Ab Initio Molecular Dynamics Simulation of Microstructure and Transport Properties of K₃AlF₆-2.2NaF-AlF₃ System

Jingkun Wang 1, Can Chen 1, Hongliang Zhang 1 and Jiaqi Li 2,*

1 School of Metallurgy and Environment, Central South University, No. 932, South Road Lushan, Changsha 410083, China; wangjingkun@csu.edu.cn (J.W.); csu15683409313@csu.edu.cn (C.C.); csu13574312788@csu.edu.cn (H.Z.)
2 School of Automation, Central South University, No. 932, South Road Lushan, Changsha 410083, China
* Correspondence: csulijiaqi@csu.edu.cn

Abstract: Researching the aluminum molten salt system has always been challenging because of the high temperature and significant corrosion seen in the aluminum electrolysis industry. This paper employs ab initio molecular dynamics simulations to investigate the ionic structure and transport features of the K₃AlF₆-2.2NaF-AlF₃ molten system. The findings indicate that the primary Al-F complex ion species present in K-rich molten salts are [AlF₄]⁻, [AlF₅]²⁻, and [AlF₆]³⁻. The fluorine atom located at the bridge site constitutes around 3% of the overall composition, suggesting a rather modest degree of polymerization for the ionic structure. The relative diffusion rates of the ions in the system are as follows: sodium (Na) has the highest diffusion ability, followed by potassium (K), fluoride (F), and aluminum (Al). With the increase in K₃AlF₆ concentration, the distribution and diffusion coefficient of complex ions in the melt change, resulting in a decrease in the transport performance of the entire system. These fundamental research findings can contribute to the optimization of the aluminum electrolysis industry in the future.

Keywords: aluminum electrolysis; K-rich salt aluminum electrolyte; molecular dynamics simulation; ion structure; transport properties

1. Introduction

Recently, the aluminum electrolysis industry based on the Hall–Héroult process has been facing the severe challenges of energy saving and emission reduction. Researchers are focusing on how to efficiently improve current efficiency and reduce the power consumption of aluminum electrolysis in order to conserve energy and reduce emissions [1–3]. The new electrolyte system of KF-NaF-AlF₃ melts [4], which has a lower crystallization temperature and better solubility of alumina, is widely regarded as a promising replacement for the traditional NaF-AlF₃ electrolyte system. On the one hand, due to the accumulation of sodium brought about by alumina in the electrolysis process, the KF-AlF₃-based electrolyte will gradually be transformed into the KF-NaF-AlF₃ electrolyte system [5,6]. On the other hand, it is inevitable that the K element from the crude materials (e.g., alumina) will be brought into the molten electrolyte system [7,8]. Therefore, it is of great significance to study the micro-mechanism of the K-rich complex molten aluminum electrolyte system for its high efficiency and low-consumption operation.

Early studies [9–11] on the molten salt system focused on experimental characterization and engineering applications, in order to achieve lower electrolysis temperature and higher current efficiency through the mechanism analysis and technical optimization. Nevertheless, the high temperature and strong corrosion have placed great limitations on the research progress of the aluminum electrolysis molten salt system; even worse, the cost of the molten salt experiment is very high [12]. In this respect, molecular dynamics (MD) simulations turn out to be very useful, and have been widely used to provide more detailed information on ionic structures and transport properties for high-temperature...
melts. It can also be noted that ab initio molecular dynamics (AIMD) has been successfully applied to the KCl-LiCl [13], LiF-NaF-KF [14], and NaF-AlF$_3$ [15] systems, and to other melts [16,17]. Recently, Lv et al. [18] implemented AIMD to simulate the ionic structure and transport properties of the KF-NaF-AlF$_3$ system. Due to the small number of ions and short simulation duration, the ionic structure cannot be reproduced in its entirety, and the chemical composition of the designed KF-NaF-AlF$_3$ system differs from that of the actual low-temperature electrolyte. Based on a particular physical model, the simulation of molecular dynamics is an effective approach for studying the structure and properties of the aluminum electrolyte melt, as the author of this paper has shown in preliminary research [19]. Generally speaking, raw materials from complicated sources cause the Ca$^{2+}$K$^-$ impurity in aluminum electrolysis cells to continuously enrich, affecting the operating stability and current efficiency of these cells. In our previous work [20], molecular dynamics simulations were applied to investigate the CaF$_2$-2.2NaF-AlF$_3$ molten salt system. It has been proved that this technique can successfully obtain the physico-chemical characteristics and ionic structure of molten salt systems.

