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Study of the tritium behavior on the surface of Li_2O by means of work function measurement

Toshihiko Yokota [a], Atsushi Suzuki [a], Kenji Yamaguchi [b,*], Takayuki Terai [a], Michio Yamawaki [a]

[a] *Department of Quantum Engineering and Systems Science, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[b] *Nuclear Engineering Research Laboratory, Graduate School of Engineering, University of Tokyo, Tokai-mura, Ibaraki-ken 319-1106, Japan*

Abstract

In the present study, the work function change of Li_2O due to change of oxygen potential of sweep gas was investigated by measuring the contact potential difference (CPD) between Li_2O and Pt electrodes with a so-called 'high temperature Kelvin probe'. The CPD change for Li_2O was generally insensitive to the oxygen partial pressure in the sweep gas. A similar insensitivity was also observed for $LiAlO_2$. Although the CPD change of Li_2O was about 200 mV when the oxygen partial pressure was changed by as much as 15 orders of magnitude, such was not the case for $LiAlO_2$. By comparing with the results obtained for other Li-bearing ceramics, it was estimated to be caused by the adsorption/desorption processes of water vapor contained in the sweep gas. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

As for solid tritium breeder materials, lithium-bearing oxide ceramics (Li_2O, $LiAlO_2$, etc) have been considered to be the principal candidates [1]. In order to enhance the tritium recovery rate from blanket, the mixing of hydrogen into inert sweep gas has been proposed [2]. It is anticipated, however, that the presence of hydrogen as well as water vapor may affect the behavior of hydrogen isotopes at the surface of solid breeders. So far, a number of studies have been performed on Li_2O, far more numbers than any other Li-bearing ceramics, mainly from the interest in fundamental physical and chemical points of view. Besides, recent studies have been mainly focused on clarifying the complex nature and behavior of the ceramic surface interaction with hydrogen isotopes which most probably plays a vital role in the tritium release process in a fusion reactor blanket. In those studies, such techniques as FT-IR [3], thermal desorption spectroscopy (TDS) [4], as well as quantum chemical calculation [5,6] were employed, but work function measurements have never been performed on Li_2O yet.

The authors have been investigating the interaction of hydrogen with the ceramic breeder material surfaces by using work function measurement at high temperature and under controlled gas atmospheres. Conventional Kelvin probes [7–9], with which the contact potential difference (CPD) between a sample and a reference electrode can be measured in vacuum, have been used for a temperature below ≈500 K. The dynamic condenser method (Kelvin method) such as employed in the present study does not need vacuum so that it can be used for the measurement of work function under atmospheric pressure. Moreover, it is capable of measuring CPD at temperatures up to 1000 K and under controlled gas atmosphere [10]. The so-called 'high temperature Kelvin probe' thus developed, was applied to investigate the interactions between the surface of ceramic breeder materials and the sweep gas. In the present study, the CPD of Li_2O as well as that of $LiAlO_2$ were measured, for the first time, at high temperature

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[*] Corresponding author. Tel.: +81-29 287 8455; fax: +81-29 287 8458.

E-mail address: yamag@tokai.t.u-tokyo.ac.jp (K. Yamaguchi).

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under controlled composition of the gas phase, where the CPD changes were measured while the sweep gas was changed from pure helium to He + H_2 mixture with various concentrations of hydrogen, and vice versa.

2. Experimental

Main features of the principle of work function measurement and the configuration of ‘high temperature Kelvin probe system’ used in this study are described elsewhere [11]. In the experiments, pure He and a He + H_2 mixture were used as the sweep gas. The concentration of H_2 was controlled by regulating the relative flow rates of He and He + H_2 gases with mass flow controllers. The oxygen partial pressure and moisture concentration in the sweep gas were measured with a Y_2O_3 stabilized ZrO_2 oxygen sensor and a hygrometer, respectively. The reference electrode and the sample support were made of Pt. The samples of Li_2O and $LiAlO_2$ in the form of pellets were supplied by Japan Atomic Energy Research Institute (JAERI) and Kawasaki Heavy Industries, respectively. The CPD between Li_2O and Pt reference electrode was measured at 823 K.

