Diffusion of oxygen interstitials in UO_{2+x} using kinetic Monte Carlo simulations: Role of O/M ratio and sensitivity analysis

Rakesh K. Behera^{1†*}, Taku Watanabe^{2‡}, David A. Andersson³, Blas P. Uberuaga³, and Chaitanya S. Deo^{1*}

1 Nuclear and Radiological Engineering Program, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

2 School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

3 Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.

[†] *Present Address: School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.*

[‡] *Present Address: Samsung R&D Institute, Japan*

**Corresponding authors: rakesh.behera@gatech.edu, chaitanya.deo@me.gatech.edu*

Abstract

Oxygen interstitials in UO_{2+x} significantly affect the thermophysical properties and microstructural evolution of the oxide nuclear fuel. In hyperstoichiometric Urania (UO_{2+x}), these oxygen interstitials form different types of defect clusters, which have different migration behavior. In this study we have used kinetic Monte Carlo (kMC) to evaluate diffusivities of oxygen interstitials accounting for mono- and di-interstitial clusters. Our results indicate that the predicted diffusivities increase significantly at higher non-stoichiometry ($x > 0.01$) for di-interstitial clusters compared to a mono-interstitial only model. The diffusivities calculated at higher temperatures compare better with experimental values than at lower temperatures (< 973 K). We have discussed the resulting activation energies achieved for diffusion with all the mono- and di-interstitial models. We have carefully performed sensitivity analysis to estimate the effect of input di-interstitial binding energies on the predicted diffusivities and activation energies. While this article only discusses mono- and di-interstitials in evaluating oxygen diffusion response in UO_{2+x} , future improvements to the model will primarily focus on including energetic definitions of larger stable interstitial clusters reported in the literature. The addition of larger clusters to the kMC model is expected to improve the comparison of oxygen transport in UO_{2+x} with experiment.

Keywords: UO_{2+x} , UO_2 , defects, diffusion, sensitivity analysis, DFT, kMC

1. Introduction

Urania is the most common fuel used for commercial nuclear energy generation. Even though urania fuel starts out stoichiometric or slightly substoichiometric, hyperstoichiometry is achieved during fabrication and operation of the fuel with a chemical formula of UO_{2+x} , where x is the concentration of excess oxygen present in the fuel [1-7]. The oxygen-to-metal (O/M) ratio of the resulting material is one of the most critical parameters in oxide nuclear fuel fabrication. Thermophysical properties of oxide nuclear fuels are significantly impacted by oxygen defects present in the system [8, 9]. In the case of UO_{2+x} , the excess oxygen atoms occupy the interstitial sites in the fluorite lattice (body centered, and edge centered positions), whereas the uranium sub-lattice maintains the FCC crystal structure. Both experimental and computational methods have investigated the structures and mechanisms of different types of clusters present in hyperstoichiometric urania. The most notable experimental work in the field was done by Willis [10], and Bevan and Willis [11], who reported the structure of di-interstitial clusters (the so-called 2:2:2 Willis cluster) and, at higher oxygen interstitial concentrations, cuboctahedral (COT) clusters using neutron diffraction. Desgranges *et al.* [12] also used neutron diffraction to demonstrate the presence of cuboctahedral clusters in U_4O_9 and U_3O_7 , which can be expressed as UO_{2+x} where $x = 0.25$ and 0.33 respectively. In addition to 2:2:2 Willis clusters and cuboctahedral clusters, He and Shoesmith [13] used various experimental techniques to show the presence of isolated interstitials, and a mixture of different clusters in UO_{2+x} , where x ranges from 0.00 to 0.33, i.e., from UO_2 to U_3O_7 . Conradson *et al.* [14] determined the presence of oxo-groups in U_4O_9 using extended x-ray adsorption fine spectroscopy. Allen *et al.* [15] proposed that the defect clusters in UO_{2+x} can be explained by a combination of 2:2:2 Willis clusters. Whapham and Sheldon [16] have also suggested the formation of COT clusters due to the formation of U_4O_9 in low radiation dose samples of UO_{2+x} . In high-dose samples, they reported the formation of 2-D interstitial dislocation loops, which lie on the $\{1\ 1\ 0\}$ planes.

Along with the experimental works, computational investigations based on first-principles calculations and atomistic simulations have been extensively used to investigate clustering in UO_{2+x} . Using density functional theory (DFT), Geng *et al.* [17] predicted the formation of stable cuboctahedral clusters with an additional oxygen atom at the body center of the unit cell (COT-o) at low temperatures and isolated interstitials at higher temperatures. Andersson *et al.* [18] used DFT to show that split di-interstitial clusters are more stable compared to the 2:2:2 Willis clusters. Andersson *et al.* [19] also reported that the split quad-interstitial cluster, which can be viewed as agglomerations of two split di-interstitial clusters, is more favorable compared to the cuboctahedral clusters. Using molecular dynamics simulations with the Basak potential [20], Aidhy *et al.* [21] have observed the formation of cuboctahedral clusters in stoichiometric UO_2 .

While the structure of the clusters in UO_{2+x} is important, it is equally critical to evaluate the transport of the interstitials and formation of interstitial clusters, which affects the thermophysical properties and the evolution of fuel under extreme irradiation environments of a nuclear reactor. Using temperature accelerated dynamics (TAD) Ichinomiya *et al.* [22] evaluated the mechanisms of oxygen interstitial migration in UO_{2+x} and reported a lower migration barrier for di-interstitials compared to mono-interstitials with the Basak potential [20]. The advantage of TAD simulations is that it does not require any *a priori* information on the migration pathways, and calculates the migration barriers of the events based on the empirical potential used in the simulation. Recently Bai *et al.* [23] have used TAD with the Basak potential [20] to examine the migration barriers for mono-, di-, tri-, tetra-, and penta-oxygen interstitial clusters and explored possible diffusion pathways for each type of cluster in UO_{2+x} . Their results indicate that out of the five possible interstitial structures ($1\text{O}_i - 5\text{O}_i$), di-interstitial clusters have the lowest energy barrier for migration. Using DFT calculations Andersson *et al.* [18] have reported that oxygen di-interstitial clusters in UO_{2+x} exhibit a faster diffusion pathway than that of mono-interstitials. The diffusivities estimated at 1073 K using kinetic Monte-Carlo (kMC) with the DFT migration barriers for mono- and di-interstitials clearly indicated that oxygen transport is significantly increased with the di-interstitial mechanism. Therefore, the comparison of the predicted diffusivities shows a better agreement with experimental data (for $x > 0.01$).

