A study of Uranium adsorption to single-crystal Tungsten

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Abstract:

In this study we explore the adsorption of uranium to the (110) plane of tungsten. Potential functions were constructed to describe the interaction of adsorbed uranium atoms with the tungsten surface and the lateral interaction between adsorbed uranium atoms. Next, the behavior of the uranium adlayer under different conditions was studied through a Monte Carlo simulation of the grand canonical Hamiltonian in an off-lattice model. Our results are consistent with available studies in the literature. The simulation results indicate that the temperature and dipole-dipole interactions play an important role in governing the adsorption process.

Introduction:

Nuclear power is a key energy alternative for efficient generation of electricity. However, an essential factor in nuclear power is the safe management of spent fuel. Electrochemical reprocessing (or Pyroprocessing) of used nuclear fuel is a promising technology that has been extensively studied (e.g [1-4]). This process allows for the selective recovery of actinides from used fuels. The process has many advantages such as compactness of process equipment and the potential of the development of the integrated irradiation- reprocessing facility which can significantly reduce the costly and complicated transport of nuclear materials [5].

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For effectively extracting actinides from the used nuclear fuel using electrochemical separation, fundamental data, such as apparent potentials of actinides in the electrolyte, must be well known. However, there is currently a shortage in the thermodynamic properties of the materials of interest especially under the extreme conditions of pyroprocessing. Cyclic Voltammetry (CV) is one of the main tools to study the reactivity of different species and is a commonly used as a tool to investigate the electrochemical behavior of uranium [6-9] in the molten salt for pyroprocessing applications. However, the molecular-scale processes that contribute to the current measured in CV are hard to determine. Moreover, it is known that adsorbed molecules can lead to changes of their electrochemical activity [10, 11] which ultimately results in difficulties in interpreting the recorded CV data. The main aim of this study is to theoretically explore the interfacial processes involved with uranium adsorption to a solid electrode. We choose to study uranium adsorption to tungsten for many reasons. First, uranium adsorption to tungsten has been studied both experimentally and theoretically in the past [12-14] and this gives us a point of reference. Second, tungsten is used as a working electrode candidate in cyclic voltammetry studies and uranium adsorption to the tungsten electrode has been known to complicate the interpretation of cyclic voltammetry measurements and models. For example, it was shown by Serrano and Taxil [15] that uranium adsorption occurs in NaCl-KCl and the formation of an insoluble compound on the electrode was detected. The studies also showed that the current followed a Langmuir isotherm. Prabhakara et al. [8] confirmed the three electron transfer process during the reduction of U(III) to U metal and the process of uranium adsorption was recognized to occur in molten LiCl-KCl

eutectic. Therefore, a clear and fundamental understanding of this phenomenon is necessary to allow the collection of reliable database, and enable more accurate modeling of electrochemical processes in pyroprocessing.

In the present study, we apply the multi-scale computational approach by combining first principles DFT calculations and statistical mechanics to understand thermodynamic mechanisms of uranium adsorption under different conditions. For our purposes it will suffice to examine static MC simulations since typical experimental sweep rates are much slower than computationally attainable sweep rates and the assumption of quasi-equilibrium is valid [16].

Computational Details:

In this study we investigate uranium electro-adsorption to both the (110) and (100) surfaces of tungsten using a $p(1\times 2)$ structure. This requires knowledge of the corrugation potential which describes the interaction of the uranium with the tungsten surface. Density functional theory calculations were employed to determine this potential. The slab supercell approach with periodic boundary conditions was applied to study the surface. The metal surface was modeled by repeated slabs of eight metal layers separated by a vacuum equivalent to eight metal layers in thickness. The density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) code within the framework of the projector augmented plane wave approach [17]. The electronic exchange-correlation were treated with the generalized gradient –corrected exchange-correlation functionals (GGA) as parametrized by Perdew, Burke and Erzenhof (PBE)[18] and the Brillouin zone was sampled using the Monkhorst-Pack method [19]. The plane wave cutoff energy was 350 eV and a k-point mesh of $9\times 9\times 1$ was used to sample the Brillouin zone. The calculations were checked for convergence

