Defect model for the Oxygen Potential of Hypo-stoichiometric Urania doped with Lutetium at 1473K

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1. Introduction

Nowadays, Nuclear fuel which is used in PWR and CANDU is oxidation Uranium(UO_2).

Rare earth elements have trivalent cation (+3). When rare earth elements is added to pure urania, oxygen potential increase.

Recently, Lu-doped urania is studied by Osaka [4]. Lu(Lutetium) is one of the rare earth elements. As a result, Oxygen potential of Lu-doped urania increased more than pure urania. And slope of ln(x) vs $\ln(P_{O2})$ graph is -5.

After assume that Point-defect Lu is added to urania in the hypo-stoichiometry region, we will explain about oxygen potential. Based on Osaka's report and pure urania defect model which is Park study.

2. Methods and Results

2.1 Defect Model of Pure Urania

By a defect structure of pure urania developed by Park, there are oxygen interstitial, oxygen vacancy, U positive polaron, U negative polaron in point defect structure of near stoichiometric region.

In this study, it's assumed that the point defect structure exists Willis cluster in hyper-stoichiometry region[2] and vacancy dimer in hyop-stoichiometry region[3].

Table 1 summarizes the defect types used in the analysis of pure urania, and Table. 2 shows the defect relations in pure urania. The nine unknown concentration ($O_i^{//}$, $V_O^{··}$, $U^/$, $U^·$, $(2:2:2)^/$, $(V:U:V)^{··}$, U_U^X, O_O^X, Po_2) are calculated by the equations of Table. 2, Table. 3 and equilibrium constants.

Table 1. The definition and effective charge of each defect used in the analysis

Notation	Definition	Effective Charge
$O_i^{//}$	Oxygen Interstitial	-2
$V_O^{··}$	Oxygen Vacancy	+2
$U^/$	(Negative) Polaron	-1
$U^·$	Hole	+1
$(2:2:2)^/$	Willis Defect	-1
$(V:U:V)^{··}$	Vacancy Dimer	+2

Table 2. Defect reactions in pure urania

$2U_U^X+1/2O_2(g)=O_i^{//}+2U^·$	$: K_{OX}$	(1)
$2U_U^X+O_O^X=1/2O_2(g)+V_O^{··}+2U^/$	$: K_{RE}$	(2)
$2O_O^X+2O_i^{//}+3U^·=(2:2:2)^/+3U_U^X$	$: K_C$	(3)
$2V_O^{··}+2U^/=(V:U:V)^{··}+U_U^X$	$: K_{CV}$	(4)

$2U_U^X=U^·+U^/$	$: K_E$	(5)
$O_O^X=O_i^{//}+V_O^{··}$	$: K_F$	(6)

Table 3. Balance equation

Uranium site balance	
$[U_U^X]+[U^/]+[U^·]=1$	(7)
Oxygen site balance	
$[O_O^X]+[V_O^{··}]+2[(V:U:V)^{··}]=2$	(8)
Stoichiometry balance	
$[O_i^{//}]+2[(2:2:2)^/]-[V_O^{··}]-2[(V:U:V)^{··}]=x$	(9)
Total charge balance	
$2[(V:U:V)^{··}]+2[V_O^{··}]+[U^·]=[(2:2:2)^/]+2[O_i^{//}]+[U^/]$	(10)

2.2 Lutetium-doped Urania($(U_{0.8}Lu_{0.2})O_{2-x}$)

In this study, Lu dopants don't exist cluster but exist point defects when added Lu in urania. Lutetium-doped pure urania is added as the trivalent cation structures of $[Lu^/]$. However pure urania doesn't change essential structure even if Lu is added on pure urania. Therefore lutetium-doped urania is regarded pure urania structure. However by lutetium the eq.(7) and (10) are changed which is:

$$[U_U^X]+[U^/]+[U^·]+[Lu^/]=1 \qquad (11)$$

its total charge balance by :

$$2[(V:U:V)^{··}]+2[V_O^{··}]+[U^·]=[(2:2:2)^/]+2[O_i^{//}]+[U^/]+[Lu^/] \qquad (12)$$

Fig.1 and Fig.2 are compared with lutetium-doped urania at 1473K and the value of $(U_{0.8}Lu_{0.2})O_{2-x}$) from Osaka[4].
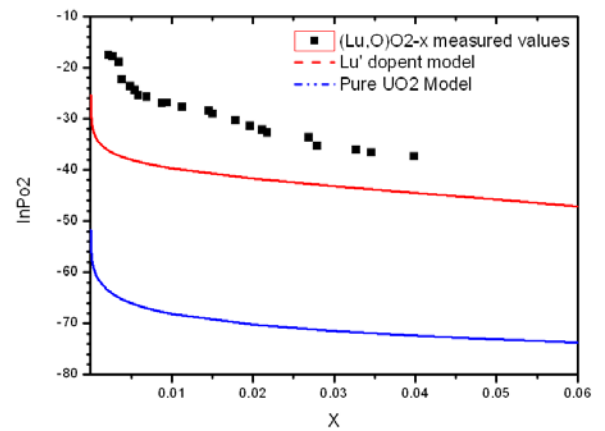

