



## 2.21 MODELLING FOR NEAR-SURFACE INTERACTION OF LITHIUM CERAMICS AND SWEEP-GAS BY USE OF CELLULAR AUTOMATION

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### Abstract

Tritium release from the lithium ceramics as a fusion reactor breeder material is strongly affected by the composition of the sweep-gas as result of its influences with the material's surface. The typical surface processes which play important roles are adsorption, desorption and interaction between vacancy site and the constituents of the sweep-gas. Among a large number of studies and models, yet it seems to be difficult to model the overall behaviour of those processes due to its complex time-transient nature. In the present work the coarse grained atomic simulation based on the Cellular Automaton (CA) is used to model the dynamics of near-surface interaction between  $\text{Li}_2\text{O}$  surface and sweep-gas that is consisting of a noble gas, hydrogen gas and water vapour.

**Keywords:** Ceramic Breeder,  $\text{Li}_2\text{O}$ , Surface Interaction, Sweep-Gas, Cellular Automaton.

### 1. Introduction

Tritium release from the lithium ceramics as a fusion reactor breeder material is strongly affected by the composition of the sweep-gas as result of its influences with the material's surface. The typical surface processes which play important roles are adsorption, desorption and interaction between vacancy site and the constituents of the sweep-gas. It is also known that addition of  $\text{H}_2\text{O}$  into the sweep-gas increases the collection rate of the tritium from the ceramic breeder material. And so there is great importance to understand the interaction of water-contained sweep-gas with a ceramic breeder material. However among a large number of studies and models, yet it seems to be difficult to model the overall behaviour of those

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processes due to its complex time-transient nature. For the purpose of describing such a complex systems, Cellular Automata (CA) are one of the very powerful tools [1][2] that has less restriction on conditioning the model compared with some methods based on differential equation such as Molecular Dynamics (MD). In general, CA are known as discrete mechanical system which is fully discrete in both independent and dependent variables. The system can be represented by some sets of so called transition rules that describe the microscopic interactions between cells. Then the states of each of those cells are updated according to the states and the corresponding rules in each time interval. Because of these characteristics, complex physical and chemical systems can be described by fairly simple manner. CA is also possible to imply highly non-linear boundary conditions in contrast to the model based on the differential equation. In the present work the coarse grained atomic simulation based on the Cellular Automaton (CA) is used to model the dynamics of near-surface interaction between  $\text{Li}_2\text{O}$  surface and sweep-gas that is considered to be consisting of a noble gas, hydrogen gas and water vapour. Moreover, in the model, adsorption and desorption of hydrogen and water at  $\text{Li}_2\text{O}$  surface is constructed and the validity and its applicability for further modelling of the tritium release are to be discussed.

## 2. Modelling

In this model, (110) surface of  $\text{Li}_2\text{O}$  which is known to be its most stable surface is considered. The ideal top three rows of the surface are shown in Fig.1.,  $\text{O}^{2-}$  ions are located on the  $\text{O}^{2-}$  lattice sites and empty sites  $E_0$  are located on the interstitial sites in the  $\text{O}^{2-}$  sub-lattice, which are arranged regularly among  $\text{Li}^+$  ions. The first step of the modelling is to discretise this surface as shown in Fig.2., For convenience,  $\text{O}^{2-}$ ,  $\text{Li}^+$  and  $E_0$  are rearranged in to the flat lattice consisting of square cells and each of those cells contain each of those ions. (110) surface of  $\text{Li}_2\text{O}$  shows an anisotropy that is the longitudinal and lateral length between the adjacent  $\text{O}^{2-}$  ions are different as illustrated in Fig.1., Thus the size of each square cells of this model is taken as the averaged size. Secondly, a lattice that represents the gaseous phase is considered on top of the surface lattice. The lattice conditions such as cell's size, number of cells and etc. are the same as those for the surface lattice. This lattice reflects the condition of the sweep-gas and desorbed particles. However, the dynamics of adsorption and desorption are implemented as local interactions between those two layers in accordance to the thermally-activated processes.

