Effect of Aluminium Fluoride on the Structure and Properties of Cryolite Alumina Molten Salt System

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Abstract. The influence of aluminium fluoride AlF₃ on the structure and properties of cryolite-Al₂O₃ melts are studied by molecular dynamics simulations at 1283 K and 0.1 MPa. The structure property such as radial distribution functions and coordination numbers, and the physical-chemical property such as density, conductivities, diffusion coefficients, and viscosities of the systems are obtained. It is shown that with the increase of aluminium fluoride content, fluorine ions in (Na₃AlF₆+4%Al₂O₃)₁₋₉(AlF₃)₉ molten salt system will replace the position of oxygen in alumina to form aluminium oxy-fluoride ion group, while aluminium ion group will form larger aluminium composite ion group through the connection of oxygen bridge and fluorine bridge. The formation of these ionic groups results in the decrease of the diffusion coefficient of anion and anion, the increase of viscosity and the decrease of conductivity in (Na₃AlF₆+4%Al₂O₃)₁₋₉(AlF₃)₉ molten salt system.

1. Introduction
Cryolite alumina molten salt electrolysis known as Hall-Héroult process is widely used in modern aluminium industry. In the cryolite alumina molten salt electrolysis method, the molten cryolite is used as the electrolyte to produce aluminium oxide. Electrolysis is generally carried out at 1213.15-1233.15 K, and the liquid aluminium is obtained on the cathode and the CO₂ is precipitated on the anode [1-2]. In the process of aluminium electrolysis, in order to improve the properties of aluminium electrolyte and improve the economic and technical indicators of the electrolysis process, various additives are often added to adjust the component of cryolite molten salt system. The addition of additives will not only affect the component and structure of aluminium electrolyte, but also affect its thermodynamic properties and transport properties, thus affecting the current efficiency and energy consumption of aluminium electrolysis process.

The additives commonly used in industry are AlF₃, CaF₂, MgF₂, LiF and NaCl etc., among which AlF₃ is an indispensable additive in cryolite molten salt system [3-7]. In recent years, Kisza et al. [8] have studied the kinetic mechanism of aluminium electrode reaction at 1000 ℃, and found that the content of aluminium fluoride in electrolyte is related to the exchange current density of cathode reaction. Lai et al. [9] prepared the AlF₃ doped anode. The study shows that adding aluminium fluoride to the anode can reduce the over-potential of the anode and improve the electrochemical activity of the anode. Fernandez et al.[10] determined the density and surface tension of cryolite aluminium fluoride system. Huang et al. [11] studied the relationship between the conductivity of Na₃AlF₆-AlF₃ melt and the concentration of AlF₃ at 1273.15K. The results show that the conductivity increases about 0.04 Ω⁻¹cm⁻¹ when the molecular ratio of electrolyte increases by 0.1. Yuan et al. [12] studied the effect of aluminium fluoride content in Na₃AlF₆-K₃AlF₆-AlF₃ on the solubility of aluminium.
However, most of the experimental reports mainly focus on the determination of the influence of aluminium fluoride on the thermodynamic properties of aluminium electrolyte. It is impossible to get the information about how aluminium fluoride affects the interaction between components in aluminium electrolyte, the existence of ion morphology, structural characteristics, ion migration and diffusion, and their influence on physical and chemical properties. The form and structure of ions and the mechanism of migration and diffusion are very important to the electrolysis process, and they are also the research hotspot and difficulty in this field. In recent years, the structure of cryolite melt and NaF-AlF₃ system melt has been studied by means of Raman spectrum, quantum chemical calculation, Monte Carlo, molecular dynamics and thermodynamic calculation. Xie et al. [13-14] used Monte Carlo method to simulate the melt structure of cryolite alumina and found that it is mainly AlF₆³⁻, AlF₄⁻ anion and Na⁺ cation. However, the mechanism of the influence of additives on the ionic morphology, structure, migration and diffusion, and the physical and chemical properties of the system is not clear, which needs further study. In addition, it is relatively difficult to study the influence of additives on the structure and properties of molten salt system in detail at a high temperature of 1213.15-1233.15 K. Therefore, it is of great significance to explore new convenient and effective methods to study the mechanism of additives in the aluminium electrolysis process, so as to screen and design additives and guide production. In this paper, the influence of aluminium fluoride on the physical and chemical properties of ions in cryolite alumina molten salt system is systematically studied by molecular dynamics method.

