

First-Principles computational study on the electrochemical recycling of used nuclear fuels through pyroprocessing technology in molten salt media

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In nuclear engineering and industry, electrochemical methods have been intensively employed in pyroprocessing technology to recycle used nuclear fuels to substantially alleviate the concern with the safe treatment of high-level radioactive nuclear wastes. Pyroprocessing is based on sequential electrochemical reactions at high temperature (typically above 700 K at ambient pressure) to enhance the efficiency for decoupling nuclear fuels from unfavourable fission fragments. Using a molten salt in electrorefining process, in which Uranium is selectively deposited in a solid cathode from solution, gives several advantages over an aqueous solution: higher thermal conductivity (it is liquid phase at high temperature, molten salt plays a role as medium at high temperature over 773 K in electrochemical reaction, lower kinetic barrier in ionic diffusion mobility and better stability against undesired side reactions with radioactive materials. Therefore, the volume of high-level nuclear wastes to be, otherwise, disposed into secured sites is dramatically reduced. Most of all it conforms to nuclear non-proliferation treaty.

Electrochemical reactions in a molten salt medium are, however, much more complicated than in aqueous solution rendering the accurate understanding of thermodynamic and kinetic properties formidably challenging. It is represented by extensive researches in experiments and computations to identify underlying mechanisms on how U and other fission fragments behave in the electrorefining system. Regardless of the researches there is a general agreement that the initial stage of the nucleation and growth process of the U deposit is critical for determining the properties of final product and the electrorefining efficiency. In spite of the focused studies it still remains unclear.

Theoretical and computational researches have been often carried out with various empirical parameter for interatomic potential energy, which are unknown variables until numerical fits to experimental measurements or just assumption is made. Thus, empirical simulations sometimes predicted outcomes are inconsistent depending on materials of interest with experimental measurements. This may be largely because the accuracy of an empirical interatomic potential energy models critically depends on the input parameters and thus, can be limited in transferability of the results. Furthermore, it may be devoid of fundamental physics or chemistry. This situation requires special caution when an electrorefining system is studied to recycle spent nuclear fuels because of the extreme difficulty in reliable acquisition of thermodynamic and kinetic data from direct experimental measurements.

In this presentation, 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 behaviours of U on Mo(110) surface in a eutectic LiCl–KCl molten salt at $T=773$ K. To rigorously investigate the effect of the molten salt electrolyte we compared the results with those calculated under vacuum condition.

To simulate electrocrystallization process of U on Mo electrode we setup model systems as shown in Figure 1. In the electrorefining system we assumed that anode is always in equilibrium state with solid U metal and U ions in the eutectic LiCl–KCl molten salt. We utilized a bulk Mo(110) surface (the most close packed plane) as a solid cathode where U ions from the molten salt are electrochemically reduced. The cathode model was composed of three atomic layers consisting of 144 Mo atoms, stacked in the direction of (110) plane in $5 \times 3 \times 1$ supercell and was open to adsorption or desorption of cations and anions in the LiCl–KCl molten salt. Mo atoms in the bottommost layer of the slab were fixed to their bulk positions, while other Mo atoms and adsorbates were fully relaxed during our calculations. We imposed a periodic boundary condition to the model system. We further divided the model into two subsystems depending on environmental conditions, either vacuum or molten salt: (i) we inserted 1.8 nm of vacuum space in the perpendicular direction of the slab to simulate vacuum condition, or (ii) we filled with Li, K and Cl ions as many as the density of LiCl–KCl reaches to the experimental value 1.62 gcm^{-3} at $T = 773 \text{ K}$ for the eutectic composition (LiCl:KCl = 0.582:0.418 by the atomic fraction). VASP was used in our calculations with a cutoff energy 341 eV for expansion of Kohn–Sham waves. Because it is well known the generalized gradient approximation (GGA) method describing exchange–correlation functional causes a spurious self-interaction error, especially for f-orbital element like U, we corrected it by the Hubbard model [34] of GGA + U scheme with $U = 1.15 \text{ eV}$. We identified the U value by comparing the enthalpy of formation of a bulk UCl_3 obtained by DFT calculations and experimental measurements 8.98 eV. Gamma point mesh of $1 \times 1 \times 1$ was applied to integrate the Brillouin zone. We carried out AIMD simulations at $T = 773 \text{ K}$ for 4 ps and generated

outcomes at every 1 fs. The algorithm of Nosé–Hoover thermostat was used corresponding to an ensemble with fixed particle number, volume and temperature. A uranium nanocluster was modelled with a cuboctahedron consisting of 13 U atoms occupying (100) or (111) facets and size of 5 Å, and adsorption energy in Mo(110) surface was calculated to determine if an instantaneous nucleation mechanism works. Using DFT calculations we estimated energetically the most stable interface between the cuboctahedral U and Mo(110) surface by computing their lattice constants. Our results indicated when a (100) facet of the U cuboctahedron and Mo(110) surface has the least lattice mismatch (5.84%) and thus, we utilized the interface configuration of $U_{\text{nano}}(100)/\text{Mo}(110)$ surface during all our calculations.