At first the following adsorption and desorption mechanisms are considered in this model. For adsorption of  $\text{H}_2\text{O}$  vapour,  $\text{H}_2\text{O}$  is dissociatively adsorbed on pair of Vs and  $\text{O}^{2-}$  site. This process and its corresponding activation energy is then,



Where Vs represents either  $E_0$  (empty site) or  $V_0$  (oxygen vacancy). Strictly speaking,  $E_0$  and

$V_0$  are energetically different but it is known that there is no significant difference in the energetics between those two [3]. And hence  $E_0$  and  $V_0$  are treated in the same way. Contrary to this, desorption of  $H_2O$  is the reverse reaction and is described as recombination process of two  $OH^-$  site to produce a  $V_s$  and  $O^{2-}$  on the surface.



The sweep-gas is considered to be consisting of  $H_2O$  vapour and  $H_2$  gas, so the next step is to make clear about  $H_2$  desorption and adsorption mechanism. The adsorption mechanism of  $H_2$  is dissociative and is as follows. One dissociative H atom is adsorbed on an  $O^{2-}$  to produce  $OH^-$  and another is adsorbed on the site existing between the two adjacent  $Li^+$  [4]. *i.e.*



Conversely desorption is then,



The above processes are now implemented into the CA rules as illustrated in Fig.3,. It means that a particular positions with the defined local configurations at given time  $t$  are modified to the defined configurations at next given time of  $t+1$  with the corresponding probability  $P_i$  ( $i \mid 1,2,3,4$ ). The probability  $P_i$  should reflect thermally-activated processes in order to make the CA model consisting with the chemical kinetics of Eq.1, Eq.2, Eq.3, and Eq.4,. Thus those can be expressed as follows.

$$P_1 = \frac{\max(E_{aH_2O}, E_{s_1}) - E_{aH_2O}}{E_s - E_{aH_2O}} \quad (5)$$

$$P_2 = \frac{\max(E_{dH_2O}, E_{s_2}) - E_{dH_2O}}{E_s - E_{dH_2O}} \quad (6)$$

$$P_3 = \frac{\max(E_{aH}, E_{s_3}) - E_{aH}}{E_s - E_{aH}} \quad (7)$$

$$P_4 = \frac{\max(E_{dH}, E_{s_4}) - E_{dH}}{E_s - E_{dH}} \quad (8)$$

Where,  $E_{s_i} = -RT \ln\left(\frac{\alpha}{\tau\nu}\right)$  ,  $\alpha$  is a random number with uniform distribution between 0 and 1.

Also,  $E_{aH_2O}$  and  $E_{dH_2O}$  are the activation energy for adsorption and desorption energy for  $H_2O$  respectively. Similarly to this  $E_{aH}$  and  $E_{dH}$  are the activation energy for adsorption and desorption energy for  $H_2$ .  $\tau$  and  $\nu$  represents time interval and the frequency factor respectively.  $E_{s_i}$  ( $i \mid 1,2,3,4$ ) are the energy of the states that are corresponding to the thermal vibration.

Those expressions of transition probabilities illustrate the probability of potential barrier crossing for given processes. However the transition rules previously introduced above are the expression of spatial positions of each particle. As consequence, for the calculation of time dependence, the whole lattice are scanned through to find the local configurations which coincide with one of the transition rules in Fig.3, then the transition process occurs with respect to those probabilities for each time step. However this algorithm is sequentially carried out until steady state is observed.