In this work we have estimated the diffusivity of oxygen interstitials as a function of stoichiometry and temperature. We have compared the diffusivities based on a mono-interstitial (1O_i _2009) and two different di-interstitial models (2O_i _2009 and 2O_i _2015). In order to determine the reliability of the predicted diffusivities, we have performed a sensitivity analysis to show the effect of input energies on the overall diffusivities. We have organized the paper as follows. The simulation details for the kMC and the migration barriers estimated with DFT are discussed in the Methodology section (Section 2). Section 3 reports the comparison of diffusivities between the three models. In particular, it provides a detailed discussion on the diffusivity of oxygen interstitials in UO_{2+x} ($x < 0.25$) for a wide range of temperatures (673 K – 1673 K). The activation energies and structural analysis are discussed for the di-interstitial models. Section 4 summarizes the sensitivity analysis by detailing the effect of di-interstitial binding energy on the predicted diffusivities and activation energies for 2O_i _2015. Section 5 highlights the summary and conclusions of this study.

2. Methodology

In this study we have used a kMC model to explore the effect of temperature and concentration of oxygen interstitials on oxygen transport in UO_{2+x} . The kMC model has the capability to investigate evolution of mono-interstitials (I_1) and a combination of mono- and di-interstitials (I_2). Table 1 lists the calculated kinetic parameters used in this study. In the mono-interstitial model (1O_i _2009), all the interstitials present in the system diffuse with a migration barrier of 0.81 eV, which is defined as the migration

energy of mono-interstitials. In order to maintain a mono-interstitial model, a blocking scheme is implemented, which restricts the occupation of all first nearest neighbor octahedral interstitial sites for each interstitial in the simulation supercell (Fig. 1(a)). This is the same blocking scheme used by the Murch model [24], and reflects the repulsion between oxygen interstitials occupying the first nearest neighbor sites. However, complex clusters of oxygen interstitials form in hyperstoichiometric urania, indicating that 1O_i_2009 will be applicable only to the very dilute limit of interstitial concentrations [13, 15, 25, 26]. The di-interstitial model, on the other hand, allows clustering of two interstitials where the interstitials can occupy one of the first nearest neighbor interstitial sites with respect to an existing mono-interstitial (Fig. 1(b)). Once a di-interstitial is formed, none of the other interstitials in the system are allowed to occupy the remaining first-nearest neighbor sites of the two interstitials forming I₂. Therefore, the di-interstitial model is an extension of the mono-interstitial model, where each mono-interstitial can be a neighbor of at most one other mono-interstitial.

In addition to the formation of the di-interstitial by the combination of two mono-interstitials ($I_1 + I_1 \rightarrow I_2$), the kMC model also accounts for the possibility of the dissociation of the di-interstitial to two mono-interstitials ($I_2 \rightarrow I_1 + I_1$). The stability of the di-interstitials is determined by the binding energy relative to two mono-interstitials. The binding energy is calculated by comparing the energy of a di-interstitial with the energies of two mono-interstitials using DFT. Assuming a diffusion-limited process, the binding energy of a di-interstitial can be expressed as a combination of the barrier to dissolve a di-interstitial (dissociation energy) and the amount of energy required to migrate a mono-interstitial to form the di-interstitial (migration energy), i.e., $BE_{di} = DE_{di} - ME_{mono}$. Using the binding energy of -0.38 eV and mono-interstitial migration energy of 0.81 eV, the effective barrier to dissolve a di-interstitial is estimated as $DE_{di} = BE_{di} + ME_{mono} = -0.38 \text{ eV} + 0.81 \text{ eV} = 0.43 \text{ eV}$ [18]. The results obtained with the binding energy of -0.38 eV is referred to as 2O_i_2009 for the rest of the discussion in this manuscript. These migration, binding, and dissociation energies are calculated based on DFT using the experimental lattice parameter of UO₂. However, first-principles calculations based on DFT have difficulties in describing strongly correlated systems such as UO₂. Therefore, calculation of the binding energy of di-interstitials as well as migration barriers within this *f*-electron system is not trivial. DFT+U has been used extensively to model the strongly correlated nature of the *f*-electrons in U. Dorado *et al.* [26] have shown that special procedures involving controlling the *f*-orbital occupation matrices must be applied to avoid meta-stable electronic solutions. This may have a significant effect on the defect energies. Applying this methodology, a more accurate binding energy of the di-interstitial is recently estimated to be -0.06 eV. The updated energy value indicates a lesser repulsion between the di-interstitials compared to 2O_i_2009. The results obtained with this updated binding energy of -0.06 eV are referred as 2O_i_2015 in this manuscript. We will present a comparison of properties estimated with both 2O_i_2009 and 2O_i_2015 description of the I₂ and rationalize the results

based on the binding energies. The effective barrier for dissolving a di-interstitial is 0.43 eV for 2O_i_2009, while it is 0.75 eV for 2O_i_2015. Therefore, the di-interstitials in 2O_i_2015 are effectively more stable than 2O_i_2009 at the same temperature.

Assuming a thermally activated process, the migration rate (k_m) is estimated using $k_m = \nu \exp(-E_m/k_b T)$, where ν is the pre-exponential or attempt frequency factor, E_m is the migration barrier, k_b is the Boltzmann constant, and T is the temperature. Following Andersson *et al.* [18], we have considered the pre-exponential or attempt frequency factor (ν) to be $1 \times 10^{12}/s$ for all species. The diffusivity of the oxygen interstitials is then estimated by measuring the mean square displacements (MSDs) of all the hyperstoichiometric oxygen ions within the kMC simulation. Using the Einstein relation $D = \langle r^2(t) \rangle / 6t$, the total diffusivity is calculated as $D = (x/(2+x)) \langle D_i \rangle$, where x is the amount of hyperstiochiometry in UO_{2+x}, and $\langle D_i \rangle$ represents the averaged diffusivity of individual oxygen ions. **It is important to note that the input energies from first principles calculations inherently reflect the charge-compensating U⁵⁺ ions due to the addition of extra oxygen(s) to the UO₂ lattice. Therefore, the kMC model accurately represents the charge state in the simulated UO_{2+x}.** In both the di-interstitial models, care was taken to distribute the oxygen interstitials in such a way that we start with a mono-interstitial configuration. Thus, no two adjacent interstitials occupy the first nearest neighbor octahedral sites in the initial interstitial arrangement. This condition of mono-interstitial distribution of the initial interstitials can be achieved till $x \leq 0.25$. In this study we have estimated the diffusivities over a range of temperature (between 673 K – 1673 K) for $x \leq 0.20$ using the energetics represented by the 1O_i_2009, 2O_i_2009, and 2O_i_2015 models.

