Comparison of the Work Function Change between Li_2ZrO_3 and Li_2TiO_3 at Elevated Temperatures.

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Abstract

The work function change of Li_2ZrO_3 and Li_2TiO_3 was measured in atmosphere of various gas compositions using a high temperature Kelvin probe. The work function change of Li_2ZrO_3 , due to change of the chemical composition of sweep gas, was found to consist of two steps: a rapid change of work function followed by its gradual change to a steady state value. Whereas in the case of Li_2TiO_3 , the work function change was very slow. The observed difference in the work function change was discussed in terms of possible surface phenomena; i.e. production/annihilation of thermal defects, adsorption/desorption of hydrogen, etc.

1 Introduction

In order to enhance the release rate of tritium from the surface of solid breeder material in a fusion reactor, addition of hydrogen to inert sweep gas has been proposed [1].

In the present study, authors have investigated the effect of hydrogen admission to a sweep gas on the surface processes of candidate ceramic breeder materials, Li_2ZrO_3 and Li_2TiO_3 by means of the work function measurement under a controlled atmosphere at elevated temperatures. The work function is sensitive to such surface phenomena as formation of a non-stoichiometric layer, adsorption/desorption processes, etc. The so-called "high temperature Kelvin probe" was first applied to YSZ, a yttria (Y₂O₃) stabilized zirconia (ZrO₂), and then was also successfully applied to Li₄SiO₄ [2].

2 Experimental

The details of a high temperature Kelvin probe has been described elsewhere [3]. with which the contact potential difference, CPD, between a sample and the reference Pt electrode was measured. The He+H₂ mixture was used as the flowing gas. The concentration of H₂ was controlled by regulating the relative flow rates of He and H₂ with mass flow controllers. The oxygen partial pressure and moisture concentration in the sweep gas were measured *in-situ* with an Y₂O₃ stabilized ZrO₂ oxygen sensor and a hygrometer, respectively. The CPD measurements were all measured at 973 K.

The samples used in the present study were pellets of Li_2ZrO_3 and Li_2TiO_3 . The latter pellet (95 % monoclinic $\text{Li}_2\text{TiO}_3 + 5$ % cubic $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 9 mm $\phi \times 1$ mm t) was supplied by CEA Saclay, France.

3 Results and Discussion

3.1 Li_2ZrO_3

Figure 1 shows the change of CPD between Li_2ZrO_3 and Pt reference electrode as caused by the change of the composition of flowing gas. The chemical composition of the sweep gas was either (O): He; (100 cc min⁻¹) or (R): He + 1.06 % H₂ (100 cc min⁻¹). It is shown in the figure that when the chemical composition of the sweep gas was changed from (O) to (R) the CPD was first (a) decreased abruptly by 500 mV, and then (b) gradually increased to a steady state value. It should be noted that the CPD change showed good correlation with the change of oxygen partial pressure, P_{O_2} . Similar trend was also observed in Li₄SiO₄ [2]. Assuming that the change (a) is due to production of oxygen vacancy, V_O, the decrease of work function and that of P_{O_2} which is determined by a defect equilibrium:

$$O_{O}^{X} \rightleftharpoons V_{O}^{n} + ne' + \frac{1}{2}O_{2}(g) , \qquad (1)$$

can be related by:

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

according to which 1/2(n+1) = 1/5.68 (n = 1.84) was obtained. This implies that doubly charged $V_{O}^{\cdot \cdot}$ is predominant.

3.2 Li_2TiO_3

Fig.2 shows the result of the CPD measurement between Li_2TiO_3 and Pt at 973K. In the case of Li_2TiO_3 , it is characterized by a single step of the CPD change whose rate was very slow compared with that of Li_4SiO_4 . Such a slow change of work function due to the change of P_{O_2} may be explained, for an example, if one assume that it is governed by adsorption/desorption of hydrogen atoms on the surface. It can be shown that the portion (c) of the work function change in fig.2 can be fitted using two rate constants, k_a and k_d , which denote the rate coefficients for adsorption and desorption, respectively.





Fig.1: The change of CPD between Li_2ZrO_3 and Pt at 943 K due to the change of chemical composition of sweep gas. Shown also here is the change of oxygen potential (dashed curve).

Fig.2: The change of CPD between Li_2TiO_3 and Pt at 933 K due to the change of chemical composition of sweep gas. See Fig.1 for comparison.

References

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