First-Principles Molecular Dynamics Simulation on High Silica Content Na$_3$AlF$_6$–Al$_2$O$_3$–SiO$_2$ Molten Salt

Yuan Feng, Mao Li, Wenyuan Hou, Benjun Cheng, Jiaoru Wang, and Hesong Li*

ABSTRACT: A new method for the disposal of the spent refractory materials by adding them directly to electrolytic cells requires our better knowledge of the Na$_3$AlF$_6$–Al$_2$O$_3$–SiO$_2$ melt system. The development of computational materials science offers us a new way to avoid the limitation of the experiment under a strong corrosive environment at high temperatures. First-principles simulation is applied to study the structure information, electronic properties, and transport properties of the system. The study reveals that the main Si and Al ions in the melt are complex ion groups such as [SiF$_2$O$_2$]$^2^−$, [SiF$_3$O$_2$]$^3^−$, [SiF$_5$O$_2$]$^3^−$, [AlF$_2$O$_2$]$^2^−$, and [AlF$_3$O]$^3^−$. Tangled structures like [SiAlO$_5$F$_4$]$^{4^+}$ also exist in the melt. The average coordination number of Al−F and Si−F is 3.21 and 2.45, respectively. O ions mainly act as bridge ions in the melt. The bonding ability of Al with O ions is stronger than that of Si with O ions. Moreover, the Al−O bond is mainly covalent, while the Al−F bond is basically ionic characters. The order of diffusion ability of ions from large to small is Na, F, Al, Si, and O. Addition of SiO$_2$ into the Na$_3$AlF$_6$–Al$_2$O$_3$ molten salt causes an increase of the viscosity and a decrease of ionic conductivity.

INTRODUCTION

The current electrolytic method of producing aluminum has been used for quite a long time. The whole process is very energy-consuming and causes severe environment pollution. One of the pollutants produced during the Hall–Héroult process is the spent pot lining (SPL). The main contents of SPL are the spent carbon cathode block and spent refractory materials (SRM). SPL is a serious pollutant because it contains some fluoride and cyanide, which greatly damage the environment. The main method to dispose SPL is the landfill method, which is expensive and results in resources being wasted. Meanwhile, our previous research has proposed a new way for the disposal of SRM. By adding SRM directly to the electrolytic cell, the Al–Si alloy can be produced directly through the electrolytic process. This process is cheaper and reclaims most of the resources from SRM. The relevant experiments have been carried on currently and have achieved the expected target.

Since the addition of SRM, the ordinary electrolyte system of aluminum–fluorine–oxygen has become a system of Na$_3$AlF$_6$–Al$_2$O$_3$–SiO$_2$. The addition of silica and alumina into a molten system of cryolite can lead to changes of physical and chemical properties. This type of electrolyte system has been rarely studied before. Elwell and Rao¹ and Keller et al.² have researched the electrodeposition of silicon using SiO$_2$/Al$_2$O$_3$ electrolytes. Grjotheim and Matiasovsky³ and Fellner and Matiasovsky⁴ have investigated the possible reactions in the molten system containing silica dissolved in cryolite and their Gibbs free energies. Tabereaux et al.⁵ and Grjotheim et al.⁶ have studied the production of aluminum–silicon alloys using bath containing silica. These research studies mainly focused on the possible chemical reactions in the melt and the optimized operation parameters for industrial production. The possible particle aggregation, electronic properties, and transport properties of the system have not been fully studied before, while these properties have a great influence on the industrial processes and require our further research.

Compared with the traditional experimental method, the computational simulation method has great advantages of obtaining microstructure and properties at a low cost. For a highly corrosive melt at high temperature (1273–1283 K), experiments upon it can be expensive and the results are strongly dependent on the experimental setting, which causes great limitations. As a classic computational simulation method, first-principles molecular dynamics simulation calculates ionic interactions directly from first-principles, while
requiring no fitting to the experimental data. It has been applied to KCl–LiCl, 28 CaO–CaSiO₃, 9 KF–NaF–AlF₃–Al₂O₃ 10 Li₂TaO₅ 11 and FeAsS 12 systems successfully. In this study, a Na₃AlF₆–Al₂O₃–SiO₂ system with a high content of SiO₂ was investigated by the first-principles molecular dynamics simulation for the first time. The structure information, electronic properties, and transport properties of the system were studied to investigate the influence of the addition of SiO₂ into the system.