This work simulates the molten salt system (also as known as the K-rich aluminum electrolyte system) at 1260 K [20] with a concentration of K$_3$AlF$_6$ varying from 5% to 25% using ab initio molecular dynamics. The analysis of structural information in molten salt electrolytes involves the utilization of quantitative data, including the radial pair distribution function, the average coordination number of Al$^{3+}$ and F$^-$, the distribution of F$^-$ type, the distribution of complex group type, and the distribution of bridge fluorine types. These metrics provide a comprehensive understanding of the structural characteristics of the electrolyte. In addition, the microscopic aspect of the ionic migration is discussed through its correlation with the local structure of different melts.

2. Computational Methods

Table 1 presents the molecular ratio of the KF and AlF$_3$ (CR), the chemical composition, and the simulation cell size of the $n$K$_3$AlF$_6$-2.2NaF-AlF$_3$ molten salt system as determined using AIMD simulation. In order to enhance computational performance, the initial model for ab initio molecular dynamics (AIMD) was chosen to be the optimized model utilizing the Buckingham force field. Using the prevailing language in the aluminum industry, this article regards K$_3$AlF$_6$ concentration as a mass percentage concentration. The molten salts are partitioned into five distinct concentrations of K$_3$AlF$_6$ by mass fractions of 5%, 10%, 15%, 20%, and 25%.

<table>
<thead>
<tr>
<th>CR</th>
<th>K$_3$AlF$_6$ (wt.%)</th>
<th>N$_{Na}$</th>
<th>N$_{Al}$</th>
<th>N$_{K}$</th>
<th>N$_{F}$</th>
<th>N$_{total}$</th>
<th>V (nm$^3$)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$N_F/N_{Al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>5</td>
<td>51</td>
<td>24</td>
<td>3</td>
<td>126</td>
<td>204</td>
<td>3.45</td>
<td>2.08</td>
<td>5.25</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>51</td>
<td>25</td>
<td>6</td>
<td>132</td>
<td>214</td>
<td>3.68</td>
<td>2.07</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>51</td>
<td>26</td>
<td>9</td>
<td>138</td>
<td>224</td>
<td>3.91</td>
<td>2.06</td>
<td>5.31</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>51</td>
<td>27</td>
<td>12</td>
<td>144</td>
<td>234</td>
<td>4.13</td>
<td>2.05</td>
<td>5.33</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>51</td>
<td>28</td>
<td>15</td>
<td>150</td>
<td>244</td>
<td>4.44</td>
<td>2.01</td>
<td>5.36</td>
</tr>
</tbody>
</table>

The CP2K programme package was utilized for conducting all simulations in this study. The molten salt system can effectively address the exchange-related interaction and van der Waals dispersion correction using the GGA-PBE functional and DFT-D3 approaches [21]. In addition, the utilization of Goedeker–Teter–Hutter (GTH) pseudopotentials is employed for the purpose of addressing the inner electrons and nuclei of atoms [20]. Our chosen approach for obtaining widespread sampling using molecular dynamics (MD) is the SGCP-MD method [22], which has been demonstrated to be accurate and efficient for sampling large condensed matter systems. As valence layer electrons, the Na3s, Al3s$^2$3p$^1$, F2s$^2$2p$^5$, and K4s$^1$ were described by the MOLOPT basis set with double $\zeta$ valence polarization [23]. The electron density of the auxiliary plane wave base group is limited to a cut-off value of
600 Ry due to the inclusion of F ions in the system. Additionally, the RELATIVE_CUTOFF value is set at 60 Ry. The temperature is maintained at 1260 K using a Nosé–Hoover thermostat with standard sampling. The NPT ensemble is employed with SCF convergence criteria of $5 \times 10^{-6}$ Hartree, a duration of 20 ps, and a time step of 1 fs. Next, the NVT ensemble is employed, where the number of particles, volume, and temperature remain constant, to simulate a duration of 40 ps. The self-consistent field (SCF) convergence threshold is set at $10^{-6}$ Hartree [24]. Finally, the simulated phase trajectory in the NVT ensemble was collected to analyze the ionic structure and transport properties of the melts.