Rather high chemical reactivity of Li_2O made it difficult to conduct experiments under wide ranges of parameters; the temperature should be high enough to avoid formation of LiOH, but not too high to enhance its vapor pressures [12]. In this sense, the temperature was fixed at 823 K, and only H_2 was used as an addition to the He sweep gas whose concentration was limited to <0.15%.

The CPD measured in the experimental system can be expressed as follows:

$$\mathrm{CPD} = \frac{\phi_{\mathrm{Li_2O}} - \phi_{\mathrm{Pt}}}{e}, \qquad (1)$$

where ϕ_A denotes the work function of material “A” and e is the electron change. Therefore, the increase of CPD may indicate that of $\phi_{\mathrm{Li_2O}}$ or the decrease of ϕ_{Pt}. In order to estimate the change of ϕ_{Pt}, the measurement of CPD between the Pt sample support and the Pt reference electrode was measured in the same condition as those for the cases of Li_2O and $LiAlO_2$. Moreover, the CPD between Au and Pt was measured in the same manner [13].

3. Results and discussion

3.1. Preliminary experiments

The same experiments under the same gas flow rate, gas compositions and specimen temperature were performed repeatedly on Li_2O to check the reproducibility of the experimental data. Only the duration of sample heating at 823 K prior to each experimental run was varied. It was confirmed that at least 6 h of pre-heating was sufficient to obtain reproducible results.

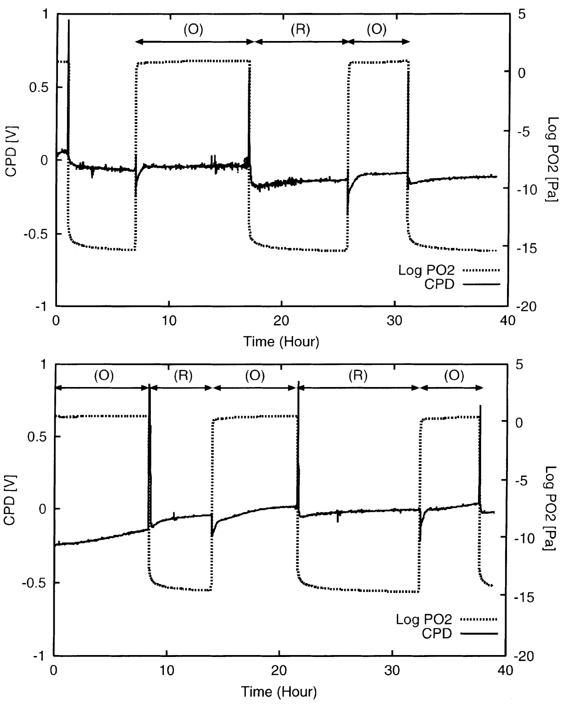

Fig. 1. Dependence of CPD of Li_2O on the gas flow rate as seen on comparing the data of 100 cm^3 min^{-1} (above) and 200 cm^3 min^{-1} (below).

Then, the gas flow rate was varied in the range between 100 and 300 cm^3 min^{-1}, where in Figs. 1(a) and (b) the experimental results on Li_2O corresponding to the flow rates of 100 and 200 cm^3 min^{-1} are compared, respectively. As can be seen from the figures, no appreciable difference was observed. In addition, the result was almost the same as that of 200 cm^3 min^{-1} (Fig. 1(b)), when the experiment was performed at 300 cm^3 min^{-1}. In the following, therefore, all the experiments were performed at the gas flow rate of 100 cm^3 min^{-1}.