2. Simulation Method and Details

The material Explorer 5.0 program [15] and born Mayer Huggins potential function are used to describe the interaction of ions in the system. The function form is (1)

\[
U_{ij}(r) = \frac{Z_i Z_j e^2}{4\pi \varepsilon_0 r} + B_{ij} \exp(-r/R_{ij}).
\]

In Eq. (1), \(Z_i\) and \(Z_j\) are respectively the charges of ion \(i\) and \(j\), where \(e\) is the basic charge, \(e = 1.6 \times 10^{-19}\) C; \(\varepsilon_0\) is the vacuum dielectric constant, \(\varepsilon_0 = 8.854 \times 10^{-19}\) F·M⁻¹; \(R\) is the distance between ions; \(B_{ij}\) is the parameter of the ion's short-range exclusion term. See Table 1 for the \(B_{ij}\) value selected in this paper, which is taken from Ref.[16,17], and all \(R_{ij}\) are 29 pm [16,17].

| \(w\) | Total | Particle numbers | NVT box length/Å | \(\rho_{l}/(\text{g cm}^{-3})\) | \(\rho_{exp}/(\text{g cm}^{-3})[1]\) |
|------|-------|----------------|-----------------|------------------|------------------|
| 0%   | 513   | Na⁺ 147, Al³⁺ 58, F⁻ 295 | 13             | 20.745           | 2.0496           |
| 5%   | 513   | Na⁺ 139, Al³⁺ 62, F⁻ 299 | 13             | 20.038           | 2.0734           |
| 10%  | 513   | Na⁺ 133, Al³⁺ 65, F⁻ 302 | 13             | 19.962           | 2.0761           |
| 15%  | 513   | Na⁺ 125, Al³⁺ 69, F⁻ 306 | 13             | 19.753           | 2.0834           |
| 20%  | 513   | Na⁺ 117, Al³⁺ 73, F⁻ 310 | 13             | 19.362           | 2.0973           |

In order to compare with the experimental results, the effect of AlF₃ with different mass fraction of aluminium fluoride \(w = 0, 5\%, 10\%, 15\%, 20\%\) on the structure and properties of \((\text{Na₃AlF₆}+\text{4%Al₂O₃})_w\text{(AlF₃)}_{1-w}\) molten salt systems were studied. The number of particles in the simulation system and the size of the simulation box in equilibrium are shown in Table 1. The particles are randomly placed in the simulation box as the initial configuration of the system. The periodic boundary condition is used, and the truncation radius is half of the box side length. The motion equation is solved by the fifth order Gear-prediction-correction algorithm. The electrostatic interaction is treated by Ewald summation technology. The simulated temperature and pressure are 1283 K and 0.1MPa respectively, and the simulation time step is 2 fs. The simulations were run in two sections. First, 40 ps was run under the \(NPT\) ensemble until the total energy converged and the temperature reached equilibrium. Then 2 ns were run under \(NVT\) ensemble to get the required physical quantity. The box size of \(NVT\) ensemble simulation is given in Table 1.
3. Results and Discussion

3.1. Density
The simulated density of (Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}$(AlF$_3$)$_w$ melt with different mass fraction of aluminium fluoride is shown in Table 1. It can be seen from the table that the simulated density value of the system is close to the experimental value [1]. It is confirmed that the potential and simulation are suitable for study the structure and the property of (Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}$(AlF$_3$)$_w$ melt.

3.2. Radial Distribution Function and Coordination Number
The radial distribution function between the mass centres of different components in the (Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}$(AlF$_3$)$_w$ molten salt system with different mass fractions of aluminium fluoride is shown in Figure 1.

