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First-principles molecular dynamics modeling of UCl_3 in LiCl-KCl eutectic

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ABSTRACT

The first principles molecular dynamics (FPMD) simulations are applied to the study of LiCl-KCl eutectic and UCl_3 in LiCl-KCl eutectic. The densities of the molten salt mixtures are optimized by FPMD simulations in NVT ensemble, and the local coordination structures are evaluated in terms of radial distribution functions and partial static structure factors. Both self-diffusion coefficients and ion conductivities are evaluated from the mean square displacements using Einstein relation for diffusion coefficients. It is conformed that the FPMD simulations give satisfactory structural and transport characteristics compared with experimental observations. Therefore, the predictability of FPMD simulations for structural and transport characteristics of molten salt mixtures is confirmed, and the FPMD simulations can be useful measurement in the establishment of database of actinide behavior in molten salt mixtures essential for the pyroprocessing of spent nuclear fuels.

1. Introduction

The pyroprocessing of spent nuclear fuels employs the molten salt mixtures, such as LiCl-KCl, NaCl-CsCl, NaCl-KCl and NaCl-$CaCl_2$, as solvent instead of water and/or organic solvents. These molten salt mixtures are noncombustible and possess high boiling points, wide liquid temperature ranges, wide electrochemical windows, extremely high radioactive resistances and nuclear transmutation resistances. Therefore, the pyroprocessing has been attracting increasingly intensive research interests in the processing of spent nuclear fuels.

The disadvantages of pyroprocessing include the high operation temperature, high corrosiveness, and sensitivity of molten salt mixtures to trace impurities, especially oxygen and moisture in air. Therefore, it is difficult to accurately acquire the basic physicochemical data about the molten salt mixtures using experimental measurements, and thermodynamic calculations and molecular dynamics (MD) simulations have stood out as important measurements for the acquiring of these data. As a matter of fact, molten salts and mixtures are among the most important systems which attracted classical MD simulation studies during the very beginning of classical MD development [1]. For example, classical MD simulations have been applied to the study of molten uranium chloride [2,3], lanthanum halides [4], rare-earth trichlorides [5], and other trivalent metal chlorides [6]. Recently, classical MD simulations were employed to study the transport characteristics in molten LiCl-KCl mixture [7–10], and transport of trivalent metallic ions in molten LiCl-KCl mixture [11], structural and transport characteristics of UCl_3 and $CeCl_3$ in molten LiCl-KCl mixture [12,13], activity coefficient of UCl_3 in molten LiCl-KCl mixture based on thermodynamic integration [14], self-diffusion coefficient and chemical diffusion coefficient of U^{3+} in molten LiCl-KCl eutectic [15], activity coefficients of a number of trivalent cations in molten LiCl-KCl mixture using polarizable ion interaction potentials [16]. For more detailed information about the classical MD simulations of molten metal halides, the readers are referred to a recent review [17].

The classical MD simulation uses force field model as the fundamental input. Thus, any classical MD simulation depends on the availability of such force field model, and the quality of classical MD simulation output depends on the accuracy of the force field model. For the classical MD simulations of pyroprocessing systems, Madden et al. have developed high quality force field models by including of polarization effects on the basis of first principles calculations and applied the force field models to simulate molten salt mixtures with satisfactory results [18–20]. Besides, polarizable interaction potential for actinoids in aqueous solutions is also explored by Spezia et al. for molecular dynamics simulations, and the simulated hydration properties and ionic radii agree well with the experimental values [21,22]. On the other hand, first principles molecular dynamics (FPMD) simulations calculate the interionic forces from first principles on-the-fly and thus avoid the use of empirical force field models. In the calculations of interatomic forces, there are a few versions of algorithms, such as the Car-Parrinello molecular dynamics (CPMD), Born-Oppenheimer molecular dynamics (BOMD) or Hellmann-Feynman molecular dynamics (HFMD), and path integral molecular dynamics (PIMD). In CPMD simulations, both electronic structures and ionic position are updated on the basis of the simultaneous integration of electronic and ionic equations of motion with the