### 3. Result and discussion

By using the above model, surface concentration of  $\text{OH}^-$ ,  $\text{O}_2^-$  and  $V_s$  are calculated for several conditions of different partial pressure of  $\text{H}_2$  and  $\text{H}_2\text{O}$  as shown in Table 1. The result is illustrated in Fig.4, through Fig.6. Moreover, Fig.4, illustrates the case of the partial pressures are taken as  $P_{\text{H}_2\text{O}} = 1 \text{ Pa}$ ,  $P_{\text{H}_2} = 100 \text{ Pa}$ . It is seen that at transition stage, adsorption of  $\text{H}_2$  is dominant since increase of  $\text{OH}^-$  and decrease of  $\text{O}_2^-$  occurs at similar rate and the increase of  $V_s$  shows the desorption of  $\text{H}_2\text{O}$  is simultaneously occurring. Also at steady state,  $V_s < \text{O}_2^- < \text{OH}^-$  has been observed because of adsorption of hydrogen is the most dominant, then desorption of hydrogen is second dominant. Lastly the adsorption and desorption of  $\text{H}_2\text{O}$  comes the least dominant. This fact can obviously be seen from the value of the partial pressure and the activation energy of each process. Secondly, the partial pressures are taken as  $P_{\text{H}_2\text{O}} = 1000 \text{ Pa}$ ,  $P_{\text{H}_2} = 1000 \text{ Pa}$ . It is seen from Fig.5, at transition stage, adsorption of  $\text{H}_2$  and  $\text{H}_2\text{O}$  are dominant since rapid increase of  $\text{OH}^-$ . After some point, the effects of desorption of  $\text{H}_2\text{O}$  and  $\text{H}_2$  appears as increase of  $V_s$  and decrease of  $\text{O}_2^-$  respectively. Then  $V_s < \text{OH}^- < \text{O}_2^-$  has been observed at steady state. The partial pressure of  $\text{H}_2$  and  $\text{H}_2\text{O}$  is the same value in this case, and so the dominant processes are adsorption of  $\text{H}_2$  and  $\text{H}_2\text{O}$ . Then desorption of  $\text{H}_2\text{O}$  comes next. The least dominant process is then desorption of  $\text{H}_2$  due to its high activation energy. Thirdly the partial pressures are taken as  $P_{\text{H}_2\text{O}} = 10000 \text{ Pa}$ ,  $P_{\text{H}_2} = 1 \text{ Pa}$ . Rapid increase of  $\text{OH}^-$  and decrease of  $\text{O}_2^-$  and  $V_s$  are seen from Fig.6. Very fast decrease of  $\text{O}_2^-$  and  $V_s$  and increase of  $\text{OH}^-$  shows the adsorption of  $\text{H}_2\text{O}$  is the most dominant in this case. This is obvious since the partial pressure of  $\text{H}_2\text{O}$  is significantly large comparing to that of  $\text{H}_2$ . It is also seen that the processes are rapidly reaching to the steady state since the rate of adsorption is so fast that sites are immediately occupied after desorption of  $\text{H}_2\text{O}$  and  $\text{H}_2$ .

### 4. Conclusions

Cellular Automaton (CA) model for adsorption and desorption of  $\text{H}_2$  and  $\text{H}_2\text{O}$  on  $\text{Li}_2\text{O}$  (110) surface is developed in this work. Preliminary calculation is made for the surface concentration of  $V_s$ ,  $\text{O}_2^-$  and  $\text{OH}^-$  are carried out for various partial pressures of the sweep-gas. Those results show a consistency with the chemical model at steady state. However, it is foreseen that inclusion of tritium effect is rather simple in order to estimate the tritium release.

Strictly speaking, in order to clarify the validation of the model, it is necessary to compare the result with other model and/or some experimental result. From this point of view it can be said that this model is still under development. But one clear point that has to be stressed here is the present work provides many insights for the capability of CA to model more complex surface processes.

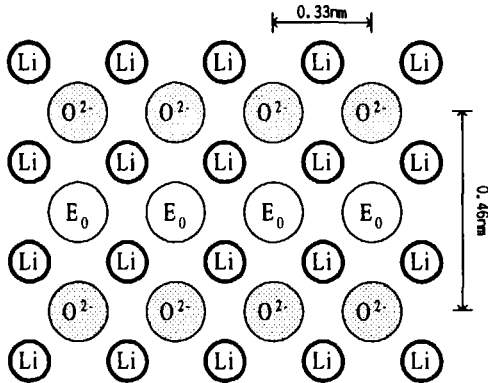


Fig.1, Li<sub>2</sub>O (110) surface.