with respect to the energy cutoff and the k-point mesh being used. Furthermore, the calculations were checked for size effects and it was determined that eight layers was sufficient to eliminate any significant size-effects. Spin-polarization was taken into account in all calculations and the Methfessel-Paxton method [20] was employed to determine electron occupancies with a smearing width of 0.1 eV. The convergence criterion for the electronic self-consistent calculations was set to 10^{-6} eV. In addition, the atomic positions of the top two layers were relaxed using the conjugate-gradient method until the difference in total energy between two consecutive ionic steps was less than 10^{-4} eV.

The surface energies for W(110) and W(100) surfaces were determined to be 3.29 J/m^2 and 4.14 J/m^2 respectively. These results are consistent with ab initio results with localized density approximation recently reported by Wang et al. [21] who reported the values of 3.649 J/m^2 and 4.403 J/m^2 . This difference is to be expected as outlined by Rikvold et al. [22] because surface energy calculations are known to be very sensitive to the form of the exchange-correlation functionals and DFT-LDA values for the surface energy are known to be larger than those calculated with DFT-GGA which are reported in this paper. Furthermore, the convergence criteria for the ionic steps used by the authors were different from our convergence criteria (converging the forces to $0.2 \text{ eV/\AA}$ vs. converging the total energy to a tolerance of 10^{-4} eV). The results are consistent with experimental values as shown in table 1.

Furthermore, the workfunction of the W(110) and W(100) surfaces were found to be 4.82 eV and 4.3 eV respectively. These values are in good agreement with recent DFT-GGA calculations

[21] which obtained the values of 4.76 eV and 4.1 eV respectively. In addition, these values are consistent with other studies. The results are summarized in table 1.

Table 1. The surface energy and work function of the (110) and (100) surfaces of W.

Surface Energy in (J/m ²)	W(110) J/m ²	W(100) J/m ²	Work function in eV	W(110) eV	W(100) eV
This work	3.30	4.14	This work	4.82	4.138
DFT-LDA [21]	3.649	4.403	DFT-GGA [21]	4.76	4.09
Experiment[23-25]	3.265-3.68	1.8-5.38	Experiment [14, 26, 27]	4.9-5.3	4.35-4.64

From the results in table 1 it can be seen that the W(110) plane is more stable than the W(100) plane in agreement with previous studies. Therefore, and considering the intensive computational resources needed for the Monte Carlo simulation of the off-lattice model, we limited our study to the W (110) plane.

After the calculations for the clean slab were completed, uranium adsorption energies were determined by using the relaxed atomic positions from the W slabs and then allowing the uranium atom to relax until the difference in energy between two ionic steps was less than 10^{-4} eV. By following this procedure, we were able to determine the optimum adsorption configurations and also the adsorption energies. It was found that the adsorption energy of uranium to the W (110) surface was (-87.33 meV). To determine the adsorption energy of uranium to the tungsten surfaces at different configurations, the uranium atom was placed at different locations on the W surfaces and the electronic self-consistent calculation was performed with a convergence criterion of 10^{-6} eV. The results are summarized in table 2. Only unique points are listed and points related by symmetry are not listed. In our notation, the x

coordinate is along the $[1\bar{1}0]$ crystal direction and the y coordinate in our terminology is along the $[001]$ crystal direction.

Table 2. DFT results of the corrugation potential for U/W(110) in terms of fractional coordinates. More negative values indicate stronger binding. In this case (0,0) indicates the on-top site for the $p(1\times 1)$ structure ($L_x = a\sqrt{2}$)

x/L_x	y/a	$U_{DFT}(x,y)$ (meV)
0	0	1435.73 (on-top site)
0	0.25	466.93
0	0.5	-87.33 (hollow site)
0.25	0	347.46
0.25	0.25	695.2
0.5	0	419.56

The results of this calculation are consistent with our expectations. The on-top sites are expected to be the most unfavorable and this is indeed reflected with the result of our calculation which shows that this site has the highest positive value for the adsorption energy. On the other hand, the hollow site is expected to be the most favorable location for adsorption and this is again confirmed by our calculations.