Computational Method. The simulation system contains 203 atoms with a chemical component of 80 wt % Na₃AlF₆, 5 wt % Al₂O₃, and 15 wt % SiO₂. It is necessary to point out that Weil and Fyfe 3 have studied the solubility of SiO₂ in the Na₃AlF₆–Al₂O₃–SiO₂ system. A small addition of Al₂O₃ can significantly increase the solubility of SiO₂. At 1010 °C, our system is located in the liquid zone of the phase diagram he has obtained. The density of the system is 2.09 g/cm³, which refers to the data from the research of Grijth et al. 6,14 The initial configuration of this simulation was obtained from Packmol software 15 by creating a random displacement of atoms into the system box. The molecular dynamic simulation was performed using the Vienna Ab-Initio Simulation Package VASP version 5.2.11. 16 Projector-augmented wave Perdew–Burke–Ernzerhof of pseudo potential supplied from the VASP package was used for Na (2p³3s¹ Na-pv 19Sep2006), Al (3s³3p² 04Jan2001), Si (3s³3p², 05Jan2001), O (2s22p⁴, 04Jan2001), and F (2s²2p², 08Apr2002). The DFT-D2 method 19 was used to add the van der Waals dispersion correction. The energy cutoff of 420 eV and the k-point grid of 1 × 1 × 1 were adopted. 20 The periodic boundary condition was used to eliminate the influence of the boundary effect. The temperature is set to 1283 K, and this simulation uses a canonical ensemble (NVT) with a Nosé thermostat 21 with a Nosé mass corresponding to a period of 40 time steps. A time step of 2 fs was chosen in order to make the energy drift less than 1 meV/(atom fs), 20 and the total simulation time was 10 ps. Bengtson et al. 20 point out that a cell of 216 ions and simulation times of 6–12 ps is sufficient for the melt system to get adequately converged results that fit the experimental data.

Computational Method. Information like partial radial distribution function (PRDF), coordination number, bond angle distribution, electronic structure, and transport properties is calculated from the simulation. PRDF describes the distribution information of one type of ions around the other. Calculated from the trajectory of the simulation, PRDF g(r) represents the probability of finding an atom in a shell dr at the distance r of another type of atom, as shown in eq 1

\[ g_j(r) = \frac{V}{N N_j} \int g_j(r, \Delta r) \frac{n_j(r, \Delta r)}{4\pi r^2} dr \]  

(1)

where V is the simulation box volume, N is the number of ions, and n_j(r, \Delta r) is the number of j ions surrounding i ions in a shell dr at the distance r of another type of atom, as shown in eq 2

\[ CN_{i-j} = 4\pi \rho \int_0^R g_j(r)^2 dr \]  

(2)

where CN_{i-j} means the coordination number of i ions surrounding by j ions, \rho is the mean density of j ions, g_j(r) is the PRDF of them, and R is the cutoff radius.

Bond angle distribution is calculated by analyzing the trajectory data of the simulation. The bond angle of F–Al–F, Al–O–Al, Si–O–Si, and F–Si–F of each frame of the trajectory is calculated and the total distribution of them is analyzed.

The electronic structure is calculated from the optimized structure of the system. A static calculation is carried on to obtain the Bader charge of the ions. The density of states (DOS) and crystal orbital Hamilton populations (COHP) are calculated to expand our knowledge of the interaction of the ions of the system.

The transport properties including self-diffusion coefficient D, viscosity \eta, and ionic conductivity \sigma can be obtained from mean square displacement (MSD). MSD represents the motion of ions in the system. The definition of MSD is as shown below: 3

\[ MSD = \langle (\Delta r(t)^2) \rangle = \frac{1}{N} \sum (r_i(t)^2 - r_i(0)^2) \]  

(3)

where r(t) is the position of ion i at time t and \langle \rangle indicates the calculation of averaging. At a large timescale, MSD should be linear with time, otherwise the system is in a state of disequilibrium.