3.2. *Effect of oxygen potential on the work function change of* Li_2O

The CPD change of Li_2O was measured at 823 K under controlled composition of the gas phase. Fig. 2 shows the change of CPD due to the change of composition of the sweep gas, where the sweep gas was changed from pure He to He + H_2 mixture of various concentrations of H_2, and vice versa. The concentrations of hydrogen in the sweep gas shown by (O) and (R) in the figure were ≈0% and 0.05%, respectively. The flow rate of the sweep gas was 100 cm^3 min^{-1} as mentioned in

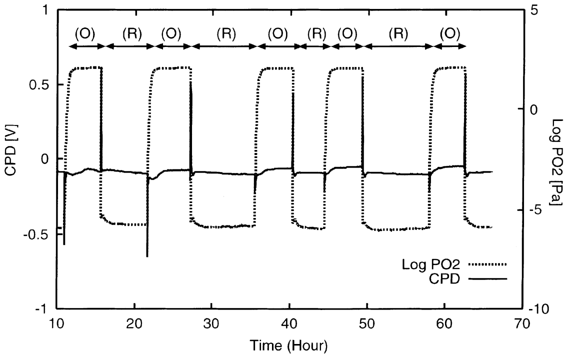

Fig. 2. The change of CPD between Li_2O and Pt with changing oxygen partial pressure, where (O) and (R) denote He and He + 0.05% H_2 gases, respectively.

the previous subsection. The oxygen partial pressure in the sweep gas (O) was $\approx 10^2$ Pa, while that in (R) was $\approx 10^{-7}$ Pa as shown in Fig. 2.

According to the results, the CPD change of Li_2O was very small when the oxygen partial pressure was changed by as much as nine orders of magnitude. On the other hand, Fig. 3 shows the change of CPD where the composition of the sweep gas was changed in a similar manner as in Fig. 2, but the concentration of hydrogen in the sweep gas shown by (O) and (R) in the figure were $\approx 0\%$ and 0.15%, respectively. The oxygen partial pressure in the sweep gas (O) was $\approx 10^2$ Pa, while that in (R) was $\approx 10^{-13}$ Pa as shown in the figure. Now, the CPD change of Li_2O was about 200 mV when the oxygen partial pressure was changed by as much as 15 orders of magnitude. Assuming that the work function change is due to the formation/annihilation of oxygen vacancies, V_O^{n+}, the change of work function and that of the oxygen partial pressure, P_{O_2} can be related by a defect equilibrium equation:

$$\frac{1}{kT}\left[\frac{\partial\phi}{\partial \ln(P_{O_2})}\right] = \frac{1}{2(n+1)}, \tag{2}$$

where k and T are the Boltzmann constant and the temperature, respectively. So long as the defect equilibria hold and the CPD change of Li_2O is attributed to the formation and annihilation of oxygen vacancies in the surface layer, the CPD ought to follow the abrupt change of oxygen potential. Although, according to Figs. 2 and 3, a steep CPD change was observed, the net change, when compared at steady states, was very small. Moreover, the CPD change shown in Fig. 3 does not obey the tendency given by Eq. (2). Therefore, it may be concluded that the formation and annihilation of the oxygen vacancies are not responsible for the observed work function change. This does not necessarily mean that the (thermal) defects are not formed in Li_2O, but if they are formed they are not large enough to affect the work function change.

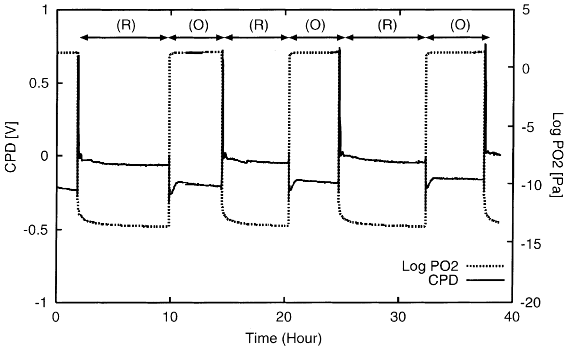

Fig. 3. The chage of CPD between Li_2O and Pt with changing oxygen partial pressure, where (O) and (R) denote He and He + 0.15% H_2 gases, respectively.