By using the symmetry of the surface and also implementing cubic spline interpolation between the calculated points, we determine the potential energy surface to describe the corrugation potential. This U/W(110) corrugation potential energy surface for the is plotted in figure 1.

Figure 1. The Potential function for the interaction of the uranium atom with W (110) surface.

Equilibrium off-lattice simulations:

In this study we will utilize an off-lattice model for adsorption similar to the one proposed by Mitchell et al. [28]. This model comprises two parallel planes. One plane represents the effective tungsten surface (the surface layer) and the other plane represents the solution near the tungsten surface (the solution layer). Periodic boundary conditions will be used in all simulations to eliminate edge effects. In this model, a particle can diffuse on the surface layer or it can transfer between the two layers through the process of adsorption/desorption. The model is illustrated in figure 2.

Figure 2. An illustration of Mitchell's off-lattice model

The grand canonical Hamiltonian is given as:

$$\mathcal{H} = -\frac{1}{2} \sum_{i \neq j} U_{int}(r_{ij}) c_i c_j + \sum_{i=1}^N U_{ext}(\mathbf{r}_i) c_i - \mu \sum_{i=1}^N c_i - k_B T \ln [(N - \sum_{i=1}^N c_i)!] \quad (1)$$

where c_i denotes whether the i th particle is in the solution layer ($c_i = 0$) or in the surface layer ($c_i = 1$), $U_{int}(r_{ij})$ is the interaction potential between two particles i and j , $U_{ext}(\mathbf{r}_i)$ is external potential which here is equivalent to the corrugation potential (which was determined through DFT calculations in the previous section), μ is the electrochemical potential and N is the total number of particles in the simulation, k_B is the Boltzmann constant and T is the temperature under which the simulation is being performed. It should be noted that all values of μ in these off-lattice simulation require a shift when compared to lattice-gas models [28].

Next, we propose a functional form for the lateral interaction potential between adsorbed uranium atoms by a truncated Lennard-Jones potential for small separations and as $1/r^3$ repulsion for large separations. As explained by Mitchell et al. [28] this $1/r^3$ potential is most likely associated with dipole-dipole and lattice mediated interactions. Due to the success of the potential functional form proposed by the authors we will use a similar form:

$$U_{int}(r) = \begin{cases} \phi_{nnn} \left(\frac{a\sqrt{2}}{D_{ion}} \right)^3 - 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - \phi_{nnn} \left(\frac{\sqrt{2}}{5} \right)^3 & \text{if } r < D_{ion} \\ \phi_{nnn} \left(\frac{a\sqrt{2}}{D_{ion}} \right)^3 - \phi_{nnn} \left(\frac{\sqrt{2}}{5} \right)^3 & \text{if } D_{ion} \leq r \leq 5a \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

Here $D_{ion} = 2R_{ion}$ is the diameter of uranium (where $R_{ion} = 2.41 \text{ \AA}$)[27], the parameter ϕ_{nnn} determines the strength of the dipolar interactions. This value is currently unknown for our case since there is currently no available experimental data to compare the simulation to. Mitchell[28] used a value of $\phi_{nnn} = -26 \text{ meV}$ for their simulations and we expect this parameter to have a similar order of magnitude in our case. Therefore, we will run the simulation for different values of the parameter and examine its effect on the results. Finally, and by requiring the continuity of the function and its first derivative at $r = D_{ion}$ we find that

$$\sigma = R_{ion} \text{ and } \epsilon = -\frac{\phi_{nnn}}{8} \left(\frac{a\sqrt{2}}{D_{ion}} \right)^3.$$

The validity of truncating the potential is illustrated in figure 2 where we plotted the interaction potential as a function of distance without the imposed truncation above. It can be clearly seen that the function approaches zero after a distance of $5a$ and that it is a reasonable assumption to truncate the potential for computational efficiency.