![Figure 1](image_url)

Figure 1. Radial distribution functions between different ions. (a) Al$^{3+}$ and F$^-$, (b) Al$^{3+}$ and O$^{2-}$, (c) Al$^{3+}$ and Al$^{3+}$, (d) O$^{2-}$ and F$^-$. Figure 1(a) shows the radial distribution function between Al$^{3+}$ and F$^-$ in the system. It can be seen from the figure that with the addition of aluminium fluoride, the first peak of Al$^{3+}$-F$^-$ radial distribution function decreases gradually, and the corresponding distance of the first peak shifts to the right, which indicates that the interaction between Al$^{3+}$-F$^-$ in the system decreases after the addition of aluminium fluoride. The radial distribution function between Al$^{3+}$ and O$^{2-}$ is shown in Figure 1(b). The peak value of the first peak of radial distribution function of Al$^{3+}$ and O$^{2-}$ is far greater than that of the first peak of that of Al$^{3+}$ and F$^-$ in Figure 1(a), and the distance value corresponding to the first peak is smaller than that of Al$^{3+}$ and F$^-$, indicating that the interaction of Al$^{3+}$ and O$^{2-}$ is significantly stronger than the interaction of Al$^{3+}$ and F$^-$. With the addition of aluminium fluoride, the peak value of the first
peak of radial distribution function of Al$^{3+}$ and O$^{2-}$ decreases gradually, indicating that the interaction between Al$^{3+}$ and O$^{2-}$ is gradually weakened due to the addition of aluminium fluoride. This may be due to the fact that F$^{-}$ is given after the aluminium fluoride enters the melt, and the position of O$^{2-}$ is replaced by F$^{-}$ in the aluminium oxygen coordination layer of Al$_2$O$_3$, which weakens the interaction between Al$^{3+}$ and O$^{2-}$.

Figure 1(c) shows the radial distribution function between Al$^{3+}$ and Al$^{3+}$ in the system. It can be seen from the figure that there are two adjacent peaks in the radial distribution function of Al$^{3+}$-Al$^{3+}$ in a short distance, and with the increase of aluminium fluoride mass fraction, the peak of the first peak gradually weakens and the peak of the second peak gradually increases. These two peaks are caused by oxygen-bridge and fluorine-bridge formed by O$^{2-}$ and F$^{-}$ linked aluminium ion groups, respectively. With the increase of the mass fraction of aluminium fluoride, the effect of oxygen-bridge decreases and that of fluorine-bridge increases. Figure 1(d) shows the radial distribution function of O$^{2-}$ and F$^{-}$ in the system. It can be seen from the figure that the peak type of the radial distribution function O$^{2-}$ and F$^{-}$ is relatively complex, and there are three peaks between $r = 1.7$ Å and 4 Å. The radial distribution function tends to be gentle after $r = 5.5$ Å. These peaks indicate that there should be a variety of aluminium oxy-fluoride ion groups in the system. These ion groups not only have simple aluminium oxy-fluoride ion groups formed by the replacement of fluorine oxy-fluoride ion, but also have the bridge structure of aluminium oxy-fluoride ion group, and even have composite aluminium oxy-fluoride ion groups.

It can be seen from the above analysis that the addition of aluminium fluoride will make the F$^{-}$ in the system replace the oxygen in alumina to form aluminium-oxygen-fluorine ion group. Aluminium ion group will be connected by oxygen-bridge and fluorine-bridge to form aluminium-oxygen-fluorine ion bridge structure.