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electronic structures being converged only approximately to the Born-Oppenheimer approximation [23]. Unlike CPMD, the electronic structure calculations in BOMD or HFMD are fully converged in the Born-Oppenheimer approximation for every time step, and the forces are evaluated according to the Hellmann–Feynman theorem [24–26]. The BOMD or HFMD allows the use of a time step similar to those normally used in classical MD simulations. For example, Galamba et al. studied the structure and dynamics of molten NaCl using HFMD based on a combination of the PBE generalized gradient approximation exchange-correlation functionals with a Troullier-Martins pseudopotential and compared the HFMD with the Born-Mayer-Huggins-Tosi-Fumi rigid-ion potential and the adiabatic shell model of Mitchell and Fincham [27]. Bengtson and Morgan et al. calculated the basic properties of volume, thermal expansion coefficient, bulk modulus, and diffusivity for molten LiCl, KCl, and LiCl-KCl eutectic at multiple temperatures using FPMD [28]. Subsequently, this group studied the structures and properties of molten LiF-BeF_2 and LiF-NaF-KF mixtures, as well as mixtures with dissolved solute Cr^{n+} ($n = 0, 1, 3$) at temperatures from 823 to 1423 K using the same method [29]. The electrodeposition of U from molten LiCl-KCl eutectic onto the Mo (110) surface and thermo-kinetic properties of molten LiCl-KCl eutectic were studied using FPMD [30,31]. Recently, we studied the dynamic fluctuation of U^{3+} coordination structure in molten LiCl-KCl eutectic using FPMD simulations [32].

In the paper, the molten LiCl-KCl eutectic and UCl_3 in molten LiCl-KCl eutectic are studied by FPMD simulations. And their structural, thermodynamic, and transport properties are evaluated.

2. Computational methods

A combination of classical MD and FPMD are carried out in this study. First, the simulation systems are prepared by insertion of component ions randomly into the simulation cells. Second, the simulation cells are pre-equilibrated using classical MD as implemented in the LAMMPS package [33]. Third, the cell volumes are optimized using FPMD in NVT ensemble as implemented in the Vienna *Ab Initio* Simulation Package (VASP) [25,34–36]. Finally, production FPMD simulations in NVT ensemble are carried out, and structural, thermodynamic, and transport properties are evaluated.

The simulated LiCl-KCl eutectic is comprised of 38 Li^+ ions, 26 K^+ ions, and 64 Cl^- ions with approximate molar fractions of LiCl and KCl at 0.594 and 0.406, respectively. For the molten LiCl-KCl-UCl_3 system, two extra UCl_3 molecules are added into the LiCl-KCl eutectic with content of UCl_3 at about 16.25 wt%. All the simulation cells are cubic with periodic boundary conditions applied to eliminate boundary effects.

The Born-Huggins-Mayer (BHM) potential, one of the most widely accepted force-field models for molten salts and mixtures, is employed in the classical MD simulations because of its appropriate balance between simplicity and accuracy. During the calculation of interionic interactions, the cutoff radius is set to approximately the half of simulation cell. The classical MD simulations are carried out using Verlet integration scheme with an integration step time of 1 fs. Initially, 500,000 steps of simulations are carried out in the NPT ensemble with Nosé-Hoover thermostat and barostat to optimize the cell volumes. And the cell volumes are evaluated as average between the 400 ps and 500 ps of simulations and used as input in the following NVT ensemble simulations. Finally, the NVT ensemble classical MD simulations are conducted for 1,000,000 steps, and the final configurations are used as input for the FPMD simulations.