The work function change may also be induced by adsorption/desorption of gaseous species. For example, the hydrogen adsorption and desorption processes are expressed as

$$H_2(g) + 2O^{2-} \rightarrow 2OH^-(surf) + 2e^- \tag{3}$$

$$2e^- + 2OH^-(surf) \rightarrow H_2(g) + 2O^{2-}, \tag{4}$$

where O^{2-}, OH^-(surf) and e^- are the oxygen ion, surface hydroxide and electron, respectively. Accordingly, in case of the adsorption of hydrogen, the CPD is considered to decrease but the experimental result shows that the CPD increased when hydrogen was introduced. One possible explanation may be to assume that the CPD change in Fig. 3 is attributed to the adsorption and desorption of water vapor. Such a process can be expressed as

$$H_2O(g) + O^{2-} + 2Li^+ \rightleftharpoons 2LiOH(surf). \tag{5}$$

Since, in the above equation, electron is transfered from H_2O(g) to solid surface, the work function should increase upon adsorption. The origin of water vapor upon H_2 admission still remains to be clarified. It has been often observed in our Kelvin probe experiments that the partial pressure of H_2O increases when the sweep gas is switched from pure He to He + H_2 mixture. Most probably the oxygen impurity in the helium gas was reacted with the admitted hydrogen to produce water vapor. Moreover, it was observed in a vaporization experiment on Li_2O that D_2O is formed due to D_2 admission to the Knudsen cell [12].

3.3. Comparison with other Li-bearing oxides

Similar experiments were also performed for $LiAlO_2$, but here the temperature had to be raised to 973 K to

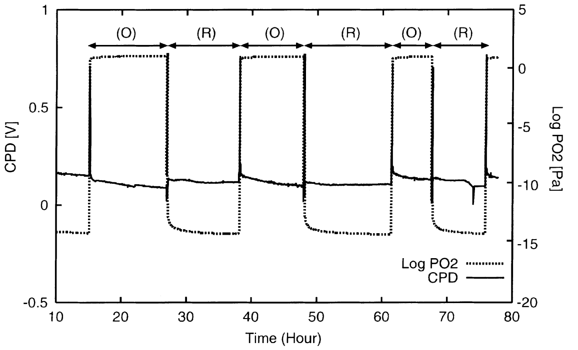

Fig. 4. The chage of CPD between $LiAlO_2$ and Pt with changing oxygen partial pressure, where (O) and (R) denote He and He + 0.15% H_2 gases, respectively.

obtain a stable signal during experiment. A typical example of the CPD change due to change of oxygen partial pressure in the sweep gas is shown in Fig. 4. Similar result as shown in Fig. 2 was observed; i.e. no significant changes of CPD were observed although the oxygen partial pressure was varied by orders of magnitude. This implies that the concentration of thermal defects in $LiAlO_2$, if any, was as small as those in Li_2O, and that adsorption and desorption of gaseous species did not play a significant role in the condition employed in the present study. In a future study, we will investigate the behavior of non-thermal, irradiation defects which may act differently from that of thermal defects and discuss their possible role in tritium release from ceramic breeders.

According to the previous results, the CPD change of Li_2TiO_3 due to the change of oxygen partial pressure was attributed to the adsorption/desorption processes of hydrogen [14], whereas in the cases of Li_4SiO_4 [13] and Li_2ZrO_3 [14], considerably large changes of the CPD occurred immediately following the change of oxygen potential, which were then ascribed to the formation of oxygen vacancies. The observed results on Li_2O (Fig. 2) and $LiAlO_2$ (Fig. 4) may be considered to be analogous to that of Li_2TiO_3, where the net CPD change was governed by its gradual change, but the absolute value of change was very small. At least they cannot be compared with those of Li_4SiO_4 or Li_2ZrO_3, where the initial abrupt change of CPD change prevailed to govern the whole CPD change.

4. Conclusion

The work function is quite sensitive to such surface phenomena as formation/annihilation of oxygen vacancies, adsorption/desorption processes, segregation etc., which can be investigated by measuring the CPD with respect to reference material. The observed CPD change of Li_2O was very small when the oxygen partial pressure in the sweep gas was varied in the range of $\approx 10^2$–10^{-7} Pa, whereas it was found to be up to about 200 mV when the oxygen partial pressure was varied in the range of $\approx 10^2$–10^{-13} Pa. In the case of Li_2O, the cause of CPD change due to H_2 admission was not attributed to formation of oxygen vacancies nor to hydrogen adsorption. Water vapor formed by hydrogen introduction was estimated to be adsorbed on the surface of Li_2O, which was ascribed to the cause for the CPD change.

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