Self-diffusion coefficient D can be obtained from the MSD curve. According to Einstein’s diffusion law, the relation between MSD slope and \sigma is as shown below: 24

\[ D = \lim_{t \to \infty} \frac{1}{6} \frac{d(\Delta r(t)^2)}{dt} \]  

(4)

The relation between viscosity \eta and self-diffusion coefficient D is demonstrated in the Einstein–Stokes equation.

\[ \eta = \frac{K_B T}{2\pi DL} \]  

(5)

where K_B is the Boltzmann constant with a value of 1.38 × 10⁻²³ J/K. T is the temperature of the system. L is the step length of ion diffusion, which is basically equal to the ion diameter. 25

The Nernst–Einstein equation depicts the relation between ionic conductivity \sigma and self-diffusion coefficient D, as shown below.

\[ \sigma = D \frac{n q^2}{K_B T} \]  

(6)

where n is the unit volume concentration of carrier ions and q is the ion charge.

Results and Discussion. Structure Information. Figure 1 is the microstructure of Na₃AlF₆–Al₂O₃–SiO₂ molten salt. The Na⁺ ions are shown in yellow, F⁻ in orange, Al³⁺ in gray, Si⁴⁺ in blue, and O²⁻ in red. The lines connecting atoms are bonds between them. Bonds are formed when the distance between atoms is less than the cutoff radius, which is the radius value at the first minimum in the radial distribution functions curve. 25 There are complex ion groups formed in the system. Al ions are connected with F and
O ions forming [AlF$_2$O]$_3$~$^-$, [AlF$_3$O]$_2$~$^-$, and [AlF$_4$O]$_3$~$^-$ ion groups. Si ions are connected with F and O ions forming [SiF$_2$O]$_3$~$^-$, [SiF$_3$O]$_2$~$^-$, and complex [SiF$_4$O]$_3$~$^-$ groups. Intricate structures like [SiAlO$_2$F$_4$]$_3$~$^-$ and [SiAl$_2$O$_2$F$_7$]$_3$~$^-$ are also formed between Al and Si groups. O ions are connected with Al or Si ions in melt, and most of them act as bridge ions connecting two ions. There are three types of F ions in the melt. Most of the F ions act as a terminal fluorine connecting one Al or Si ion, some act as free fluorine randomly distributed in the melt, and only a few numbers of F ions act as a bridge ion connecting two ions. [AlF$_3$]$_3$~$^-$ and [AlF$_4$O]$_3$~$^-$ ion groups, which are the prevailing ones in ordinary Na$_3$AlF$_6$ melt, also exist in the system, but they are in the minority. The presence of [SiF$_2$O]$_3$~$^-$ and [SiO$_2$F$_3$]$_3$~$^-$ ion groups is consistent with the research by Dolejs and Baker.

Partial Radial Distribution Functions and Coordination Number. The PRDFs of this system are shown in Figure 2. For a radius greater than 6 Å, the g(r) value of each PRDF tends to reach a constant value of 1, which suggests the long-range disorder in the melt. The first peak value of Si−O, Si−F, Al−F, and Al−O are quite sharp and the locations of peaks are all less than 2 Å. It suggests the strong bonding ability of Si with F, Si with O, Al with F, and Al with O ions and the presence of complex ion groups of them in the system. The g(r) value of Si−O is nearly twice as large as that of Al−O and the radius at the peak is smaller, which means the formation of the Si−O bond is easier than that of the Al−O bond. A sharp peak also exists in the RDF of the Si−Si pair at the radius of 3.09 Å, which is very large to form a bond, indicating that most Si ions are in an orderly form where two Si ions are linked by a bridge ion in the system. The average bond length of the ion pair can be represented by the radius of the first peak in the PRDF. The average bond length of each pair is shown in Table 1. Because of the lack of experimental data on the Na$_3$AlF$_6$−Al$_2$O$_3$−SiO$_2$ system, we compare these data with the values from two references, one is based on a Na$_3$AlF$_6$−Al$_2$O$_3$ system containing 5 wt % Al$_2$O$_3$ and the other is on a KF−NaF−AlF$_3$−Al$_2$O$_3$ system containing 6.6 wt % Al$_2$O$_3$. Compared with the data from reference, the average bond length of most ion pairs matches that of the reference. The addition of SiO$_2$ into the system only affects a few ion pairs. A decrease of O−O is observed, which was due to the formation of the Si−O bond, which is relatively shorter than the Al−O bond, in the system. The average bond length of Al−Al is smaller than 3.46 and 3.52 Å, which are twice the bond lengths of Al−O and Al−F, respectively, indicating the possible presence of O ions or F ions as bridge ions in the Al−O−Al or Al−F−Al groups with a bond angle smaller than 180°. The presence of O or F as bridge ions in Si−O−Si or Si−F−Si ion groups is also possible.