3.3. Diffusion Coefficient
Figure 3 shows the diffusion coefficients of Na$^+$, F$^-$, Al-F ion groups and Al-O-F composite ion groups in (Na$_3$AlF$_6$+$4\%$Al$_2$O$_3$)$_{1-x}$(AlF$_3$)$_x$ molten salt system with different mass fractions of aluminium fluoride. It can be seen from the figure that the diffusion coefficients of the four ions decrease with the increase of the mass fraction of aluminium fluoride, and the diffusion coefficients of Na$^+$ are obviously larger than those of other ions. Combined with the results of radial distribution function and coordination number, it can be seen that this is due to the formation of aluminium complex ion groups in the melt with the addition of aluminium fluoride, and the large-scale complex ion groups lead to the slow diffusion of ions. Among these ions and ionic groups, the aluminium oxy-fluoride ion group has the largest size, so its diffusion coefficient is also the smallest. The size of Na$^+$ is the smallest, and Na$^+$ is still the main diffusion ion in the system. However, due to the hindrance of large-scale aluminium composite ion group, the diffusion coefficient of Na$^+$ decreases with the increase of aluminium fluoride mass fraction.

3.4. Conductivity and Viscosity
Figure 2 shows the effect of different mass fraction of aluminium fluoride additives on the conductivity and viscosity of (Na$_3$AlF$_6$+$4\%$Al$_2$O$_3$)$_{1-x}$(AlF$_3$)$_x$ molten salt system. It can be seen from Figure 2(a) that the simulated conductivity shows the same change trend as the experimental result [2], and the conductivity decreases with the increase of aluminium fluoride mass fraction. The conductivity of molten salt system is mainly related to the conductivity of simple cations in the system. Combined with the analysis of the radial distribution function and ion diffusion coefficient, it can be seen that with the increase of aluminium fluoride content, large-scale aluminium composite ion groups will be formed in the system. This will reduce the number of charged ions and ion migration in the system, and hinder the diffusion of the main carrier Na$^+$ in the system, thus reducing the conductivity of the system. From Figure 2(b), it can be seen that the simulated viscosity and conductivity do show the opposite trend. With the increase of aluminium fluoride mass fraction, the viscosity of (Na$_3$AlF$_6$+$4\%$Al$_2$O$_3$)$_{1-x}$(AlF$_3$)$_x$ molten salt system increases continuously. This is mainly because with the increase of the mass fraction of aluminium fluoride, the fluorine anion and aluminium oxide in the system forms the aluminium fluoride ion group and aluminium oxy-fluoride ion group. These
aluminium ion groups will form a larger space network structure through the connection of oxygen-bridge and fluorine-bridge. The viscosity of molten salt system mainly depends on the mobility of large-scale polymer ion groups in the melt. In the system, the internal friction between the melts will be increased by the large size of the polymer ion group, which makes the viscosity of the melts increase and the flow speed slow down. In (Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}$molten salt system, the viscosity of the system is increased mainly due to the action of aluminium complex ion group.

![Figure 2](image_url)\(\text{Figure 2. Effect of AlF}_3\text{ on conductivities (a) and viscosities (b) of (Na}_3\text{AlF}_6+4\%\text{Al}_2\text{O}_3)_{1-w}(\text{AlF}_3)\)w molten salt system.\]

4. Conclusion
The effect of different mass fraction of AlF$_3$ on the structure and properties of cryolite molten salt system was studied by molecular dynamics method at 1283k and 0.1MPa. The effects of AlF$_3$ on the ionic forms, mobility, ionic interactions, and diffusion mechanisms of cryolite melts are revealed, which is important for the production of aluminium by electrolysis. The density and conductivity of the simulated system are in good agreement with the experimental values. With the increase of aluminium fluoride content, fluorine ions in (Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}(\text{AlF}_3)w$ molten salt system will replace the position of oxygen in alumina to form aluminium oxy-fluoride ion group, while aluminium ion group will form larger aluminium composite ion group through the connection of oxygen bridge and fluorine bridge. The oxy-fluoride complex of Al$_2$OF$_2^{2-}$and the mixture of aluminium oxy-fluoride may also exist in the system. The formation of these ionic groups results in the decrease of the diffusion coefficient of anion and anion, the increase of viscosity and the decrease of conductivity in(Na$_3$AlF$_6$+4%Al$_2$O$_3$)$_{1-w}(\text{AlF}_3)w$ molten salt system.