Fig 1. Comparison of oxygen potentials of present model with those of Pure Urania and Osaka's paper (x vs $\ln(P_{O2})$)
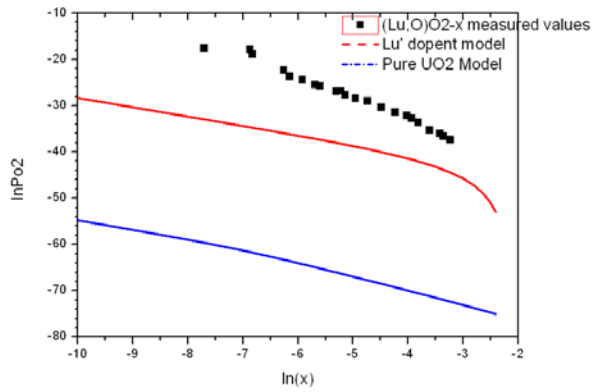
Fig 2. Comparison of oxygen potentials of present model with those of Pure Urania and Osaka's paper $(\ln(x) vs \ln(p_{O_2}))$

Fig. 3 and Fig.4 are shown the point defects concentration of pure urania and lutetium-doped urania.

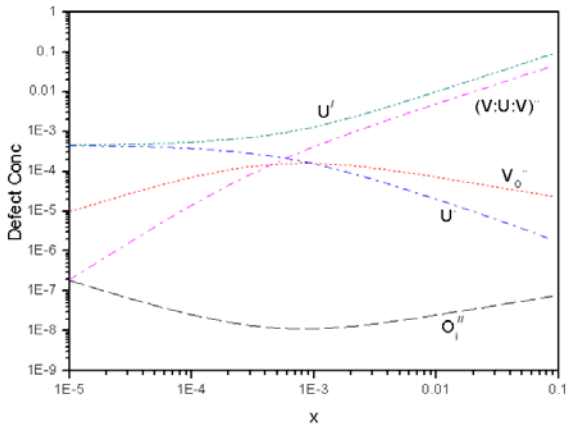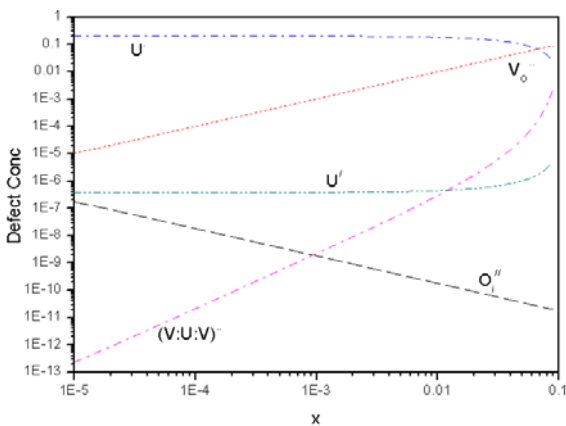
Fig 3. Defect concentration of pure urania.

Fig 4. Defect concentration of Lu-doped urania(present model).

The slop of $\ln(x)$ vs $\ln(P_{O2})$ from $(U_{0.8}Lu_{0.2})O_{2-x}$ of Osaka[4] is -5 but the slop from this study is -2.6 in Fig.2. Also the slop of pure urania is -2.6 in Fig.2

In Fig.3, With increasing hyper stoichiometry x, the oxygen vacancies are increased and effect as the important point defects while vacancy dimers effect as the important point defect the region of $x>10^{-2}$. In Fig.4, however, the slop of [U·] defect concentration is about 0.2 due to effect of added [$Lu^/$] and effect as the

important point defect. Thus, Lu does exist cluster when Lu is added to pure urania.

Slope of $\ln(x)$ vs $\ln(P_{O2})$ graph of defect model of Lu-doped urania to form cluster by Lu have to be -5. Therefore, the possible form of cluster is $[(Lu:(2/5)V_O)^/]$.

3. Conclusions

After assumming that urania which is contain point-defect Lu is based on pure Urania point-defect structure and Lu does exist point defects when Lu is added to pure urania, this study compared oxygen potential of Urania which is contain point-defect Lu with that of Lu-doped Uraina which is studied by Osaka[4] and pure urania.

It exist cluster not point-defect due to slope of $\ln(x)$ vs $\ln(P_{O2})$ graph is -2.6 when point-defect Lu is added to Urania. And at this time the possible form of cluster is $[(Lu:(2/5)V_O)^/]$

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