Figure 3. The lateral interaction potential plotted as a function of distance. It can be clearly seen that the proposed truncation of the interactions is justified since the potential approaches zero at a distance of $5a$.

Furthermore, and to do another test of this approximate potential function, two uranium atoms were placed at different hollow sites (adsorption sites) in the $p(1 \times 2)$ slab that was used previously, and the interaction energy was estimated. The results were also compared with the predictions from the potential function and are summarized in table 3 below.

Table 3. Comparison between the DFT estimates for the pair interaction energy for adsorbed uranium atoms and predictions based on the proposed lateral interaction potential

Distance	DFT	Potential with $\phi_{nnn} = -10 \text{ meV}$	Potential with $\phi_{nnn} = -26 \text{ meV}$	Potential with $\phi_{nnn} = -40 \text{ meV}$
$r = 2.74 \text{ \AA}$	7.2 eV	2.71 eV	7 eV	10.8 eV
$r = 3.165 \text{ \AA}$	1.8 eV	0.6 eV	1.52 eV	2.33 eV

These results suggest that the potential function and the parameters used are a reasonable first approximation to be used in this parametric study to explore the important role different mechanisms play in governing the adsorption process.

The Monte Carlo Simulation:

The Metropolis Monte Carlo algorithm is used for our simulations to describe the equilibrium properties of both the adsorbed uranium on the W (110) surface. Furthermore, the effects of the temperature and the dipolar interactions on the adsorption process will be explored.

Monte Carlo simulations were performed on systems with $L = 32$ where the dimensions of the W(110) lattice were $(L \times a\sqrt{2}, La)$ and the absence of significant size-effects was checked by additional simulations for $L = 40$. Our simulations account for adsorption/desorption and lateral diffusion of adsorbed particles on the surface layer. This is an important detail that was not previously accounted for in theoretical investigations of uranium adsorption. Including the surface diffusion in the model is important in light of recent experimental evidence from impedance spectra[29]. When attempting a diffusion move for particle i , a random displacement vector $d\mathbf{r}$ (uniformly distributed within a circle of radius $R_{ion}/4$) is added to the position vector of particle i $\mathbf{r}_i$. In the simulation, we randomly select a uranium atom. If the atom is adsorbed to the surface then lateral diffusion on the surface or desorption are attempted, otherwise adsorption to the surface layer is attempted. According to the Metropolis algorithm the new configuration of the system is accepted with a probability:

$$P = \min \left[1, \exp \left(-\Delta\mathcal{H}/k_B T \right) \right] \quad (3)$$

where $\Delta\mathcal{H}$ is the change in the Hamiltonian that would result from the acceptance of the proposed move. In our simulations it was determined that 4000 sweeps of the lattice were sufficient to achieve equilibrium at each μ value.

Results and discussion:

The Monte Carlo simulations were performed using the off-lattice grand canonical Hamiltonian described in the previous section. To study the effects of temperature on the adsorption process from a fundamental point of view, simulations were performed at two different temperatures. In figure 4, the adsorption isotherm at temperatures $T = 290$ K and $T = 773$ K are recorded with the dipolar interaction parameter set to $\phi_{nnn} = -26$ meV. Room temperature is clearly not relevant for pyroprocessing applications, but it was chosen so that the temperature effects on the adsorption process can be clearly observed. The results indicate that the coverage of the tungsten surface reaches a plateau value of about 0.4 ML for the simulation at 773 K and about 0.31 ML at 290 K. In addition, we notice that simulation at 290 K levels off faster than the simulation at the higher temperature and this observation agrees with our understanding of the metropolis algorithm since we are more likely to reject energetically unfavorable moves for a smaller temperature. In the case of a higher temperature simulation, the thermal energy allows for a greater likelihood of acceptance of energetically unfavorable moves and as a result the isotherm continues to display appreciable change at higher values of the chemical potential.

Figure 4. Simulated coverage isotherms vs. electrochemical potential, computed for uranium adsorption on a 32x32 W(110) at T=290 K and T=773 K with the value of the parameter for the dipolar interaction set to (-26 meV).