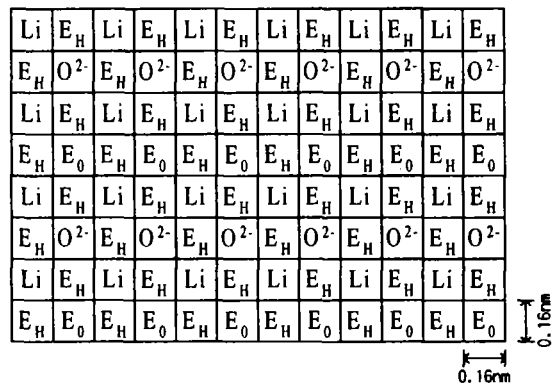


Fig.2, Discretised surface of Li<sub>2</sub>O (110).

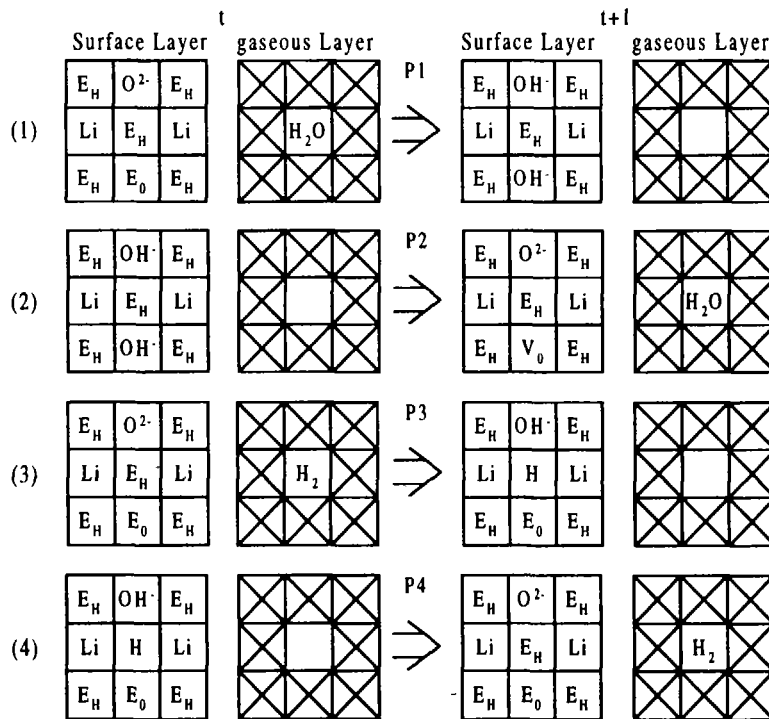
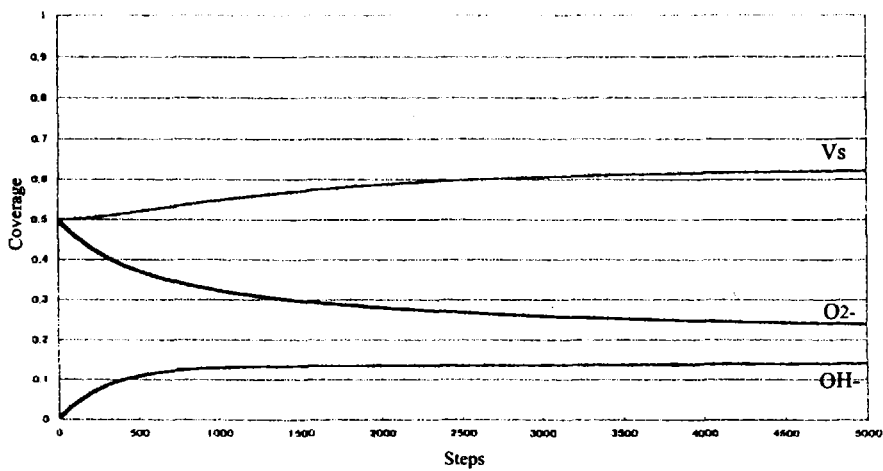


