ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Investigation on Structures and Properties of (Li, Na, K, Cs)Cl Quaternary Molten Alkali Chlorides System by MD Simulation

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Highlights

- The transport properties and local structures of quaternary system have been calculated.
- The performance of LMB can be evaluated by using MD simulation method.
- The influence of ionic radius in quaternary systems has been revealed.

1. Introduction

Liquid metal battery(LMB) proposed by professor Sadoway[1] will be competitive in the field of grid-scale energy storage technology in the future. LMB as a new technology has some shiny advantages, such as fast reaction kinetics, low ohmic losses, high current density and high voltage efficiency[2]. LMB consists of a unique three-layer structure, which comprising a negative metal electrode on the top, a molten salt electrolyte in the middle, and a positive metal electrode in the bottom. It's a practical assume to improve the transport and structural performance of molten salt electrolyte by adjusting the composition of the electrolyte. Then the current efficiency will be increased and the energy consumption will be reduced in LMB.

In this study, the transport and structural properties of molten alkali quaternary chlorides (Li, Na, K, Cs)Cl at 700-1000K have been calculated in details by molecular dynamics(MD) simulation. Masahiko Matsumiya et al.[3] have reported the effects of temperature and CsCl concentration on electrical properties of molten quaternary systems by MD simulation. More work need to be accomplished to optimize the performance of molten salt in LMB. The influence of CsCl concentration in (Li, Na, K, Cs)Cl system and temperature on transport properties as well as local structures(mainly density, ionic conductivity and self-diffusion coefficients) have been investigated in this paper by MD simulation.

2. Methods

Born-Mayer-Huggins potential has been successfully used to calculating the interaction between ions in the simulation. The LAMMPS code was adopted to perform the simulation process. The self-diffusion coefficients can be calculated from the mean square displacement through Einstein expression. The ionic conductivity can be calculated from the time integral of the charge flux auto-correlation function in a steady state equilibrated MD simulation by using Green-Kubo(GK) relationship.

3. Results and discussion

The radial distribution functions(RDFs) and running coordination numbers with increasing ratios of CsCl for the molten quaternary system (Li, Na, K, Cs)Cl are indicated in Figure 1. Almost all RDFs demonstrate common features: the positions of the first peak $g_{Li\text{-}Cl}<g_{Na\text{-}Cl}<g_{K\text{-}Cl}<g_{Cs\text{-}Cl}$, the heights of first peak $g_{Li\text{-}Cl}>g_{Na\text{-}Cl}>g_{K\text{-}Cl}>g_{Cs\text{-}Cl}$, the position of the first valley $g_{Li\text{-}Cl}<g_{Na\text{-}Cl}<g_{K\text{-}Cl}<g_{Cs\text{-}Cl}$. As shown in Figure 2, the ionic conductivity of the (Li, Na, K, Cs)Cl quaternary molten alkali chlorides system decrease monotonically with the enrichment of CsCl. Due to the ion radius of Cs^+ is larger than Li^+, Na^+, K^+, the interaction between anion and cation in the quaternary system will be enhanced, then the migration ability of the ions will be weakened, and the ionic conductivity of the molten salt will decrease gradually.

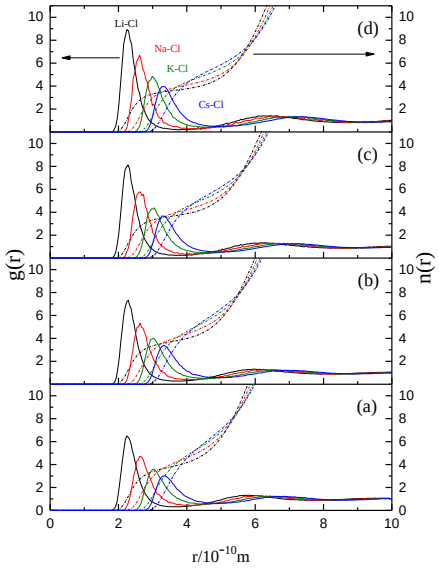

Figure 1. The radial distribution functions, g(r) and running coordination numbers, n(r) of the molten quaternary system (Li, Na, K, Cs)Cl at 1000K, g_{LiCl}; solid black line, g_{NaCl}; solid red line, g_{KCl}; solid green line, g_{CsCl}; solid blue line: (a) (Li/Na/ K/Cs)/ (42.6:7.0:30.4:20); (b) (Li/Na/K/Cs) /(31.9:5.3:22.8:40); (c) (Li/Na/K/Cs)/(21.3:3.5:15.2:60); (d)(Li/Na/K/Cs)/(10.6:1.8: 7.6:80).

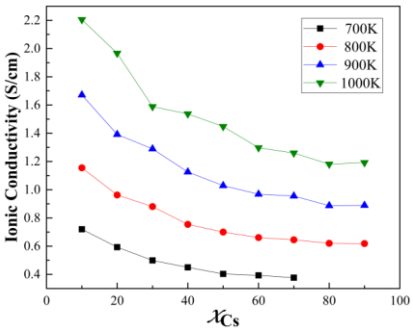

Figure 2. Ionic Conductivities of Molten (Li, Na, K, Cs)Cl at Different Temperatures

4. Conclusions

The calculated results show as follows, and the simulation results can provide reference for selecting a suitable molten salt mixture as the electrolyte in a LMB. The calculated results for the density of molten salt mixture indicate that the addition of CsCl to (Li, Na, K, Cs)Cl system increases the density markedly and lifting the temperature decreases the density. Analysis of RDFs and coordination numbers indicates that the increased amount of CsCl in quaternary mixtures strengthens interactions between A-Cl pairs. Diffusion coefficients of individual ions have a positive dependence on temperature and a negative dependence on concentration of CsCl. Viscosities have a negative dependence on temperature, and the increment of CsCl concentration influences viscosity slightly. Ionic conductivity of the quaternary system decreases monotonically with the enrichment of CsCl, while increases with the temperature promote.

References

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Keywords
molten quaternary system; molecular dynamics simulation; ionic conductivity; self-diffusion coefficients