The migration energies of mono- and di-interstitials are taken as 0.81 eV and 0.47 eV respectively [18]. Other studies have predicted slightly higher magnitudes of migration barriers [26, 27], but the relative ordering of mono- and di-interstitial migration barriers remain the same. The lower migration barrier for di-interstitials compared to mono-interstitials clearly indicates that faster diffusion is expected with di-interstitials in UO_{2+x}. However, the magnitude of the binding energy of the di-interstitial clusters is expected to affect the predicted diffusivities. In order to evaluate the effect of input binding energies on diffusivity, we have systematically varied the binding energies to represent a totally repulsive to totally attractive nature of di-interstitials. The results of this sensitivity analysis are useful in evaluating the mechanisms at work in UO_{2+x} at specific non-stoichiometry.

Approximation and Model Limitation: Before discussing the results it is necessary to point out the key approximations and limitations of the current model. While we have discussed results related to di-interstitials (I₂), it is necessary to report the type of I₂ considered in this study. Following the work by Andersson *et al.* [18, 19], it is clear

that I_2 clusters can be described as either undistorted di-interstitial (I_2^0) or split di-interstitial (I_2^X) (Fig. 2). I_2^0 is composed of two oxygen interstitials (a and b) residing in nearest neighbor octahedral sites, while a third oxygen (c) remains in a more or less perfect lattice site. I_2^X is created when the two nearest neighbor interstitial ions (a and b) move towards a common regular oxygen site (c) and displace it to form split di-interstitial with configuration presented as $A-B-C$ in Fig. 2. Therefore, I_2^X consists of three oxygen ions arranged along the $\{111\}$ plane in an equiaxed or equilateral triangle centered around a vacant regular oxygen site. Using DFT, Andersson *et al.* [18] have established that I_2^X configuration is more favorable compared to the I_2^0 configuration for di-interstitials.

Due to the structural variation of the two di-interstitial configurations with respect to the host UO_2 lattice, an off-lattice kMC model is ideal to describe the I_2^X configuration, while an on-lattice kMC model is ideal to describe the I_2^0 configuration. While the off-lattice model provides the possibility to include the atomic description of I_2^X configuration, the model cannot explicitly define host- UO_2 lattice and mono-interstitials in the model simultaneously. The on-lattice model on the other hand, can handle the atomic description of both the host UO_2 lattice, along with the mono-interstitials and I_2^0 configuration, but not the I_2^X configuration. Understanding the complexity of having a hybrid on-lattice and off-lattice kMC model, we have selected the on-lattice kMC model for this study. This approximation is guided by our choice of explicitly describing both the uranium and oxygen lattice atoms in the model. This approximation can be justified based on the diffusion mechanism of I_2^X clusters. While mono-interstitials migrate by the interstitialcy mechanism, diffusion of di-interstitial clusters actually involves both I_2^0 and I_2^X configurations as discussed by Andersson *et al.* [18]. Starting from the I_2^X configuration shown in Fig. 2 ($A-B-C$), the structure transforms to I_2^0 ($a-b-c$). Figure 2 only represents one of the three I_2^0 possible configurations where the I_2^0 forms with C occupying the vacant c site. The other two possibilities are A can occupy the vacant c site or B can occupy the vacant c site while going from I_2^X to I_2^0 configuration. From the I_2^0 configuration ($a-b-c$) the di-interstitial can transform back to the original I_2^X configuration by kicking out the oxygen at the c site or form a new I_2^X configuration by kicking out the d site. This transformation from I_2^0 to I_2^X for migration has four energetically equivalent possibilities, e.g., if c site is kicked out, then either a or b can occupy the vacant c site, else if d site is kicked out, then either a or b can occupy the vacant d site. From the diffusion mechanism of di-interstitials it is clear that I_2^0 acts as an intermediate state for I_2^X migration. Hence, the diffusivities estimated assuming I_2^0 structure with 0.47 eV barrier for migration is expected to be comparable to considering I_2^X structure for migration.

The other approximation in our study is related to the size of the interstitial clusters. In order to enhance the fundamental understanding of the effect of various interstitial clusters on overall diffusivities, we have estimated the effect of I_1 and I_2 clusters on the overall diffusivity in UO_{2+x} . Establishing the individual effect of mono- and di-interstitials on the diffusivities is one of the most powerful attributes of

computational models, which is difficult to separate with experiments. However, this advantage can result in some limitation of the computational model compared to the experimental scenarios. For example, in our current model we have implemented a blocking scheme to obtain the response of only mono- and di-interstitials on oxygen ion diffusivities in UO_{2+x} . Therefore, it is important to point out that our model does not include the description of other larger clusters possible in hyperstoichiometric UO_2 . For example, Andersson *et al.* [19] reported the structure of split quad-interstitials, which are energetically more favorable compared to I_2^x or mono-interstitials. The split quad-interstitial structure is formed by a combination of two split di-interstitials. Incorporation of such larger interstitial clusters to the kMC model will be a logical extension of the current work.

3. Results and discussions

In order to estimate the effect of the updated di-interstitial binding energies on oxygen transport, we have calculated the diffusivities for 2O_i _2015 and reproduced the results for 1O_i _2009 and 2O_i _2009 published by Andersson *et al.* [18] with non-stoichiometry (x) ≤ 0.20 at 1073 K. Fig. 3 compares the oxygen interstitial diffusivities (D) in UO_{2+x} predicted by the mono- and di-interstitial models with experiment [28, 29]. The calculations show an initial increase and then a decrease in D with x , which can be attributed to the implemented blocking mechanisms. While the predicted diffusivities compare well with experiment at low x , larger deviations are observed for higher x . Comparing the mono- and di-interstitial results, the addition of di-interstitial cluster formation increases oxygen diffusivity for $x > 0.01$. Consequently, the diffusivity values are more pronounced at higher x values with the I_2 models, where the comparison with experiment is improved significantly. Comparing the two I_2 models, the updated di-interstitial binding energy in 2O_i _2015 increases the effective diffusivities (for $x > 0.01$) even further compared to 2O_i _2009. This increase is attributed to the relatively stronger binding and thus a longer lifetime of the di-interstitials in 2O_i _2015. We have primarily discussed the results obtained with 2O_i _2015 for the remaining discussion.