There are many different types of atoms in the aluminum molten salt system, and its structural makeup is intricate. The statistical technique used in this study completely takes into account the periodicity influence on each statistic, ensuring that the structural distribution is in good agreement with the simulation results. To minimize mistakes brought on by periodic changes in atomic coordinates, all the atoms were periodized prior to computing the diffusion parameters of the ions in the orbital files. In addition, the ion self-diffusion coefficients were calculated by importing trajectory files into the Gromacs software. The radial pair distribution function (RDF) and average coordination number (CN) were then computed using the VMD software. The TkConsole module of the VMD software provided statistics relating to additional structural data. In order to completely account for the influence of the periodic structure, all the statistical findings in this study were collected using the statistics of the final 5000 frames of the last 5 ps of the stable structure.

3. Results and Discussion

3.1. Micro-Structure of Molten Salt System

Information on the micro-structure and coordination of molten salts deepens the understanding of the elementary elements of the micro-structure of matter. Herein, a stable ionic configuration of a K$_3$AlF$_6$-2.2NaF-AlF$_3$ system containing 5 wt% K$_3$AlF$_6$ is illustrated in Figure 1. It can be seen that the K and Na ions are randomly distributed without covalent characteristics because of the small polarity differences. As a result of the presence of bridge F ions and bridge O ions, these Al-F-O complex groups form a complex spatial arrangement. In general, the [AlF$_5$]$^{2−}$ complex ions exhibit a higher prevalence within the observed composition of the molten salts. However, it is worth noting that [AlF$_6$]$^{3−}$ and [AlF$_4$]$^{−}$ are also present, but with a very limited distribution. The dimer of the Al-F complex ions, denoted as [Al$_2$F$_4$]$(8−6)−$, can be seen directly. This result is in agreement with several previous studies. When comparing conventional triangular double-cone, octahedral, and tetrahedral configurations, it is observed that the majority of the aluminum fluoride complexing group configurations exhibit significant distortion. The extent of distortion is shown to be greater in the molecular structure of the [AlF$_5$]$^{2−}$ complex ion. Despite the loss of its long-range ordered state, the system maintains a short-range ordered state in its local ionic structure.

3.2. Radial Distribution Function

The radial distribution function (RDF) is a fundamental tool in the research of the structural properties of molten salts, as it offers initial insights into their arrangement [25]. A molecular dynamics simulation trajectory’s radial distribution function (RDF) can examine a fluoride melt’s local ionic structure. As shown in Equation (1), the RDF quantifies the possibility of discovering another particle within $r$ of a reference particle.

$$g_{ij}(r) = \frac{V}{N_iN_j} \sum_j \left\langle \frac{n_{ij}(r, \Delta r)}{4\pi r^2} \right\rangle$$

where $V$ is the volume of simulation box, $N$ is the number of particles, and $n_{ij}(r, \Delta r)$ is the average number of ions $j$ surrounding a central ion $i$ within a defined cut-off distance $\Delta r$. To examine the distribution of ions and the change in their action intensity in molten salt
systems, the radial pair distribution functions of a few ion pairs in the final 5 ps structure are counted. The radial pair distribution functions of certain ion pairs within the final 5 ps structure are quantified in order to analyze the spatial distribution of ions and assess variations in their interaction strength. Figure 2 displays the statistical outcomes pertaining to specific ion pairs observed in a molten environment. When the cut-off radius exceeds 7 Å, the RDF values of various ion pairs gradually approach 1, which is consistent with the short-range ordered and long-range disordered structure of the system. The RDF of the Al-F ion pair presents a high and sharp peak at 1.7Å that corresponds to the average bond length of the Al-F [18], indicative of a strong interaction that leads to the construction of well-defined coordination complexes. Table 2 shows the average ion pair bond length calculated from the RDF’s first peak radius. The potential parameters calculate ion pair bond lengths that match references [2,24], which indicates that the potential parameters constructed in this paper are reasonable.

