

# First-principles Computational Study on Nucleation and Growth Mechanisms of U on Mo(110) Surface Solvated in an Eutectic LiCl-KCl Molten Salt

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## 1. Introduction

In this paper, we extensively utilized first principles density functional theory (DFT) calculations and ab-initio molecular dynamic (AIMD) simulations to figure out underlying mechanisms of the initial stage of nucleation and growth behaviors of U on Mo(110) surface in a eutectic LiCl-KCl molten salt at  $T = 773$  K. To rigorously investigate effect of the molten salt electrolyte we compared the results with those calculated under vacuum condition.

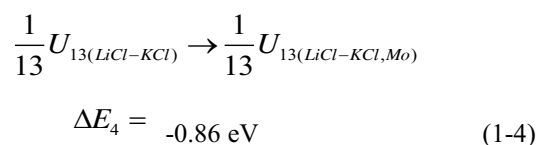
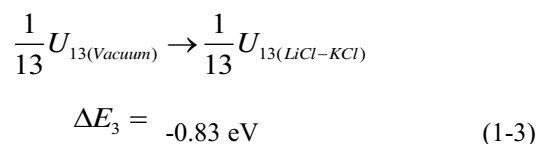
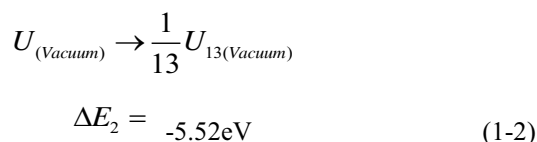
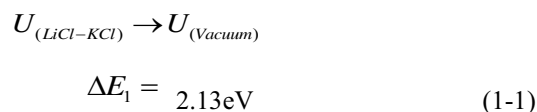
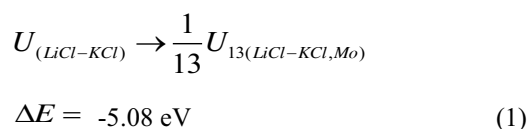
## 2. Model systems

Deposition of U on Mo occurs with bordering on three phases, which are LiCl-KCl molten salt, Mo(110) electrode and nucleus of U. LiCl-KCl molten salt were modeled based on density at 773 K based on experimental value. Mo electrode was constructed by stacking five layers of (110) plane. The last layers were fixed to simulate the bulk of Mo. Cuboctahedron shape of U nanocluster was assumed as nuclei of U while electrocrystalization occurs.

## 3. Results and Discussion

Thermoelectrochemical processes where U ions solvated in eutectic LiCl-KCl molten salt coalesce into a U nanocluster, followed by its adsorption on Mo(110) surface in LiCl-KCl eutectic molten salt.

Equation (1) describes the overall reaction for uranium atom to be adsorbed in form of U nanocluster in molten salt system, and the reaction can be separated into several steps, from equation (1-1) to equation (1-4).



U and  $U_{13}$  means an U atom and a U nanocluster, respectively. Round bracket means the state of U:  $X_{(vacuum)}$  means the X is in vacuum while  $X_{(LiCl-KCl)}$  does the X is in eutectic LiCl-KCl molten salt,  $X_{(LiCl-KCl,Mo)}$  indicate the X is adsorbed on Mo(110) surface in eutectic LiCl-KCl molten salt.  $\Delta E$  is energy change of the reaction (1).  $\Delta E_n$  is energy change for

the elementary reactions from (1-1) to (1-4). The equation (1-1) is the reversal reaction of a U solvation into eutectic LiCl-KCl molten salt from vacuum, and the energy change  $\Delta E_1$  equals to 2.13 eV implying the reaction is thermodynamically unfavorable. The second step, reaction (1-2) describes the formation of a U nanocluster from U gas in vacuum. It is exothermic reaction with -5.52 eV. Third reaction step of the equation (1-3) indicates that the solvation of U nanocluster from vacuum into the eutectic LiCl-KCl molten salt releases heat of -0.83 eV. The magnitude of  $\Delta E_1$  is bigger than  $-\Delta E_3$ .  $-\Delta E_1$  represents the solvation energy of a U atom into eutectic LiCl-KCl molten salt while the  $\Delta E_3$  does for a U nanocluster. This makes sense since the chemical potential of U in the eutectic molten salt increases as U composition increases. Equation (1-4) represents adsorption of the U nanocluster on Mo(110) surface in the LiCl-KCl molten salt. It indicates that the U nanocluster is stable as much as -0.86 eV. Using these sequential steps the energy change ( $\Delta E$ ) for the reaction described at Equation (1) was calculated by summing  $\Delta E_1$ ,  $\Delta E_2$ ,  $\Delta E_3$  and  $\Delta E_4$ , which is equal to -5.08 eV. It means that the nucleation of U in LiCl-KCl molten salt favorably occurs and adsorption of U nanocluster on Mo(110) surface in eutectic LiCl-KCl molten salt is also a spontaneous reaction. These results support the instantaneous nucleation mechanism of U in eutectic LiCl-KCl molten salt.

#### 4. Conclusion

Our results clearly unveiled surprisingly different mechanisms govern the nucleation and growth behaviors depending on the kinds of environmental conditions. Under vacuum U favored a uniform atomic layers electrodeposition on Mo(110) surface,

while strong chemical interaction between U nanocluster with Cl ions stabilized and tapered the U nanocluster into sharp tip like an atomic-scale dendrite. Our results fully based on ab-initio methods accurately captured the structural evolution as a function of time on atomic scale, which is invaluable for understanding fundamental principles on not only the electrorefining process for recycling spent nuclear fuels but also on other electrochemical reactions involving various electrolytes potentially leading to design of efficient electrochemical systems.

#### REFERENCES

- [1] Kwon, Choah, Joonhee Kang, and Byungchan Han. "First- principles based computational study on nucleation and growth mechanisms of U on Mo (110) surface solvated in an eutectic LiCl-KCl molten salt." *International Journal of Energy Research* 40.10 (2016): 1381-1388.