All the calculations presented in Fig. 3 are performed with a $10 \times 10 \times 10$ supercell of the fluorite lattice. In order to estimate the effect of system size, we have calculated the magnitudes of the average oxygen diffusivities with varying system sizes. Fig. 4(a) summarizes the D values estimated for four different system sizes $4 \times 4 \times 4$, $6 \times 6 \times 6$, $8 \times 8 \times 8$, and $10 \times 10 \times 10$ supercell using 2O_i _2015. The system size effect on the D values at 1073 K is observed to be very minimal. We have performed a structural analysis by calculating the average number of 1st nearest neighbor (1NN) oxygen interstitials present after reaching equilibrium at 1073 K with 2O_i _2015 (Fig. 4(b)). The average number of 1NN indicates the fraction of di-interstitials generated with respect to the total oxygen interstitials present in the system. If all the interstitials present in the system form stable di-interstitials, then the average 1NN number will reach a value of 1.0. In general the plots show a linear increase in the number of di-interstitials with non-stoichiometry. The total number of di-interstitials in the

system is observed to be between 65% – 70% at $x = 0.20$. Due to the small number of interstitials present in the system in the dilute regime ($x < 0.01$), a large statistical error is observed in the average 1NN. Comparing all the system sizes, $4 \times 4 \times 4$ system shows the largest fluctuation in the number of di-interstitial clusters present at different concentrations. These fluctuations are reduced for larger system sizes. Therefore, a $6 \times 6 \times 6$ system size is considered for most of the remaining calculations, which has an improved computational efficiency compared to the $10 \times 10 \times 10$ supercell.

Using a $6 \times 6 \times 6$ supercell, we have calculated the effect of temperature on the overall diffusivities. Fig. 5 illustrates the D values at $T = 673$ K, 773 K, 873 K, 973 K, 1073 K, 1273 K, 1473 K, and 1673 K at all non-stoichiometry. As would be expected, the results show a systematic increase in the diffusivities with temperature, typical of an Arrhenius process. However, in addition to a simple increase in rate due to the higher temperature, the relative populations of I_1 and I_2 also change with temperature, compounding the temperature effect. The mobility of the oxygen interstitials is higher at higher temperatures, which increases the possibility of I_2 formation at higher temperatures. Since the migration energy of I_2 is smaller than I_1 , an overall increase in diffusivities is realized at higher temperatures. In Fig. 6 we have compared the calculated kMC diffusivities with experiment between 673 K - 1073 K and $x < 0.25$. The predicted diffusivities are close to the experimental values at very low concentrations ($x < 0.01$). At these low concentrations the probability of I_2 cluster formation is minimal, and diffusion is expected to be dominated by the contribution from mono-interstitials. From the data it is clear that the diffusivities compare well with the experiment at higher temperatures (e.g., 1073 K), while it deviates more at lower temperatures (e.g., 673 K). This suggests that I_1 and I_2 description only is not sufficient to describe the diffusion dynamics at lower temperatures. The addition of even larger interstitial clusters (e.g., quad clusters) to the model will improve the physical basis of the model, and thereby is expected to improve the comparison with experimental diffusivities.

The predicted diffusivities with respect to temperature and stoichiometry can be used to estimate the effective activation energies. The activation barrier is obtained by fitting the data to $D = D_0 \exp(-E_a/k_B T)$, where D_0 is the temperature independent pre-exponential factor, E_a is the activation barrier, k_B is the Boltzmann constant, and T is the temperature. Fig. 7 plots the diffusivities with respect to $1/T$ for $2O_i$ _2015, where the slope of the lines fitted to the data points at each concentration provides the activation energies. The effective activation energies predicted by all the models are then plotted against non-stoichiometry (Fig. 8(a)). The mono-interstitial activation energy is 0.81 eV, which is the model input. Surprisingly, the effective activation energies predicted by $2O_i$ _2009 are comparable to the mono-interstitial model. This indicates that most of the diffusion in $2O_i$ _2009 for different non-stoichiometry (x) is guided by mono-interstitials present in the system. This is possible since the

di-interstitials experience a stronger repulsion, which indicates that di-interstitials form and quickly dissociate back to mono-interstitials. In order to support this possibility, we have estimated the fraction of di-interstitials present in the final structure for all the non-stoichiometry at 1073 K. Fig. 8(b) illustrates that the average 1NN oxygen interstitials in the final structure are < 0.05 for $2O_i$ _2009, indicating less than 5% of the total interstitials are in the I_2 form. The effect of concentration is also observed to have no effect on the stabilization of I_2 clusters in $2O_i$ _2009. Therefore, the effective migration barrier is similar to $1O_i$ _2009, even though the diffusivities are much larger for $2O_i$ _2009 compared to $1O_i$ _2009. In $2O_i$ _2009 the primary role of the di-interstitial clusters is not to migrate as a cluster, but to facilitate the migration of mono-interstitials by reducing the effect of blocking.

In contrast, the activation energy response for $2O_i$ _2015 in Fig. 8(a) shows a combined mono- and di-interstitial diffusion mechanism, where the formation and stabilization of di-interstitials are substantially enhanced (Fig. 8(b)). Fig. 8(a) can be divided into three distinct regions of effective activation energies, which are labeled as Regions I, II, and III. The effective activation energies decrease with increase in non-stoichiometry in Region I ($x < 0.04$), remain nearly constant in Region II ($0.04 < x < 0.12$), and increase towards the mono-interstitial activation energy in Region III ($x > 0.12$).