Figure 1. The stable ionic configuration of K₃AlF₆-2.2NaF-AlF₃ molten salt system.

Figure 2. Radial distribution functions of typical ion pairs in the molten salt system at various K₃AlF₆ concentrations: (a) Al-F, (b) K-F, (c) Na-F, and (d) Al-Al.
Table 2. The average bond length (Å) of ion pairs and the average CN of Al-F ions in $nK_3AlF_6\cdot2.2NaF\cdotAlF_3$ system.

<table>
<thead>
<tr>
<th>Ion Pair</th>
<th>5 wt.%</th>
<th>10 wt.%</th>
<th>15 wt.%</th>
<th>20 wt.%</th>
<th>25 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-F</td>
<td>1.76</td>
<td>1.76</td>
<td>1.76</td>
<td>1.76</td>
<td>1.76</td>
</tr>
<tr>
<td>K-F</td>
<td>2.72</td>
<td>2.72</td>
<td>2.7</td>
<td>2.68</td>
<td>2.72</td>
</tr>
<tr>
<td>Na-F</td>
<td>2.3</td>
<td>2.28</td>
<td>2.28</td>
<td>2.28</td>
<td>2.28</td>
</tr>
<tr>
<td>Na-Na</td>
<td>3.88</td>
<td>3.84</td>
<td>3.84</td>
<td>3.82</td>
<td>3.88</td>
</tr>
<tr>
<td>Al-Al</td>
<td>5.88</td>
<td>5.86</td>
<td>6.04</td>
<td>5.94</td>
<td>5.94</td>
</tr>
<tr>
<td>CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-F</td>
<td>5.12</td>
<td>5.17</td>
<td>5.09</td>
<td>5.12</td>
<td>5.20</td>
</tr>
</tbody>
</table>

3.3. Coordination Number and Bond Angles Distributions

In order to study the effect of increasing $K_3AlF_6$ concentration on the coordination number of melts, we integrated the radial pair distribution function of ion pair to obtain the coordination number curve. The average coordination number of Al-F complex ion groups in the $nK_3AlF_6\cdot2.2NaF\cdotAlF_3$ system can be obtained by integrating the RDF curves. In this paper, the cutoff radius of Al-F is 2.465 Å and the CN values range from 5.09 to 5.20, as shown in Table 2. The overall pattern is an increase, followed by a decline, and finally an increase, with the lowest value of 5.09 being achieved at a concentration of 15% $K_3AlF_6$. On the whole, the Al-fluorine pentacentate complex ion is the predominant conformation of complex ions in the molten salt system.

As is shown in Figure 3, the bond angle distribution of F-Al-F in the molten salt system is calculated. According to the literature [20], the [AlF$_6$]$^{3-}$ octahedron exhibits eight F-Al-F bond angles of 90° and three bond angles of 180°. Similarly, the [AlF$_5$]$^{2-}$ triangular bipyramid demonstrates six F-Al-F bond angles of 90°, three bond angles of 120°, and one bond angle of 180°. Lastly, the [AlF$_4$]- regular tetrahedron displays six F-Al-F bond angles of 109.5°. The bond angle distribution curve of the F-Al-F has a prominent peak at approximately 90° and 80°, indicating the prevalence of Al-F complex ions adopting octahedral or triangular bipyramidal structures. The first peak radius of the bond angle distribution appears near 90°, and does not shift significantly with the increase in $K_3AlF_6$ concentration.

