could give more favorable sites and reaction path (Eq. (5)).

The high level of carbon shown in Table 1 is a strong indication of the presence of 'carbonates' due to the pebble annealing in air. Their decomposition–reduction to volatile species and H_2O during *R* gas sweeping starts at 600–650°C (Fig. 1) and causes the complete removal of carbon from the pebbles at 800°C. Such a complex decomposition–transformation process occurs at a rate comparable or slower than that characterizing the sole O-vacancies generation (1).

It must be also remarked that the x_{eq} values in Table 2 are lower than those reported by Kawamura et al. [6], ($x_{eq} = 3 \times 10^{-3}$ at 800°C) but the agreement should be much better if we would have considered the whole H_2O generated by the reduction (i.e. by including the contribution due to the carbonate impurities decomposition–reduction).

4. Effects on tritium release properties

TPD tritium release tests from 98/2-1 (Fig. 3) pebbles were performed after their irradiation in the TRIGA reactor as already described [3,8]. Both the 'reduced' and 're-oxidized' pebble bed forms were tested. The TPD peaks result from a convolution of many peaks (desorption sites); however their distribution and weight are not affected by the reduction status of the specimens. Similar results were obtained for the thermally annealed (OSi-C6/98) specimens. Since the microstructure of the specimens do not change during the reduction and reoxidation runs, probably the microstructural features (texture, grain size, etc.) is confirmed to be the main parameter governing the tritium release properties of the materials, as generally observed for the Li-ceramics as well as for Li_2TiO_3 pebbles [8].

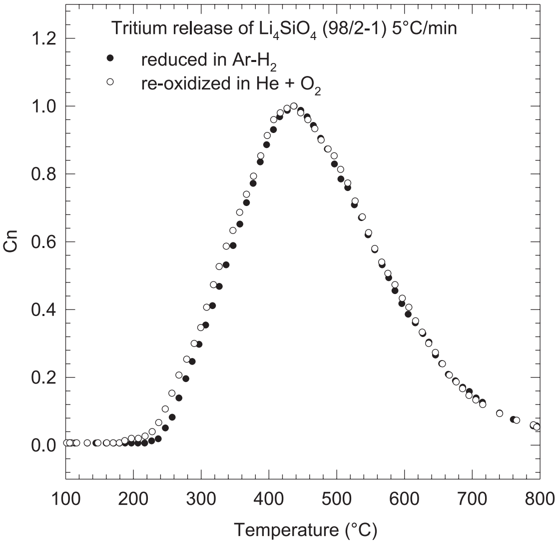

Fig. 3. Tritium release TPD signals (as normalized to the peaks values) for the reduced and reoxidized 'as fabricated' (98/2-1) pebbles.

5. Conclusion

A quantitative analysis has been performed to characterize the Li_4SiO_4 pebbles reduction due to the H_2 added to the He purge at 800°C. The 'stabilization' treatment planned and performed by FzK was found to increase the amount of O-vacancy formation at the steady-state (x_{eq} in Table 2) and to change the mechanism (kinetics) of the process. However once the specimens were completely 'reduced' their tritium release properties were found unchanged with respect to the 'oxidized' form. Hence the reduction process (1) does not seem to affect tritium release mechanism in a significant way.

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