Superimposing the effective activation energies with $I_2/(I_1+I_2)$ values obtained for $2O_i$ _2015 (Fig. 8), we can relate the structural configuration of the interstitials with the observed response of the activation energies. In Region I, the concentration of di-interstitials increases with increasing x . For extremely low interstitial concentrations, e.g. $x = 0.005$, there are very few oxygen interstitials present in the supercell. Therefore, the chance of I_2 formation is significantly reduced in this dilute limit. The diffusion in these low concentrations is guided mostly by mono-interstitial migration. Hence, the activation energy in this concentration regime is similar to the mono-interstitial migration energy. However, with the increase in x , the resulting activation energies are in between the mono- and di-interstitial migration energies (0.81 eV and 0.47 eV respectively). This indicates that diffusion for $x > 0.005$ in Region I is realized via mixed I_1 and I_2 migration. Structural analysis in this region confirms a significant increase in I_2 concentration for $x = 0.04$ compared to $x = 0.005$ at 1073 K. The probability of blocking during diffusion is expected to be relatively smaller due to the low concentration of the defects in Region I.

The effective activation energies remain almost constant in Region II, which can be explained by two major factors. First, the number of I_2 clusters in this region increases linearly with the increase in concentration. This effect is expected to reduce the activation energy. Second, the probability of blocking increases in Region II compared to Region I as the total number of interstitials increases with the increase in concentration. This increased blocking is expected to reduce diffusion, thereby increasing the activation energy. This interplay between the increase in diffusion due

to di-interstitial formation and decrease in diffusion due to blocking results in the plateau region in effective activation energy for $0.04 < x < 0.12$, where $I_2/(I_1+I_2)$ varies approximately between 0.2 - 0.5.

In Region III, the total number of I_2 cluster increases further for $x > 0.12$. The ratio of I_2 to the total interstitials (I_1+I_2) is greater than 0.5, which indicates that there are more di-interstitials present in the system than mono-interstitials. Ideally this increase in the number of I_2 clusters should increase the overall diffusivities due to a smaller migration barrier. However, the realized blocking between mono-di, and di-di interstitials due to the increased concentration significantly reduces the overall diffusivity. Even though there are many mobile clusters present in the system, there are less available spots for diffusion. Therefore, the effective activation energy in Region III increases with respect to Region II. This activation energy is still in between I_1 and I_2 migration energies, which indicates a mixed mono- and di-interstitial response to the overall diffusion.

In order to show the effect of temperature on the ratio of di-interstitials present in the system, we have performed the structural analysis at all the temperatures considered in this study for $2O_i$ _2015. Fig. 9 reports the ratio of I_2 clusters present in the system with respect to the total interstitials (I_1+I_2) with temperature for a $6 \times 6 \times 6$ supercell. The data shows a larger fluctuation of the ratio at 673 K. In addition, the fluctuation at relatively low non-stoichiometry ($x < 0.01$) is also observed to be large, which arises due to the statistical error associated with the small number of oxygen interstitials present in the system. Therefore, in order to estimate the effect of temperature and concentration we have considered $x > 0.01$ and $T > 673$ K for discussion.

First we have considered the effect of temperature on I_2 formation. The results are presented by comparing the I_2 concentration between 773 K and 1673 K. For $x = 0.04$ (Region I), increasing the temperature from 773 K to 1673 K results in a ~6% increase in the di-interstitial concentration (~19% I_2 in the system at 773 K, ~25% I_2 at 1673 K). Similar analysis at $x = 0.08$ and 0.12 (Region II) results in an increase of ~2% and 10% I_2 concentration respectively. In Region III, the di-interstitial concentration increases by ~9% and 3% for $x = 0.16$ and 0.20 respectively. Therefore, a maximum of 10% variation is observed in the hyperstoichiometric systems by increasing the temperature from 773 K to 1673 K at any concentration. In order to check the effect of concentration, we have selected a representative temperature of 1073 K for discussion. This analysis is performed by comparing the change in di-interstitial concentration with respect to $x = 0.04$ at 1073 K. We obtained an overall 9%, 28%, 33%, and 45% increase in di-interstitial concentrations for $x = 0.08, 0.12, 0.16$, and 0.20 respectively. Therefore, change in stoichiometry is observed to have a more pronounced effect on the defect structure than temperature. It is important to point out that the overall trend on I_2 concentration with respect to x is similar for the rest of the temperatures.

4. Sensitivity analysis

While the effect of temperature and concentration on overall diffusivities and activation energies are important, it is equally important to estimate the effect of model input energetics on the resulting defect dynamics. Since the kMC results are dependent on the accuracy of the energy barriers predicted from first-principles calculations, an evaluation of the confidence of the model is good modeling practice. Confidence of a model may be evaluated by quantifying the uncertainty in any model results (uncertainty analysis) and by evaluating how much each input is contributing to the output uncertainty [30, 31]. Sensitivity analysis addresses the second of these issues by performing the role of ordering by importance of the strength and relevance of the inputs in determining the variation in the output [32]. The choice of method of sensitivity analysis is typically dictated by a number of problem constraints or settings. Hence, there are a large number of approaches for performing sensitivity analysis of a computational model. In the context of kMC simulations of defect diffusion, as is the case in our investigation, where the input consists of a catalog of rate events (rate of migration of defects with energy barriers and attempt frequencies), the one-at-a-time/one-factor-at-a-time (OAT/OFAT) approach appears appropriate. In this approach, one input variable is changed, keeping others at their baseline values. This is repeated for other inputs in the same way, where sensitivity is measured by monitoring the changes in the output. Any observed change can be traced back to a single variable as all other variables are fixed to their central or baseline values. A limitation of OFAT is that the process could produce a large amount of data which will scale with the number of input parameters. Therefore, it is necessary to use the physics of the model to reduce the number of parameters to explore.

Based on our DFT predictions and other literature values, the difference between the I_1 and I_2 migration barriers are fairly accurately captured. Therefore, we have performed a limited OFAT sensitivity analysis by varying one variable input, the binding energy of the O-O interstitials. The choice of this parameter was guided by the varying binding energy values predicted with DFT (Table 1). In this sensitivity analysis, we have focused on the effect of I_2 binding energies on the overall diffusivities and activation energies.