The average coordination number of Al−F groups and Si−F groups can be calculated from the integration of RDF curves of each pair at the cutoff radius. Figure 3 shows the integration function of Al−F and Si−F. The cutoff radius of PRDF of the Al−F pair is 2.55 Å, which is the radius at the first minimum.

![Figure 1. Microstructure of the Na$_3$AlF$_6$−Al$_2$O$_3$−SiO$_2$ melt.](https://dx.doi.org/10.1021/acsomega.0c05339)

![Figure 2. PRDFs of the Na$_3$AlF$_6$−Al$_2$O$_3$−SiO$_2$ melt.](https://dx.doi.org/10.1021/acsomega.0c05339)

| ion pair | result | ref 25 | ref 10 |
|----------|--------|--------|--------|
| bond length(Å) |        |        |        |
| Al−Al    | 3.19   | 3.21   | 3.69   |
| Al−F     | 1.76   | 1.82   | 1.77   |
| Al−Na    | 3.27   | 3.59   | 3.65   |
| Al−O     | 1.73   | 1.73   | 1.61   |
| Al−Si    | 3.14   |        |        |
| F−F      | 2.64   | 2.51   | 2.51   |
| F−Si     | 1.62   |        |        |
| F−Na     | 2.28   | 2.41   | 2.43   |
| F−O      | 2.69   | 2.69   | 2.73   |
| Na−Na    | 3.56   | 3.53   | 3.75   |
| Na−O     | 2.34   | 2.35   | 2.25   |
| Na−Si    | 3.54   |        |        |
| O−O      | 2.74   | 2.94   | 2.93   |
| O−Si     | 1.63   |        |        |
| Si−Si    | 3.09   |        |        |
The average CN of Al−F is 3.21. Compared with the CN value of 4−5 in an ordinary Na₃AlF₆−Al₂O₃ system, this value is smaller. The main reason is that the high content of SiO₂ in the system leads to a comparatively rich O ion environment in the system. The strong bonding ability between Al and O ions cause O ions replace some F ions in ion groups like [AlF₆]³⁻ and [AlF₅]²⁻, leading to the widespread presence of complex Al−O ion groups, such as [AlF₂O₂]²⁻, [AlF₃O]²⁻, and [AlF₄O]³⁻. Ordinary ion groups of [AlF₆]³⁻ and [AlF₅]²⁻ are rare in cryolite melt. The average CN of Si−F is 2.28, which is the integration value of PRDF of Si−F at the cutoff radius of 2.45 Å, corresponding to the large presence of [SiF₂O₂]⁻² and some [SiO₂F₃]³⁻ ion groups in the system.

Bond Angle Distributions. The bond angle distribution is calculated using a self-made Python script by analyzing the trajectory information of the simulation. The bond angle distribution of each frame in the trajectory of the simulation is calculated, and the total bond distribution is analyzed. The first 250 frames of the trajectory are neglected to avoid the influence of the initial structure. Figure 4 shows the bond angle distribution of F−Al−F, Al−O−Al, Si−O−Si, and F−Si−F in the system. The ideal octahedron [AlF₆]³⁻ group has eight 90° and three 180° F−Al−F bond angles, and the ideal triangular bipyramid [AlF₅]²⁻ group has six 90°, three 120°, and one 180° F−Al−F bond angles. There are two types of triangular bipyramid [AlOF₄]³⁻ groups formed in the system, one has four 90° and one 120° F−Al−F bond angles and one 180° F−Al−F bond angle and the other has three 90° and three 120° F−Al−F bond angles. The tetrahedron [AlOF₃]³⁻ group formed in this system has one 109° F−Al−F bond angle. The main peak of F−Al−F angle distribution is large and relatively smooth, and it is located in the area 80−110°, indicating the presence of those ion groups in the system. A small peak also exists at 160−180°, corresponding to the triangular bipyramid [AlF₅]²⁻ and [AlOF₄]³⁻ groups in the system. The Al−O−Al bond angle distribution is mainly located in the area from 120 to 140°, with a peak value at 130°. The average bond lengths of Al−O and Al−Al are 1.73 and 3.19. This means that most of the Al ions are connected by bridge O ions in the system in a form of Al−O−Al. The peak of the Si−O−Si bond angle is located at 135°, and the average bond lengths of Si−O and Si−Si are 1.63 and 3.09, indicating that most of the Si ions are connected by O ion-forming complex ion groups. The [SiOF₃]²⁻ ion group has one 90° F−Si−F bond angle, and the [SiOF₄]³⁻ group has two 90° and one 180° F−Si−F bond angles, corresponding to the main peak at 90° and a small peak at 170° in the distribution curve.

