Vacancy mediated cation migration in uranium dioxide: The influence of cluster configuration

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ABSTRACT

The effect of cluster configuration on vacancy mediated uranium migration is investigated for stoichiometric UO_2 and hyper-stoichiometric UO_{2+x}. The minimum enthalpy pathway involves reconfiguration of the most stable cluster to a metastable configuration, in stoichiometric and hyper-stoichiometric systems. Additionally, a much larger number of alternative metastable configurations were identified for UO_{2+x} compared to UO_2. This would lead to a larger contribution to the Arrhenius pre-exponential term with hyper-stoichiometry. Consequently, the often made assumption that re-orientation of the ground state cluster offers access to the migration activation energy cannot be assumed to be valid.

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1. Introduction

The migration of uranium in uranium dioxide is an important factor in determining the mobility and release of fission gases from nuclear fuel pellets [1–4]. Xe, Kr and other fission products migrate via the uranium sublattice where vacancy mediated diffusion controls species release. The transport of intrinsic point defects is also a key parameter in the recovery from radiation damage. By understanding the mechanisms underpinning uranium vacancy migration, fuel performance predictions can be improved.

Experiments by Matzke [5] estimated the Arrhenius activation enthalpy for uranium vacancy migration as 5.6 eV in UO_2 and 2.6 eV in UO_{2+x}. The migration enthalpies were determined by measuring the diffusion of ^{238}Pu in uranium dioxide and were, therefore, not strictly indicative of uranium cation movement, especially considering that Pu can be in the 3 + rather than 4 + charge state in the stoichiometric case. Reimann and Lundy [6], for example, calculated the Arrhenius activation enthalpy value to be 4.3 eV in UO_2. Although other experimental work has been carried out, it often focused on mixed oxides such as $(U,Pu)O_{2\pm x}$ [7]. Thus, despite efforts to understand the effect of non-stoichiometry and temperature on the contribution of uranium vacancies, the underlying migration mechanisms in UO_2 and UO_{2+x} are still not well defined.

Difficulties with experimental studies have meant that a great deal of theoretical work has been carried out to understand the transport of cations in UO_2. Early work by Catlow [8] used empirical potentials to estimate the vacancy migration enthalpy in $UO_{2\pm x}$ for transport with and without charge balancing oxygen vacancies, but it did not consider charge compensation by U^{5+} cations. The results agreed with the UO_2 and UO_{2+x} experimental values, especially that the peak in activation enthalpy occurred at the stoichiometric composition. The enthalpy barrier was calculated to be ~5.3 eV. Similarly, Jackson et al. [9] used empirical potentials but included the migration of U^{3+} and U^{5+} cations in UO_2 as well as U^{4+} cations. They predicted the migration enthalpy to increase as a function of U ion charge, so that, U^{3+}, U^{4+} and U^{5+} cations exhibited migration enthalpies of 3.32 eV, 4.85 eV and 7.32 eV, respectively.

More recently, 19 different empirical potentials have been compared by Govers et al. [4] and validated against density functional theory (DFT) and experimental data where available. Depending on the empirical model, uranium vacancy (V_U''' in Kröger Vink notation [10]) migration was computed to proceed with at enthalpy ranging from 0.6 eV to 8.2 eV, quite an extra-ordinary spread. There was no obvious correlation between those models that employed formal charges (i.e. the uranium and oxygen charges set to $+4e$ and $-2e$, respectively) and those models that used partial charge models. Notably, the calculations presented by Govers et al. [4] did not consider cluster configurations using charge compensating defects, due to computational limitations, lack of information and that it was not the main focus of the study.

The DFT calculations of Dorado et al. [11] investigated uranium vacancy migration enthalpy using a form of orbital occupancy control to ensure the lowest enthalpy arrangement was attained. During electronic structure optimisation of a uranium vacancy within a charge

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neutral supercell the charge compensating U^{5+} defects can be investigated. However, Dorado et al. [11] used a 4+ background charged supercell negating the necessity for charge balancing U^{5+} defects. The energies reported for migration enthalpy are dependent on the oxygen displacement and exchange correlation used; the lowest enthalpy barrier of 3.6 eV employed GGA exchange correlation with a Hubbard correction. Although nudged elastic band methods implemented in DFT would be capable of capturing the behaviour of the small polaron rearrangement of the U^{5+} cation (as the electronic structure is optimised separately in each step of the uranium vacancy migration) it is not possible to identify multiple U^{5+} arrangements which have migration enthalpies very close to the lowest enthalpy pathway and could contribute to diffusion. Furthermore, due to the high computational cost and large number of cluster configurations needed, DFT is not yet suitable for studying the effect of the large number of possible oxygen vacancy reconfiguration during uranium vacancy migration within Schottky clusters. Currently, DFT studies are usually limited to a 2×2×2 supercell containing 96 lattice sites [11–14] but improvements in computational power will allow the enhancement in accuracy that stem from use of ab-initio methods to be combined with the methods developed using current empirical approaches.

A very recent paper by Andersson et al. has used a combination of empirical potentials and ab-initio methods to investigate radiation-enhanced fission gas diffusion in $UO_{2\pm x}$ [15]. They restate that the diffusion of Xe through the UO_2 lattice is highly related to the mobility of uranium vacancies. Not only do they find that a uranium vacancy migrates with an energy of 4.72 eV (similar to previous studies) but also show that double uranium vacancies (bound) give migration activation energies of 2.54 eV and 3.26 eV (when the vacancy cluster is considered fully charged or charge neutral, respectively).