In order to evaluate the uncertainties associated with our input energetics, we have varied the binding energy of I_2 clusters through the entire range of completely unbound ($BE = -0.81$ eV) to strongly bound ($BE = +1.09$ eV) with a step of 0.10 eV. This corresponds to di-interstitial dissociation energies of 0.00 eV to 1.90 eV respectively. It is important to point out that the BE for $2O_i_{2009}$ is -0.38 eV and for $2O_i_{2015}$ it is -0.06 eV. In addition to the binding energies, we have varied the non-stoichiometry and temperature to estimate the uncertainties associated with the overall diffusivities. Therefore, at each temperature (673 K, 773 K, 873 K, 973 K, 1073 K, 1273 K, 1473 K, and 1673 K), and each concentration ($x = 0.005, 0.01, 0.04, 0.08, 0.12, 0.16, \text{ and } 0.20$) we performed runs with 20 different di-interstitial binding energies to estimate the sensitivity. Fig. 10 illustrates the uncertainty in diffusivities at

three representative temperatures (673 K, 1073 K, and 1673 K). At the relatively low temperature (Fig. 10(a)), we can observe three distinct regions of diffusivities. For low di-interstitial binding energies ($BE < -0.10$ eV) the diffusivities are relatively low. This is consistent with the fact that for low BE the di-interstitials will form and quickly dissociate to mono-interstitials. Thus, diffusivities are mostly dominated by I_1 migration. For intermediate binding energies ($-0.10 < BE < +0.19$ eV), the diffusivities are guided by a combined effect of I_1 and I_2 migration energies. In this range of binding energies, the I_2 clusters are relatively weakly repulsive. For the high binding energy regimes ($BE > +0.19$ eV), the diffusivities are predicted to be the highest. This is because in this regime I_2 clusters are relatively stable due to a stronger attraction. As the migration energy of I_2 is less than I_1 , the overall diffusivities in this region of binding energies are predicted to be the highest. Similar behavior is observed for 1073 K and 1673 K. However, the gap between the three distinct regimes of binding energy on diffusivities becomes less pronounced with the increase in temperature.

In addition to the diffusivities, we have estimated the sensitivity of the activation energies based on the binding energy. Fig. 11 reports the effective activation energies estimated for the entire range of binding energies. The data shows three distinct regions of activation energies. It is clear that at lower binding energies (< -0.4 eV) the activation energies remain almost identical to the I_1 migration energy of 0.81 eV, and at higher binding energies (> 0.4 eV) the activation energies are much closer to the I_2 migration energy of 0.47 eV. Interestingly, the effective activation energies show a combined I_1 and I_2 response only within a limited intermediate range of binding energies. The sensitivity analysis of activation energies also indicates a concentration dependent variation in the three regions, which is clear from the 2D representation of the effective activation energy plot in Fig. 11(b). For very low concentrations ($x < 0.01$), the effective I_1 activation energy is realized for $BE < -0.10$ eV; while the effective I_2 activation energy is realized for $BE > 0.20$ eV. For $x < 0.01$, the mixed I_1 and I_2 activation energy response is observed for $-0.10 < BE < +0.20$. For high non-stoichiometry, e.g. $x = 0.20$, the mixed I_1 and I_2 activation energy is observed over a larger range of binding energies ($-0.30 < BE < +0.40$).

Considering the case of $x = 0.20$, we have further analyzed the probability of different events taking place during the kMC simulation at 1073 K. The possible events in the kMC model are I_1 migration, I_2 migration, and I_2 dissociation ($I_2 \rightarrow I_1 + I_1$). The data is plotted as a percentage of individual events taking place by tracking all the events during simulation (Fig. 12). The results show that for $BE < -0.30$ eV, I_1 migration and I_2 dissociation dominates, which means that within this range of BE di-interstitial clusters are unstable and dissociate as soon as they form. BE of -0.38 eV in model 2O_i_2009 falls in this range. The I_2 migration event dominates for $BE > +0.30$ eV. In this region of BE, the di-interstitials once formed are mostly stable. The events show a mixed character of I_1 migration, I_2 migration, and I_2 dissociation in the intermediate range of BE, which includes the BE of -0.06 eV with 2O_i_2015. Even though the data

is shown for a particular concentration and temperature ($x = 0.20$ and 1073 K), the overall trend of the individual events at other concentrations and temperatures are similar.

5. Summary and conclusions

We have performed a detailed analysis of the effect of temperature and non-stoichiometry on the overall oxygen transport in hyperstoichiometric urania fuel (UO_{2+x}) using a kMC model based on DFT energetics for oxygen interstitial clusters. Our results show that incorporation of di-interstitial cluster formation in to the model enhanced the oxygen interstitial diffusivities compared to the mono-interstitial model. The predicted diffusivities from di-interstitial models compare well with the experimental results for $x > 0.1$. The diffusivity-concentration relation shows a maximum in diffusivity due to the competition between the diffusing species and blocking. Since the migration energy of di-interstitials is lower than the migration energy of mono-interstitials, an increase in the total number of di-interstitials in 2O_i_{2015} compared to 2O_i_{2009} increased the diffusivities even further. While diffusivities increase with the increase in temperature for the di-interstitial models, it is clear that the binding energy of di-interstitials strongly influences the nature/mechanism of diffusion. This is due to the fact that the magnitude of binding energy guides the stability of the di-interstitials in the system.

A sensitivity analysis was performed to evaluate the influence of binding energies on the overall diffusivities. The activation energies calculated from the sensitivity analysis show three distinct regions based on the binding energy of I_2 : (i) for low binding energies, diffusion is dominated by mono-interstitial migrations, (ii) for high binding energies, oxygen transport is dominated by di-interstitial migrations, while (iii) for intermediate binding energies, oxygen diffusion is guided by a combination of mono- and di-interstitial migrations. The range of low, intermediate, and high binding energy varies with non-stoichiometry. The intermediate range is smaller at lower non-stoichiometry ($x < 0.01$ eV), and increases with the increase in non-stoichiometry ($x = 0.20$).

From this analysis it is clear that only within a small range of binding energies of I_2 , a combined effect of I_1 and I_2 migration events contribute significantly to the diffusion of oxygen interstitials. The binding energy of -0.38 eV for 2O_i_{2009} falls in the low binding energy region (data joined by dotted lines in Fig. 11), which results in an effective activation energy close to that of mono-interstitials. The binding energy of -0.06 eV for Model 2O_i_{2015} falls in the intermediate region. Therefore, the effective activation energies for 2O_i_{2015} show a combined effect of I_1 and I_2 migration barrier that results in an activation energy that is sensitive to non-stoichiometry and temperature (data joined by solid line in Fig. 11). Outside of this intermediate range of binding energies, the effective activation energy is independent of non-stoichiometry and temperature. This analysis shows that the input binding energy affects the predicted interstitial structures and migration.