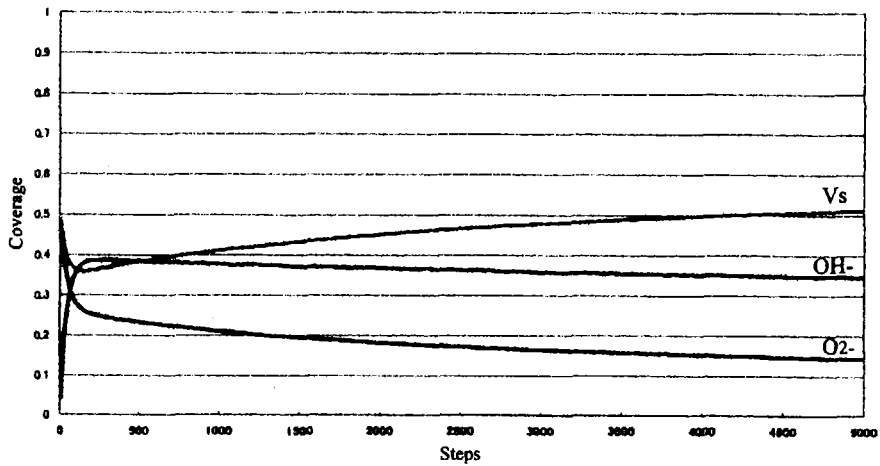
Fig.3, The transition rules of CA for each process. Where t represents the time before the transition, t+1 represents the time after the transition and also P<sub>1</sub> through P<sub>4</sub> represent the transition probabilities. See text for explanation of the symbols.

**Table 1.** The calculation conditions for this model.

H <sub>2</sub> O partial pressure	H <sub>2</sub> partial pressure	Temperature
1 [Pa]	100 [Pa]	773K
1000 [Pa]	1000 [Pa]	773K
10000 [Pa]	1 [Pa]	773K



**Fig.4.** Result of CA calculation for  $P_{H_2O} = 1$  Pa,  $P_{H_2} = 100$  Pa.



**Fig.5.** Result of CA calculation for  $P_{H_2O} = 1000$  Pa,  $P_{H_2} = 1000$  Pa.

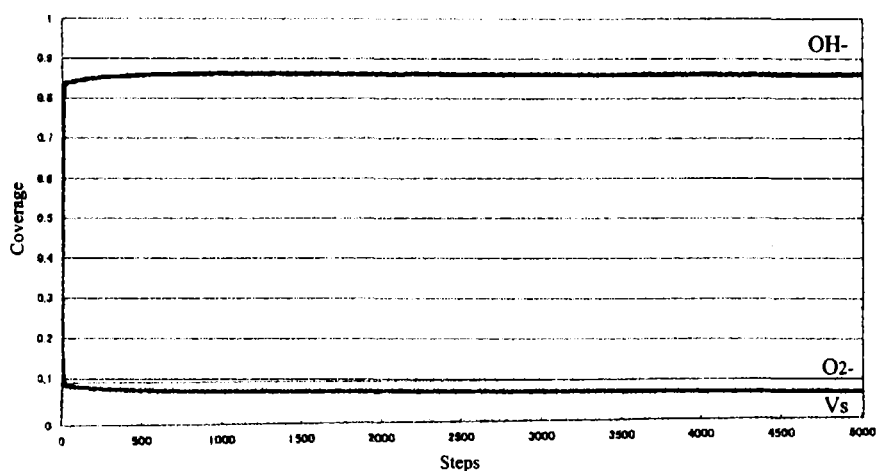


Fig.6, Result of CA calculation for  $P_{H_2O} = 10000$  Pa,  $P_{H_2} = 1$  Pa.

### References

- [1] N. Boccara, G.Y. Vichniac, and R. Bidaux, Springer Proceedings in Physics **46**, (1989)
- [2] S. Wolfram, *Cellular Automata and Complexity*, (Addison-Wesley, 1994)
- [3] D. Yamaki et al., Key Engineering Materials, **83**, 111-112 (1995)
- [4] M.Taniguchi et al, Proc. of the 7th International Workshop on Ceramic Breeder Blanket Interaction (CBBI-7), Petten, Netherlands, Sep.14-16, 1998, 6(1999)