In addition, it is observed that at higher temperatures, a higher chemical potential is needed to initiate adsorption. Figure 4 shows that adsorption for the 290 K simulation starts around 200 meV whereas it barely begins at 400 meV for the 773 K simulation. This observation may have some implications for investigators studying thermodynamic properties of certain species using electrochemical measurements (such as cyclic voltammetry) where adsorption to the electrode typically poses a challenge and complicates the interpretation of the recorded data. If feasible for the materials under scrutiny and if the range of the needed potential scan is not large, it may be possible to avoid the complications that arise with adsorption by performing the experiment at higher temperatures.

Next, the effects of the dipole-dipole interaction on adsorption were explored. Three different simulations were performed at 773 K with the dipolar interaction parameter ϕ_{nnn} set to (-10 meV, -26 meV and -40 meV). The results are shown in figure 5.

Figure 5. Simulated coverage isotherms vs. electrochemical potential, computed for uranium adsorption on a 32x32 W(110) at T=773 K with three different value of the parameter for the dipolar interaction.

Upon examination of figure 5 it is clear that the long range dipolar interaction plays an important role in governing the adsorption process. We observe that for a more negative dipolar strength parameter, the adsorption isotherm appears to level off at smaller coverage values. This observation agrees with our intuition as larger dipole-dipole interactions lead to a larger repulsion between adsorbing uranium atoms. This means that much higher values of the chemical potential would be needed to overcome this repulsion to allow larger values of coverage.

Moreover, it should be pointed out that our results are consistent with the ones recently reported by Kwak et al. [12]. In that work, the authors used the coupled cluster expansion of Cl/U/W(100) surface to develop a potential surface which was consequently used in Monte Carlo simulations using the grand canonical Hamiltonian. The investigators included the chlorine ions in the simulation but the effects of surface diffusion were not accounted for and the authors used a lattice-gas model which is different from our approach. The authors reported that the uranium adsorption isotherm levels off at around 0.33 ML and they give the explanation that the uranium adsorption sites are blocked by chloride ions which adsorb more easily. Therefore, a direct comparison with that study is not possible since we did not account for the chloride in our simulations. Nevertheless, the adsorption isotherm curves show qualitative agreement with Kwak's study. In our simulation, it is clear that the coverage continues to rise after the initial levelling off and this is also observed in Kwak's study. This observation might be unique to uranium as it is not observed in halide adsorption studies where the isotherm curves usually level off at the saturation point immediately as was observed from both experimental studies and off-lattice and lattice simulations [16, 28, 30]. However, our study indicates that even in the absence of chloride, and despite exploring the adsorption process under different conditions and scanning a large range of the chemical potential, the electrode coverage appears to level off at 0.5 ML. This observation agrees with previous experimental studies [14] and means that large radius of uranium atoms and the dipole-dipole interactions between these atoms also plays an important role in limiting the adsorption process. A more rigorous analysis would require comparison with experimental data

for electrode coverage, but in the absence of such data using different values of the parameters is a useful method to investigate the behavior of the adlayer.

Moreover, the final configurations for the different situations studied are included in figure 6 below.

(a)

(b)

(c)

(d)

Figure 6. The equilibrium configurations for adsorbed uranium atoms on the Tungsten (110) plane (a) $T = 773$ K and $\phi_{nnn} = 40$ meV (b) $T = 773$ K and $\phi_{nnn} = 26$ meV (c) $T = 290$ K and $\phi_{nnn} = 26$ meV (d) $T = 773$ K and $\phi_{nnn} = 10$ meV.

Conclusions:

In this study we examine the adsorption of uranium to the (110) plane of tungsten. We utilize an off-lattice model to investigate the behavior of the adlayer. This required constructing

potential functions to describe the different interactions in the system. The grand canonical Hamiltonian was used in the Monte Carlo simulations and the behavior of the adlayer under different conditions was investigated. Higher values of coverage were observed at higher temperatures. Moreover, stronger dipole-dipole interactions were found to limit the adsorption process. These findings may have implications for adsorption processes which occur during electrochemical measurements.

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