Since we have performed only a limited OFAT sensitivity analysis, this work may be extended to sample the entire rate catalog, and determine the sensitivity of all the input parameters. In that case, sensitivity may then be measured by monitoring changes in the output, e.g. by partial derivatives or linear regression of the output results with respect to the model input variables. This sensitivity analysis approach can be directly applied to a wide variety of systems to quantitatively examine the influence of input model parameters on the predicted properties.

It is important to emphasize that the current kMC models only include mono- and di-interstitials in evaluating oxygen diffusion response in UO_{2+x} . With the aim of understanding individual contributions to the experimentally observed oxygen diffusivities in hyperstoichiometric urania, we have performed a systematic investigation to estimate the influence of I_1 and I_2 on the overall diffusivities. While the model shows a lot of promise, from the range of diffusivities calculated for each concentration at various temperatures in our sensitivity analysis, it is clear that only I_1 and I_2 description of the interstitial clusters is not enough to completely describe the experimentally observed oxygen diffusion response in hyperstoichiometric Urania. For example, first principles calculations by Andersson *et al.* [19] have shown that quad-interstitial clusters (I_4) have a higher stability and will impact the oxygen ion diffusivities. Therefore, the addition of other energetically stable clusters reported in the literature [19, 23] to the kMC model is expected to improve the comparison of oxygen transport in UO_{2+x} with experiment.

6. Acknowledgements

This research is being performed using funding received from the DOE Office of Nuclear Energy's Nuclear Energy University Programs. [D.A.A. and B.P.U. were funded by the U.S. Department of Energy, Office of Nuclear Energy, Nuclear Energy Advanced Modeling and Simulation \(NEAMS\) program.](#)

References:

- [1] J. Wang, R.C. Ewing, U. Becker, Scientific Reports 4 (2014) 1-5.
- [2] H.R. Hoekstra, A. Santoro, S. Siegel, Journal of Inorganic & Nuclear Chemistry 18 (1961) 166-178.
- [3] P.E. Blackburn, J. Weissbart, E.A. Gulbranson, Journal of Physical Chemistry 62 (1958) 902-908.
- [4] J.S. Anderson, L.E.J. Roberts, E.A. Harper, Journal of the Chemical Society (Resumed) (1955) 3946-3959.
- [5] R.J. McEachern, P. Taylor, Journal of Nuclear Materials 254 (1998) 87-121.
- [6] F. Gronvold, Journal of Inorganic & Nuclear Chemistry 1 (1955) 357-370.
- [7] B.E. Schaner, Journal of Nuclear Materials 2 (1960) 110-120.
- [8] J.K. Fink, Journal of Nuclear Materials 279 (2000) 1-18.
- [9] J.T. White, A.T. Nelson, Journal of Nuclear Materials 443 (2013) 342-350.
- [10] B.T.M. Willis, Acta Crystallographica Section A 34 (1978) 88-90.
- [11] D.J.M. Bevan, I.E. Grey, B.T.M. Willis, Journal of Solid State Chemistry 61 (1986) 1-7.

- [12] L. Desgranges, G. Baldinozzi, G. Rousseau, J.-C. Niepce, G. Calvarin, *Inorganic Chemistry* 48 (2009) 7585-7592.
- [13] H. He, D. Shoesmith, *Physical Chemistry Chemical Physics* 12 (2010) 8108-8117.
- [14] S.D. Conradson, D. Manara, F. Wastin, D.L. Clark, G.H. Lander, L.A. Morales, J. Rebizant, V.V. Rondinella, *Inorganic Chemistry* 43 (2004) 6922-6935.
- [15] G.C. Allen, P.A. Tempest, J.W. Tyler, *Nature* 295 (1982) 48-49.
- [16] A.D. Whapham, B.E. Sheldon, *Philosophical Magazine* 12 (1965) 1179-1192.
- [17] H.Y. Geng, Y. Chen, Y. Kaneta, M. Kinoshita, *Physical Review B* 77 (2008) 180101(R).
- [18] D.A. Andersson, T. Watanabe, C. Deo, B.P. Uberuaga, *Physical Review B* 80 (2009) 060101(R).
- [19] D.A. Andersson, J. Lezama, B.P. Uberuaga, C. Deo, S.D. Conradson, *Physical Review B* 79 (2009) 024110.
- [20] C.B. Basak, A.K. Sengupta, H.S. Kamath, *Journal of Alloys and Compounds* 360 (2003) 210-216.
- [21] D.S. Aidhy, P.C. Millett, T. Desai, D. Wolf, S.R. Phillpot, *Physical Review B* 80 (2009) 104107.
- [22] T. Ichinomiya, B.P. Uberuaga, K.E. Sickafus, Y. Nishiura, M. Itakura, Y. Chen, Y. Kaneta, M. Kinoshita, *Journal of Nuclear Materials* 384 (2009) 315-321.
- [23] X.M. Bai, A. El-Azab, J.G. Yu, T.R. Allen, *Journal of Physics-Condensed Matter* 25 (2013) 015003.
- [24] G.E. Murch, D.H. Bradhurst, H.J. Debruin, *Philosophical Magazine* 32 (1975) 1141-1150.
- [25] B. Dorado, D.A. Andersson, C.R. Stanek, M. Bertolus, B.P. Uberuaga, G. Martin, M. Freyss, P. Garcia, *Physical Review B* 86 (2012) 035110.
- [26] B. Dorado, P. Garcia, G. Carlot, C. Davoisne, M. Fraczekiewicz, B. Pasquet, M. Freyss, C. Valot, G. Baldinozzi, D. Simeone, M. Bertolus, *Physical Review B* 83 (2011) 035126.
- [27] D.A. Andersson, F.J. Espinosa-Faller, B.P. Uberuaga, S.D. Conradson, *Journal of Chemical Physics* 136 (2012) 234702.
- [28] P. Contamin, J.J. Bacmann, J.F. Marin, *Journal of Nuclear Materials* 42 (1972) 54-64.
- [29] J.F. Marin, P. Contamin, *Journal of Nuclear Materials* 30 (1969) 16-25.
- [30] J.C. Helton, J.D. Johnson, C.J. Sallaberry, C.B. Storlie, *Reliability Engineering & System Safety* 91 (2006) 1175-1209.
- [31] A.D. Kiureghian, O. Ditlevsen, *Structural Safety* 31 (2009) 105-112.
- [32] A. Saltelli, M. Ratto, T. Andres, F. Campolongo, J. Cariboni, D. Gatelli, M. Saisana, S. Tarantola, *Global Sensitivity Analysis: The Primer*, John Wiley & Sons, Ltd, West Sussex, England, 2008, p. 304.