In addition, the configuration deformation of complex ions is more pronounced due to the intense interionic force. To examine the bond angle distribution of complex ions with different configurations and their contribution to the total bond angle distribution, the bond angle distribution of complex ions with different coordination numbers (CN) was also statistically analyzed, and the results are depicted in Figure 4. As can be seen from Figure 4b, there are more pentacentates in the complex ions, which correspond well to the CN values mentioned above. The bond angle distribution curve of the tetracoordinate complex ions is depicted in Figure 4a, and it can be seen that its smoothness is substantially lower than those of Figure 4b,c. This is because the concentration of tetracoordinate complex ions in this molten salt system is low, and the bond angle distribution curve for complex ions with the same coordination number that contain Al complex ions is relatively steep. This demonstrates that, despite the fact that complex ions are affected by the surrounding ions in the melt environment, their deformation trend is very consistent, indicating that their configuration is relatively uniform. Moreover, the peak of the major bond angle of the complex ion shifts to about 170°, indicating that the anions at both ends of the pentacoordinate and hexacoordinate ions are more easily attracted.
The bond angle distribution curve of the F-Al-F has a prominent peak at approximately 90° and 80°, indicating the prevalence of Al-F complexes adopting octahedral or triangular bipyramidal structures. The first peak radius of the bond angle distribution appears near 90°, and does not shift significantly with the increase in K₃AlF₆ concentration.

Figure 3. (a) Average CN integral curve of Al-F ion pairs, (b) Bond angle distribution of F-Al-F under different K₃AlF₆ concentrations.

3.4. Distribution of F Ion Type and Al-F Complex Ion Group

In this section, the distribution of the Al-F complex ion groups in the molten system is calculated, as shown in Figure 5. On the one hand, the F-type distribution statistic was derived by enumerating the quantities of Al³⁺ and K⁺ ions inside a spherical region centered on F. The determination of the limiting radii of the Al-F and K-F facilitated this analysis. The element F can be categorized into distinct forms, namely, free fluorine (Fᶠ), terminal fluorine (Fᵗ), and bridge fluorine (Fᵇ), among others. The classification is determined by the concentrations of Al³⁺ and K⁺ within a specific range. Bridge fluorine (Fᵇ) can exist in various configurations, such as Al-F-Al, Al-F-K, and K-F-K. On the other hand, the distribution of the complex ion types was determined by identifying core chains in the structure. In order to maintain the statistical integrity of the computation results for each frame, ions that had already been identified and counted were not be subjected to further search or enumeration. To examine the cross-linking of the complex ions, we analyzed the distribution of the F⁻ ions in the calculation results of 1,000 frame structures, as depicted in Figure 6. The classification of F⁻ can be delineated into three distinct categories based on the count of cations present within its cut-off radius (Bridge fluorine Fᵇ, F ion connects two Al ions in the form of Al-F-Al; terminal fluorine Fᵗ, F ion connects with an adjacent Al ion; free fluorine Fᶠ, F ion does not interact with neighboring Al ions) [15]. With the increasing concentration of K₃AlF₆, the concentration of [AlF₆]³⁻ and [AlF₅]²⁻ exhibits a steady increase, but the concentration of [AlF₄]⁻ experiences a slow reduction and remains consistently low.
Figure 4. Bond angle distribution of F-Al-F under different coordination numbers: (a) CN = 4, (b) CN = 5, (c) CN = 6.