The BHM potential is not satisfactory for the evaluation of properties of our molten salt systems attributing to the strong polarization effects [19]. However, the use of BHM potential for equilibrating the systems is satisfactory since the ionic positions are well rearranged in their coordination shell during the preparation FPMD simulations. For example, the mean square displacements are about 5.51 and 1.06 $Å^2$, respectively, for Cl^- and U^{3+} in the molten LiCl-KCl-UCl_3 mixture at 960 K, corresponding a root mean square displacements of 2.35 and 1.03 Å, after 2000 time steps of FPMD simulations. For details about the mean square displacements, the readers are referred to Section 3.3 and Fig. 6.

The FPMD simulations are carried out within the framework of Born-Oppenheimer molecular dynamics simulation. The PBE functionals are employed, and the energy is evaluated with a $1 \times 1 \times 1$ k-point mesh [37]. The wave functions of valent electrons, Li($2s^1$), Cl($3s^23p^5$), K_sv($3s^23p^64s^1$) and U_s($5f^36s^26p^66d^17s^2$), are expanded in plane wave basis set with a cutoff energy of 420 eV, and the core electrons are approximated by projector-augmented wave (PAW) pseudopotentials [38]. The spin polarization is always applied for all the FPMD simulations to properly describe the unpaired electrons in valent shells. The ionic coordinates are integrated with a relatively small time step of 1 fs to reduce energy drift.

In order to optimize the equilibrium volumes of the simulation cells, the NVT ensemble FPMD simulations are carried out at five fixed volumes for each given temperature. The internal energy (U) is evaluated as the average over 2000 time steps after 2000 steps of preparation simulation. For each temperature, the internal energies are fitted to a quadratic polynomial of cell volumes, and the equilibrium volume is evaluated as cell volume with the minimum internal energy. And these equilibrium volumes are used during the final production FPMD simulations in NVT ensemble.

The final FPMD simulations are conducted in NVT ensemble at five preset temperatures at 858, 886, 921, 960, and 1019 K, and five corresponding equilibrium volumes for both LiCl-KCl and LiCl-KCl-UCl_3 systems. After 5000 steps of initial simulations, the structural, thermodynamic and transport properties are generated from the following 10,000 steps of FPMD simulations.

Compared with the classical MD simulations, our simulation system is very small and simulation time is very short attributing to the great calculation cost of FPMD simulations. This simulation time is reasonable compared with FPMD simulations reported in literatures [28,29]. From the root mean square displacements, the ions have moved, a simulation time of 15 ps, for about 6.02, 6.58, 7.95 and 3.77 Å for Cl^-, K^+, Li^+ and U^{3+} in the molten LiCl-KCl-UCl_3 mixture at 960 K. Therefore, it can be concluded that our simulated systems have reached equilibrium in the relatively short simulation time and the simulation results are reasonable.

3. Results and discussion

3.1.1. Densities of the molten salt mixtures

The dependencies of internal energies on cell volumes evaluated from the FPMD simulations in NVT ensemble are depicted in Fig. 1, and the equilibrium volumes are optimized by fitting these dependencies to quadratic polynomials. Moreover, we tried to deduce the second derivatives from these dependencies of internal energies on cell volumes as the second derivatives are related to bulk modulus for solid state materials. However, we cannot get reasonable results from these second derivatives attributing to the stricter calculation requirement compared with the first derivative calculation which corresponds to the equilibrium volume of the molten salt mixture.

In order to compare the FPMD results with experimental measurements, the equilibrium densities of the simulation cells are evaluated from these equilibrium cell volumes as shown in Fig. 2a.

The FPMD density decreases from 1.630 to 1.497 g cm^{-3} for the molten LiCl-KCl mixture as the temperature increases from 858 to 1019 K. Meanwhile, the corresponding experimental density, as suggested by van Artsdalen and Yaffe, decreases from 1.575 to 1.486 g cm^{-3} [39]. Our FPMD density is slightly overestimated compared with the experimental density with deviation between 0.33% and 3.13%, reflecting the slight overestimation of interionic interaction in molten LiCl-KCl mixture by the PBE functionals. The temperature dependence of density can be fitted satisfactorily to a linear relationship,

$$\rho = a - bT \quad (1)$$