TABLE**Table 1.** List of mono- and di-interstitial energies used in the kMC models

Interstitials	Migration Barrier (eV)	Binding Energy (eV)	
		2O _i _2009	2O _i _2015
Mono (I ₁)	0.81	-	-
Di (I ₂)	0.47	-0.38 (0.43 eV)*	-0.06 (0.75 eV)*

* Values in parenthesis represent the effective barrier for dissolving a di-interstitial, which is also referred as the dissociation energy.

FIGURES

Fig. 1. (Color online) Structure of the defect clusters presented by highlighting the oxygen sublattices in UO_{2+x} . For clarity face-centered U-atoms are not shown. The interstitial oxygen atoms are shown by the multi-colored spheres. Fig. (a) represents a typical case of mono-interstitials, where the interstitials are not occupying the first nearest neighbor interstitial sites ($> 3.866 \text{ \AA}$, assuming the UO_2 lattice parameter of $5.468 \text{ \AA}$). For each oxygen mono-interstitial there are 12 un-occupied first nearest neighbor sites. Fig. (b) illustrates a di-interstitial cluster, where two oxygen interstitials are occupying the first nearest neighbor site, which is at $3.866 \text{ \AA}$. The di-interstitial can migrate or split into two mono-interstitials during defect evolution. The displacements known to occur for these interstitials are not shown for clarity. The plot is generated following Ref. [1].

Fig. 2. (Color online) Schematic representation of the structure of undistorted di-interstitial I_2^0 (represented by lower case letters a , b , and c), and split di-interstitial I_2^X (represented by upper case letters A , B , and C). Only oxygen sublattice is shown for clarity. The I_2^0 structure is generated by two oxygen interstitials (a and b) in the octahedral interstitial sites with one lattice oxygen (c) in the Urania lattice, while the I_2^X structure constitutes an equiaxed or equilateral triangle situated on top of an empty fluorite lattice oxygen site (c) shown by the blue dashed line connecting A - B - C . The lattice site d is indicated to explain the mechanism of di-interstitial migration. The plot is adapted from Ref. [19].

Fig. 3. (Color online) Change in diffusivity of oxygen interstitials with non-stoichiometry (x) in UO_{2+x} at $T = 1073 \text{ K}$. The predicted diffusivities from mono-interstitial and two different di-interstitial models are compared with experiment [28, 29].

Fig. 4. (Color online) Effect of system size on (a) diffusivity and (b) the evolution of di-interstitials at 1073 K for UO_{2+x} where $x \leq 0.20$ with 2O_i_2015. The system sizes computed for comparison are $4 \times 4 \times 4$; $6 \times 6 \times 6$; $8 \times 8 \times 8$; and $10 \times 10 \times 10$ cubic supercells. A $6 \times 6 \times 6$ system size is enough to describe the structural evolution.

Fig. 5. (Color online) Effect of temperature on diffusivity, where the temperatures considered are $T = 673 - 1073$ K with a 100 K increment and at 1273 K - 1673 K with a 200 K increment with $2O_{i_2015}$ for $x < 0.25$. The diffusivities systematically increase with the increase in temperature.

Fig. 6. (Color online) Comparison of experimental diffusivities with diffusivities predicted using $2O_i$ _2015 between 673 K - 1073 K. The solid symbols are the kMC predicted values while the respective open symbols correspond to the experimental results. Most of the experimental results are taken from Contamin *et al.* [28]. The experimental data at 1073 K contains a mixture of data from Contamin *et al.* [28] and Marin *et al.* [29]. The comparison of predicted diffusivities with experiment is better at higher temperatures and deviates more at lower temperatures (e.g. at 673 K)

Fig. 7. (Color online) The effect of temperature on diffusivity is plotted with a reciprocal of temperature to show the Arrhenius relationship. Activation energy at each concentration is calculated using the slope of the fitted lines. The data plotted here are presented for $2O_i_{2015}$.

Fig. 8. (Color online) (a) The variation of effective activation energies with concentration predicted by all the models. While $2O_i$ _2009 predict migration energies of ~ 0.81 eV (same as $1O_i$ _2009), $2O_i$ _2015 shows a combined effect of mono- and di-interstitial migration barriers. (b) The structural analysis indicates the ratio of di-interstitials increases almost linearly with the increase in non-stoichiometry in $2O_i$ _2015, while the ratio remains constant (nearly zero) with $2O_i$ _2009 at 1073 K.

Fig. 9. (Color online) The effect of temperature on the evolution of mono- and di-interstitials is calculated for $2O_i_{2015}$. The results show that concentration effect is more pronounced than temperature in stabilizing di-interstitials.

Fig. 10. (Color online) The overall variation of diffusivities calculated at three different representative temperatures (673 K, 1073 K, and 1673 K) using the KMC model with binding energies varying between -0.81 eV – +1.09 eV. The available experimental results (shown as filled circles) are included for comparison.

Fig. 11. (Color online) Sensitivity analysis of the effective activation energies with respect to binding energies varying between -0.81 eV – +1.09 eV. The activation energy data joined with dotted line corresponds to 2O_i_2009, while the data joined with solid line is for 2O_i_2015. Fig. (a) represents the 3D surface plot while (b) represents the 2D surface plot for the activation energies. While Fig. (a) provides a better visual guidance of binding energy dependence on activation energy, Fig. (b) provides a better representation of the intermediate range of binding energy dependence on stoichiometry.

Fig. 12. (Color online) Illustration of the sensitivity in frequency of mono-interstitial (I_1) migration, di-interstitial (I_2) migration, and di-interstitial dissociation ($I_2 \rightarrow I_1 + I_1$) events estimated at a typical temperature of 1073 K and $x = 0.20$. I_1 migration and I_2 dissociation are the primary events with 2O_i_2009 (BE = -0.38 eV, highlighted by the triangle on the BE axis), while I_2 migration is the most frequent event with model 2O_i_2015 (BE = -0.06 eV, represented by the star symbol). Similar event frequencies are observed for all other investigated temperatures and concentrations.