Due to the small interaction between the K ions and F ions, the statistical target cation in this system is only Al ions, and the statistical cutoff radius is 2.465 Å, which corresponds to the radius of the first valley value in the RDF statistical results. As shown in Figure 6, the predominant type of fluorine ion in the molten salt system is terminal fluorine, accounting for more than 90%. As the mass proportion of K₃AlF₆ increases, the terminal fluorine first decreases and then increases, with a minimum value of 90.78% at a mass proportion of K₃AlF₆. As the mass proportion of K₃AlF₆ increased, the proportion of bridge fluorine Fₖ first increased and then decreased, reaching a maximum of 3.1% at the mass proportion of K₃AlF₆. In addition, the free fluorine F increased progressively as the K₃AlF₆ mass proportion increased.
In order to conduct a more comprehensive examination of the impact of different concentrations of K$_3$AlF$_6$ on the dispersion of complex ions, a detailed analysis was performed to identify the specific types of complex ions present. The statistical findings are represented in Figure 6a, illustrating the alteration in the concentration ratio of aluminum inside each complex ion. The coexistence of four-coordination, five-coordination, six-coordination,
and massive complex ions is apparent in the molten salt system. Moreover, the relationship between the distribution of Al-F complex ions lacking coordination numbers and the concentration of K$_3$AlF$_6$ is consistently proportionate. The molten salt structure system consists of a significant quantity of [AlF$_4$]$^-$, [AlF$_3$$^2$]$^-$, and [AlF$_6$]$^{3-}$, with a lesser quantity of Al$_2$F$_7$$^{3-}$, [Al$_2$F$_{10}$]$^{4-}$, [Al$_3$F$_{15}$]$^{5-}$, and [Al$_3$F$_{14}$]$^{5-}$. With increasing K$_3$AlF$_6$ concentration, the number of pentacenate complex ions in the molten salt first decreases and then increases, whereas the number of large complex ions first increases and then decreases; the maximum value is attained when the K$_3$AlF$_6$ concentration is 20%. Further, the quantification of Fb in the [AlF$_6$]$^{3-}$, [AlF$_3$$^2$]$^-$, and [AlF$_4$]$^-$ is conducted in order to investigate the extent of cross-linking in complex ions with varying coordination numbers, as depicted in Figure 6b. Globally, the proportion of fluorine on the six-coordination [AlF$_6$]$^{3-}$ is comparatively high, and as the concentration of K$_3$AlF$_6$ rises, it first rises and then falls. To clarify, it may be inferred that a decrease in the concentration ratio (CR) may result in a reduction in the extent of cross-linking of complex ions inside the molten salt, particularly when there is a continuous enrichment of potassium ions (K$^+$) in the molten salt.

3.5. Transport Properties

The transport properties of the nK$_3$AlF$_6$-NaF-AlF$_3$ system are very important to the aluminum electrolysis process. Due to the high temperature and strong corrosion of aluminum electrolyte, relevant data are scarce at present. Meanwhile, the lack of data on partial transport properties severely limits the optimization of energy efficiency. In principle, the electrical conductivity of molten electrolytes is of an ionic nature, that is, the overall charge transport is performed by the individual ionic migrations. For such partially dissociated mixtures with a significant short-range ordering, several solutions have been reported in the literature. Among them, the self-diffusion coefficients of each species can be calculated from the slope of the mean-squared displacements (MSDs) over time. The results indicate that this approach can predict the transport properties of molten salt with appreciable accuracy.

Through analyzing the particle trajectory data produced by FPMD, the self-diffusion coefficient of the ions in the system are obtained from the slope of the mean-squared displacements (MSDs) over time [26]. In this context, MSDs are employed to model the motion over an extended period, ensuring its temporal linearity and mitigating the occurrence of collision-free motion.

\[ D_s = \frac{1}{6N_i} \lim_{t \to \infty} \frac{d}{dt} \langle \sum_i (r_i^\alpha(t) - r_i^\alpha(0))^2 \rangle \]  

(2)

where $N_i$ is the number of species $i$ in the system and $r_i(t)$ is the displacement of a given ion $\alpha$ of species $i$ in time $t$, while $r_i(0)$ denotes its initial position in the Cartesian space.

As shown in Figure 7, the relative diffusion rates of the various ions in the molten state can be observed to follow the order of Na > K > F > Al. The high diffusion capacity of the Na and K ions suggests that they do not readily form complex ion groups with F anions. Instead, they are evenly dispersed throughout the entire system in a state of free diffusion. However, the diffusion capacity of the potassium ions is slightly lower than that of the sodium ions due to their larger volume and mass [27,28]. Nevertheless, the diffusion capacity of the Al and F ions is limited due to the significant polarity disparity between these ions and the O ions. Additionally, the formation of intricate complex ion groups further hampers their diffusion ability [29,30]. With the increasing concentration of K$_3$AlF$_6$, the diffusion coefficient of each ion reaches a maximum value of 15–20%, while, when the concentration of K$_3$AlF$_6$ is greater than 15%, a larger volume of Al-F-Al complex ion groups is formed, making the diffusion of ions more difficult. Referring to our previous research [20], the order of diffusion performance of Al$^{3+}$ in Al-F complex ion groups with varying coordination numbers is as follows: [AlF$_6$]$^{3-}$ > [AlF$_3$$^2$]$^-$ > [AlF$_4$]$^-$ when the concentration of K$^+$ increases in the molten salt, decreasing the value of CR can result in a reduction in the degree of cross-linking of the complex ions in the molten salt. This
reduction can significantly improve the diffusion performance of Al\(^{3+}\) and consequently raise the current efficiency. Even aluminum–fluorine complex ions (mainly [AlF\(_5\)]\(^{2-}\)) and free fluorine (single F\(^-\)) are more favorable to discharge on the anode surface at this stage [30–32].