Figure 2 shows structural evolutions showing the formation of a U nanocluster from randomly distributed 13 U in the eutectic molten salt. Our DFT results clearly indicate that U ions favor clustering into various crystallite as UCl_n ($n=3-6$), mediated by chemical bonding with Cl ions in the eutectic LiCl–KCl molten salt. The overall topology of the U nanocluster does not change with only marginal modification around the outmost shell by the interaction with Cl ions nearby. The U nanocluster is in solid metallic state chemically interacting with mostly Cl ions in the eutectic molten salt. Our DFT calculations indicated that the formation energy of the U nanocluster is 1.89 eV, which is more negative than addition of the formation energies of all U crystallite in the molten salt. This implies that the crystallite thermodynamically favors agglomeration into a bigger nanocluster. Our results strongly represent that fundamental mechanism of the nucleation of U substantially depend on environmental conditions. In vacuum U gas directly form the nanocluster via an interatomic clustering, while in the eutectic molten salt U ions first configure crystallite through chemical bondings with Cl ions followed by formation of the nanoclusters as agglomerates of crystallite.

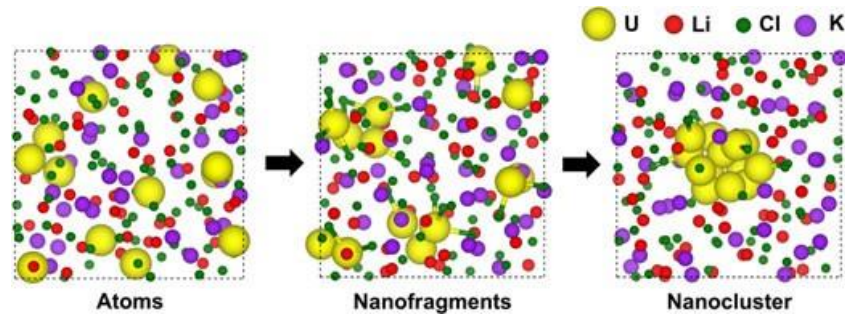


Fig. 1. Structural evolution from U fragments to U nanocluster in eutectic LiCl–KCl molten salt calculated by DFT method. Yellow, red, green and purple represent U, Li, Cl and K ions, respectively.

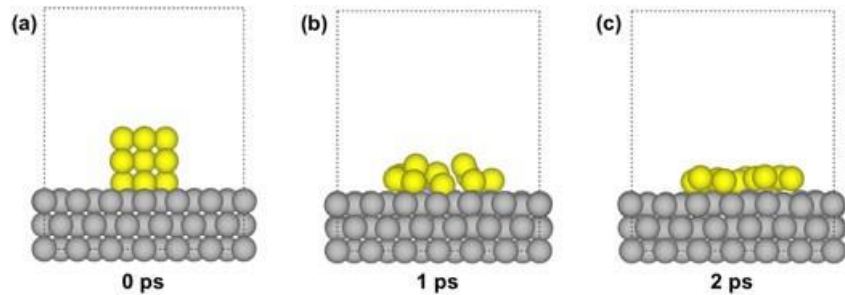


Fig. 2. Structural evolution of a U nanocluster adsorbed on Mo(110) surface under vacuum condition as a function of time of AIMD simulation. Yellow circles represent U and grey do Mo atoms.

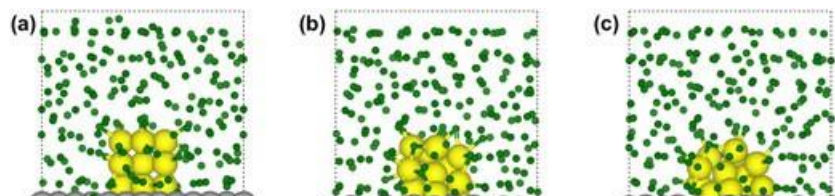


Fig.3. Structural evolution of U nanocluster adsorbed on Mo(110) surface in eutectic LiCl–KCl molten salt captured by AIMD simulations. Yellow, grey and green circles represent U, Mo and Cl atoms, respectively. Li and K atoms were removed on purpose to more clearly show atomic-level interactions between the U nanocluster and Cl^- ions.

Reference

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