

First principles thermodynamic studies for recycling spent nuclear fuels using electrorefining with a molten salt electrolyte



Seunghyo Noh^a, Joonhee Kang^a, Dohyun Kwak^a, Peter Fischer^b, Byungchan Han^{a,c,*}

^a Department of Energy Systems Engineering, DGIST, Daegu 711-873, Republic of Korea

^b CXRO/LBNL, MS 2-400 1, Cyclotron Rd., Berkeley, CA 94720, USA

^c DGIST-LBNL Joint Research Center, DGIST, Daegu 711-873, Republic of Korea

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ABSTRACT

Using first principles DFT (density functional theory), we have examined the thermochemical mechanism of electrorefining spent uranium (U) from a LiCl–KCl molten salt on a tungsten (W) surface. We calculated 197 different U/W(110) surfaces to identify the most thermodynamically and electrochemically stable structures as a function of U and Cl coverages. The results indicate that local structures of the double-layer interface between the W(110) surface and the LiCl–KCl salt are the key factors governing the electrorefining performance. The results also provide important thermodynamic properties for the design of efficient recycling systems for spent nuclear fuels, such as pyroprocessing technologies, and may be applicable as well to general electrochemical applications involving strong redox reactions of transition metals exposed to non-aqueous solutions.

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1. Introduction

Decreasing the use of fossil fuels is a key challenge. Although fuel cells, solar cells and Li-ion batteries provide renewable energy solutions, widespread commercialization to meet the large-scale energy demand has many bottlenecks, largely because of inefficiency and the high cost of materials [1].

Nuclear power efficiently generates significant amounts of electricity without greenhouse gas emissions. These merits were, however, seriously damaged by the recent catastrophe in Japan. In addition to safe operation, the other essential factor needed for a resurgence of nuclear power is the safe management of spent nuclear fuels. In Korea, the storage capacity for spent nuclear fuels is expected to reach saturation in the near future, and the search for new storage locations is very challenging because of social resistance.

Another, possibly better, option for handling spent nuclear fuels is to make the fuel cycle closed by recycling the spent fuels. For this purpose, pyroprocessing methods with molten salt electrolytes have attracted considerable attention. These technologies enable us

to selectively recover actinides among spent nuclear fuels through a series of pyrometallurgical and electrochemical processes [2].

Electrorefining, in which actinide ions in molten salts are electroplated onto metallic cathodes, is the key step in pyroprocessing of spent nuclear fuels [3,4]. Electrorefining is critically dependent on the thermodynamic and kinetic properties of the spent nuclear fuels and the molten salts. Essential variables include electroreduction potentials, chemical activity, and diffusion coefficients of actinide ions [5,6].

Accurate characterization of the thermodynamic information is, therefore, the most important consideration in the design of highly functional electrorefining systems. However, direct experimental measurements may be difficult to perform in radiation environments and may be time consuming as well. An alternative approach is to use first principles DFT (density functional theory). If combined with rigorous statistical mechanics, DFT makes it possible to calculate potential energy surfaces on an atomic scale, which are needed for the understanding of detailed electrochemical reaction mechanisms for the eventual design of engineering-scale materials for electrochemical applications [7–14].

In this paper, we apply first principles DFT to the electrorefining of uranium (U) with a KCl–LiCl molten salt and a tungsten (W) cathode. We obtain thermodynamically stable structures of U electroplated on a W(110) surface, and evaluate its electrochemical

* Corresponding author. Department of Energy Systems Engineering, DGIST, Daegu 711-873, Republic of Korea. Tel.: +82 53 785 6412; fax: +82 53 785 6409.
E-mail address: hanbc@dgist.ac.kr (B. Han).

stability by calculating the activity coefficient of U. Our results clearly show that chlorine (Cl) ions, being at the double-layer interface between the LiCl–KCl molten salt and the W(110) surface, are critical for stabilizing the electrodeposition layers of U on the W surface.

2. Computations

2.1. Model system

Fig. 1 illustrates our model system to simulate the electro-refining step in the pyroprocessing of spent nuclear fuels. Here, U ions in molten KCl–LiCl are electrically deposited on a metallic cathode. A slab model composed of five atomic layers of body-centered cubic W in the (110) direction represents the cathode surface that adsorbs U and Cl ions. To minimize interactions with slab images, we imposed a periodic boundary condition to the slab with 20 Å thick vacuum spaces perpendicular to the W(110) surface. We fully relaxed adsorbed U, Cl and all atoms in the W(110) slab except those in the bottommost two layers that were fixed to their bulk positions.