![Figure 7. Self-diffusion coefficients of different ions in nK\(_3\)AlF\(_6\)–NaF–AlF\(_3\) system.](image)

4. Conclusions

The present study used the ab initio molecular dynamics (AIMD) methodology to investigate the ionic micro-structure and transport characteristics of the nK\(_3\)AlF\(_6\)-2.2NaF-AlF\(_3\) system. Furthermore, it provides clarification on the evolving patterns and mechanisms of production for the various representative ionic structures present in the system. The results show that the average bond length and cut-off radius for the Al-F bond are reported as 1.76 Å and 2.422 Å, respectively. Similarly, the average bond length and maximum cut-off radius for the K-F bond are documented as 2.31 Å and 3.06 Å, respectively. The mean coordination number of the Al-F bond ranges from 5.12 to 5.20. The interaction between aluminum and fluorine is characterized by a significant degree of strength, mostly attributed to the presence of covalent bonds. This results in the formation of a considerable quantity of complex ion groups, such as [AlF\(_4\)]\(^-\), [AlF\(_5\)]\(^{2-}\), and [AlF\(_6\)]\(^{3-}\). The bond angle distribution of the complex ions mainly occurs between 65° and 180°, and there is essentially no bond angle distribution less than 65°. The diffusion ability of the ions in the system is Na > K > F > Al. The distribution and diffusion coefficient of the complex ions in the melt is influenced by the concentration of K\(_3\)AlF\(_6\). An increase in the concentration of K\(_3\)AlF\(_6\) beyond 20% leads to a highly unstable electrolysis process.

Subsequent investigations will prioritize the introduction of Al\(_2\)O\(_3\) into the K\(_3\)AlF\(_6\)-2.2NaF-AlF\(_3\) molten salt system, with a particular emphasis on exploring the ionic structure and transport features of the KF-NaF-AlF\(_3\)-Al\(_2\)O\(_3\) system. The findings of this study hold significant practical implications for the experimental investigation of low-temperature aluminum electrolytes that incorporate potassium salts.

Author Contributions: Conceptualization and methodology, J.L.; Software, validation and data curation, C.C.; Investigation, visualization, writing—original draft preparation, J.W.; Supervision and project administration H.Z. All authors have read and agreed to the published version of the manuscript.
Funding: This research was funded by the National Key R&D Program of China (2022YFB3304902), the National Natural Science Foundation of China (U2202253, 62133016, 51974373), the Yunnan Province Science and Technology Planning Project (202202AB080017), and the Frontier Cross-disciplines Project of CSU (2023QYJC007).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

7. Li, J.; Li, J.; Wang, J.; Zhang, H. Insight into sodium penetration with mechanical behaviors of carbon electrodes by large-scale reactive molecular dynamics simulations. Chem. Phys. Lett. 2022, 800, 139657. [CrossRef]
15. Lv, X.; Xu, Z.; Li, J.; Chen, J.; Liu, Q. First-principles molecular dynamics investigation on Na3AlF6 molten salt. J. Fluor. Chem. 2016, 185, 42–47. [CrossRef]
24. Lv, X.; Xu, Z.; Li, J.; Chen, J.; Liu, Q. Molecular dynamics investigation on structural and transport properties of Na3AlF6–Al2O3 molten salt. J. Mol. Liq. 2016, 221, 26–32. [CrossRef]


Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.