Here we consider the role of uranium vacancies for uranium ion transport in stoichiometric and hyper-stoichiometric uranium dioxide. Unlike previous empirical studies, we include charge compensating defects in UO_2 and also in UO_{2+x}. As shown previously, the dominant positive charge compensating species in stoichiometric UO_2 is the oxygen vacancy ($V_O^{\bullet\bullet}$) [16]. In hyper-stoichiometric UO_{2+x}, accommodation of excess oxygen by the formation of oxygen interstitials means the oxygen vacancy concentration is very small (due to the Schottky equilibrium). U^{5+} defects ($U_U^{\bullet}$) will, therefore, be the dominant positively charged species compensating the negatively charge uranium vacancies in UO_{2+x}. Thus, the vacancy mediated uranium migration enthalpy is investigated in $\{V_U''':2V_O^{\bullet\bullet}\}^\times$ and $\{V_U''':4U_U^{\bullet}\}^\times$ defects clusters, representing UO_2 and UO_{2+x} respectively. Rather than only considering the most stable arrangement, as has previously been the case, the uranium vacancy migration enthalpy is also calculated for a large number of configurations to understand whether a metastable arrangement of the defect cluster may dominate, or at least contribute, to the migration mechanism despite the enthalpy penalty.

2. Methodology

Atomistic simulations have been carried out using the General Utility Lattice Program (GULP) [17]. The energy of interaction between two ions, i and j, is described by the short range Buckingham potential [18] with long range Coulombic interactions,

$$E_{\alpha\beta}\left(r_{ij}\right) = \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{ij}} + A_{\alpha\beta}exp\left(\frac{-r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6} \tag{1}$$

where α and β represent ions i and j respectively. The first term describes the long range Coulombic interactions where q_α and q_β are the charges on the two ions (e.g. O^{2-}). The second term represents repulsive short range interactions and the third term describes the attractive van der Waals interactions [19]. The $A_{\alpha\beta}$, $\rho_{\alpha\beta}$ and $C_{\alpha\beta}$ parameters used here are those derived by Busker et al. [20,21] — a very

flexible potential that will allow the effects of extrinsic defects to be considered in future work.

Defect cluster enthalpies were calculated using energy minimisation calculations within the Mott–Littleton approach [22], with regions I and IIa radii of 13.0 Å and 34.0 Å, respectively (as used with this potential set previously [5,23]). Defect enthalpies were determined for all possible configurations of the $\{V_U''':2V_O^{\bullet\bullet}\}^\times$ and $\{V_U''':V_O^{\bullet\bullet}\}''$ clusters that fit within a 2×2×2 cubic fluorite full unit cell volume (consisting of 96 atoms). By including the isolated oxygen vacancy defect enthalpy, the latter cluster is considered as a partially bound version of the former (note the change in cluster charge). As discussed in Section 1, this cluster, which incorporates oxygen vacancies, establishes the state in stoichiometric UO_2. Equivalently, hyper-stoichiometric UO_{2+x} was investigated by determining the defect enthalpies of the $\{V_U''':4U_U^{\bullet}\}^\times$, $\{V_U''':3U_U^{\bullet}\}'$, $\{V_U''':2U_U^{\bullet}\}''$ and $\{V_U''':U_U^{\bullet}\}'''$ clusters again for all configurations it is possible to form within the $2 \times 2 \times 2$ fluorite supercell volume; this time the charged clusters are partly bound with additional isolated U^{5+} ions.

For each cluster configuration, a rational functional optimisation (RFO) [24] calculation was used to determine the system enthalpy at the saddle point for the migration of a U^{4+} ion into a first nearest neighbour uranium vacancy in the ⟨110⟩ direction. The enthalpy barrier was determined by subtracting the saddle point enthalpy from the associated defect cluster enthalpy in a similar manner to the previous study of vacancy migration in UO_2 carried out by Govers et al. [4]. Care was taken to include only saddle points that would facilitate migration of the species into the vacancy as the RFO method may find other points that fulfil the stopping criterion of the saddle point finder.

We investigated the possibility that during vacancy migration reconfiguration of a cluster from its most stable configuration into a metastable arrangement results in a lower enthalpy barrier. If the reduction in the enthalpy barrier is greater than the change in enthalpy of the cluster due to reconfiguration (the reconfiguration enthalpy), a lower overall uranium vacancy migration enthalpy has been identified. Thus, from now on migration enthalpy refers to the combination of reconfiguration enthalpy plus the enthalpy barrier for a given cluster configuration. A number of approximations have been made, in particular, that the oxygen sub-lattice is able to move far more rapidly than the uranium vacancy, which allows a metastable arrangement of the $\{V_U:2V_O^{\bullet\bullet}\}^\times$ cluster to exist for the migration event. This is acceptable given that experimental and modelling studies report oxygen migration to be orders of magnitude faster than for uranium [8,9,25]. Similarly, we assume that the hole on the uranium sub-lattice (which is responsible for U^{5+} being 5+) is very mobile compared to uranium vacancies — a sensible approximation given the small-polaron behaviour of U^{5+} in the lattice [26].

Migration of the U^{3+} cation and U^{5+} cation into a vacancy were also considered as these species may exist due to variations in stoichiometry or via the endothermic reaction $U^{4+} \rightarrow \frac{1}{2}U^{3+} + \frac{1}{2}U^{5+}$ (the Catlow–MacInnes process [27]) with an enthalpy of ~1.7 eV (obtained using DFT methods [11]) or ~1.9 eV (using empirical and experimental methods [9]).

Molecular dynamics methods were not chosen as uranium vacancy migration is known to be slow and therefore difficult to model using standard dynamics methods. Temperature accelerated dynamics [28] could prove useful in related studies, however, the small-polaron behaviour of the U^{5+} cation would be difficult to capture without a reliable and computationally economical empirical charge transfer model.

3. Results and discussion

3.1. UO_2

Using the RFO technique, the enthalpy barrier for uranium migration via a vacancy mechanism in with the ⟨110⟩ direction has been