2.2. Computational details

We used the VASP (Vienna *ab-initio* simulation package) [15] to calculate total energies, and utilize the GGA (generalized gradient approximation) to calculate the exchange–correlation energy [16,17]. We solve the governing, the Kohn–Sham equation, as implemented in the VASP as Eq. (1) [18].

$$E[n(r)] = T_s[n(r)] + V_H[n(r)] + E_{xc}[n(r)] + V_{ext}[n(r)] \quad (1)$$

where, $T_s[n(r)]$ is the kinetic energy of non-interacting electrons with density $n(r)$ in the model system. $V_H[n(r)]$ and $V_{ext}[n(r)]$ mean a Hartree term caused by electrostatic interactions and the external potential induced by nuclei, respectively. $E_{xc}[n(r)]$ is an exchange–correlation energy of electrons, which is a purely quantum mechanical nature.

It is well known, however, that the spurious electron self-interaction error is not adequately corrected with the standard GGA in first principles DFT. The error is particularly substantial in the calculations of redox reaction energies for many transition metals, including lanthanides and actinide compounds, and it

Table 1

Ab-initio calculated adsorption energies of U and Cl atoms on the W(110) surface at various sites. The sites are depicted in Fig. 1.

E_{ad} (eV)	Atop	Long-bridge	Short-bridge	Hollow
U	−4.63	−5.21	−4.90	−4.95
Cl	−3.69	−3.73	−3.98	−4.05

sometimes leads to an improper description of electronic and structural properties [19–23]. To correct strong correlations between the 5f electrons of uranium, we utilized the DFT + U method, as described previously [24,25]. We calibrated the U value by using the standard enthalpy of formation of uranium–chloride (UCl_3). To obtain the enthalpy, we integrated the product of the heat capacity and the temperature (T) over $T = 0$ –298 K, and added it to the *ab-initio*-calculated total energies of UCl_3 (s), U (s) and Cl (g). We determined that 1.5 eV for U gives the best match with the experimental enthalpy of formation [26]. The PAW (projector augmented wave) pseudopotential [27] was used to replace the interaction potentials of the core electrons. Atoms were relaxed to get the optimized structure with a cutoff energy of 350 eV for the plane wave basis. A gamma-point mesh of $11 \times 11 \times 1$ k-points was used for a unit cell and a smaller number was used for larger cells to integrate the Brillouin zone. To simulate the electrochemical environment of the double layer interface between the W(110) surface and the LiCl–KCl molten salt, we imposed an electric field of 0.483 eV/Å, which corresponds to that existing within a 3 Å-thick double layer for a −1.449 V U reduction potential (vs. Ag/AgCl) [28].

3. Results and discussion

3.1. Thermodynamically stable structures

To identify thermodynamically stable adsorption sites for U and Cl, we calculated their adsorption energies on the available W(110) sites: atop, long- and short-bridges, and hollow sites. It was found that U and Cl adsorb most strongly at long-bridge and hollow sites, respectively (Table 1).

By adsorbing U and Cl at the long-bridge and hollow sites, we calculated mixing enthalpies, ΔH_{mix} , for 197 different U/W(110) structures at $T = 773$ K. The structures included supercell sizes of (1×1) , (2×2) and (3×3) , with respect to the unit cell, to

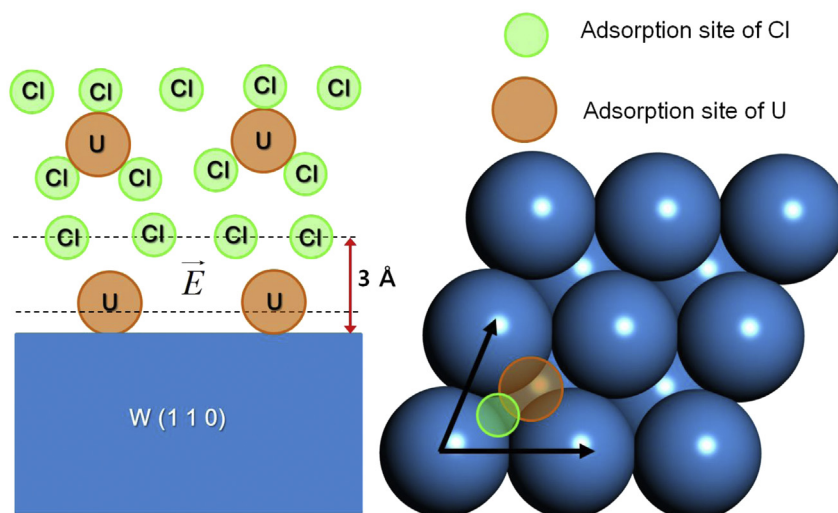


Fig. 1. (Left) Model systems for a Cl/U/W(110) surface. (Right) Adsorption sites for Cl and U. Two arrows indicate a unit cell vector.

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