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6. References
[1] Qiu Z X 1998 Principle and application of aluminium electrolysis (Beijing: China University of Mining and Technology Press)
[2] Liu Y X, Li J 2008 Modern aluminium electrolysis (Beijing: Metallurgical Industry Press)
[3] Hu X W, Qu J Y, Gao B, Shi Z, Liu F, Wang Z 2011 Raman spectroscopy and ionic structure of Na$_3$AlF$_6$-Al$_2$O$_3$ melts. Transactions of Nonferrous Metals Society of China, 21(2), 402-406.
[4] Fu J, Wu W Y, Peng K W, Wang Z W, Tu G F 2004 Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$-CaF$_2$-MgF$_2$-NaCl Investigation of electrolyte density in low temperature aluminium electrolysis, Journal of Materials and Metallurgy, 3(2), 113-117.
[5] Fu Q W, Wang Z W, Yang Y J, Yang D J, Liu J C, Liao Y S, Li H R 2013 Study of the liquidus temperature of Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$-CaF$_2$-KCl aluminium electrolyte. *Metallurgical analysis*, 33, 28-35.

[6] Liu S Y, Li W Z, Wang Z W, Shi Z N 2010 Influence of aluminium electrolyte component on permeation behaviour of sodium and electrolyte. *Nonferrous Metals*, 62, 57-62.

[7] Shi S, Gao B L, Wang Z W, Shi Z N, Hu X W, Huang C S, Wang X X 2014 Influence of KF on the determination of cryolite ratio of aluminium electrolyte. *Light metals*, 4, 22-28.

[8] Kisza A, Kaźmierczak J, Thonstad J, et al. 2002 Influence of CaF$_2$ and AlF$_3$ on the kinetics and mechanism of the Al electrode reaction in cryolite melts with various alumina contents. *Journal of Applied Electrochemistry*, 32, 305-309.

[9] Lai Y Q, Qin Q W, Li Q Y, et al. 2003 Effect of AlF$_3$ dopant and baking temperature on overpotential of carbon anode in aluminium electrolysis, *Chinese Journal of Non-ferrous Metals*, 13, 764-770.

[10] Fernandez R, Ostvold T 1989 Surface-tension and density of molten fluorides and fluoride mixtures containing cryolite, *Acta Chemica Scandinavica*, 43, 151-155.

[11] Huang Y G, Tian Z L, Lai Y Q, et al. 2008 Advances in research on electrical conductivity of aluminium electrolyte melts. *Light metals*, 6, 28-34.

[12] Yuan M J, He S R, Meng Q Y, et al. 2011 Solubility of Aluminium in Na$_3$AlF$_6$-K$_3$AlF$_6$-AlF$_3$ electrolyte system. *Rare metals*, 35, 312-318.

[13] Xie G, Qiu Z X. 1991 Structure of alumina dissolved in cryolite melt [J]. *Journal of Kunming University of Technology (Science and Technology Edition)*, 6, 30-36.

[14] Xie G, Yan J F, Li R X 2006 *Computer simulation of structure and properties of metallurgical melts*. (Beijing: Metallurgical Industry Press).

[15] http://www.fqs.pl/chemistry_materials_life_science/products/materials_expplorer

[16] Belashchenko D K, Ostrovski O I, Saposznikova S Y 1998 Computer study of structure, thermodynamic and electrical transport properties of Na$_3$AlF$_6$-K$_3$AlF$_6$-AlF$_3$ melts. *Metallurgical and Materials Transactions B*, 29, 105-110.

[17] Belashchenko D K, Ostrovski O I, Utochkin Y I 1998 Molecular dynamics simulation of dilute solutions of MeO and MeF$_2$ in the CaO-CaF$_2$ system. *ISIJ International*, 38, 673-678.

[18] Picard G C, Bouyer F C, Leroy M 1996 Structures of oxy-fluorooxaluminates in molten cryolite-alumina mixtures investigated by DFT-based calculations. *Journal of Molecular Structure: THEOCHEM*, 368, 67-75.