Electronic Structure. The electronic structure of the system is calculated from the optimized final structure of the dynamics calculation using the same setting as dynamics simulation. Properties like the DOS, Bader charge, and COHP are analyzed. Figures 5 and 6 show the total and partial DOSs of the system, respectively. The electron orbitals at the energy level from −27 to −20 eV are occupied by Na 2p and F 2s states. F 2p and O 2p states, hybridization of Al 3p and Al 3s, and a combination of Si 3s and Si 3p occupy the orbits near the Fermi level. It indicates that interactions of Al−O, Al−F, Si−O, and Si−F exist in this melt and electrons transfer from Al 3s and 3p and Si 3s and 3p to O 2p and F 2p. The average Bader charges of five ions are Na (+1.01e), Al (+2.47e), Si (+3.12e), O (−1.52e), and F (−0.86e).

In order to know the interaction of these ion pairs, the COHP of the system is calculated using LOBSTER software.28 Figure 7 shows the −COHP plot of the system. Below the Fermi level (0 eV), the −COHP value of Al−O and Si−O is mainly positive, and the integration value of Al−O is greater than that of Si−O, suggesting that the bonding ability of Al with O ions is stronger than that of Si with O ions and Al−O bond is comparatively stable than that of Si−O bond. The curve of Al−F fluctuates around 0, indicating that covalent interactions between Al and F ions are relatively weak. The bond between Al and F is mainly ionic. The integration of −COHP of Si−F is positive, suggesting that covalent bond interaction exists between them. The presence of a negative part of the curve suggests that the Si−F covalent bond interaction is relatively more unstable than Al−O and Si−O.

Transport Properties. Transport properties like self-diffusion coefficient D, viscosity η, and ionic conductivity σ are calculated from the MSD curves of the simulation. These properties significantly influence the industrial production process of Al−Si alloy production. The MSD curves of Na, Al, Si, O, and F ions are obtained from trajectory data of the simulation using the R.I.N.G.S. code.29 Figure 8 shows the MSD and linear fitting curves of five ions. The trajectory data of the initial 1.5 ps simulation are withdrawn to avoid the impact of the initial structure to the result. MSD curves of Na, Al, Si, O, and F ions are basically straight lines. The linear fitting of MSD curves with R-square all above 0.98 suggests that these ions are generally in a free diffusion state and the diffusion coefficients of Na, Al, and F have very similar values, which are greater than the Si and O ions. Figure 8 shows that Na, Al, and F have the highest diffusion coefficients, indicating that these ions have the highest mobility in this system.
The self-diffusion coefficients $D$ can be calculated from MSD curves. Table 2 lists the ion self-diffusion coefficients $D$ ($10^{-9}$ m$^2$/s), viscosity $\eta$ (mPa·s), and ionic conduction $\sigma$ (S/cm) in the Na$_3$AlF$_6$–Al$_2$O$_3$–SiO$_2$ melt. The order of diffusion ability of five ions from large to small is Na, F, Al, Si, and O. The large diffusion coefficient of Na suggests that Na ions mainly exist in a free diffusion state in the system without interacting with other ions forming the complex ion group. The relatively weak bonding interaction between Al–F and Si–F in the melt and the presence of free fluorine make the diffusion ability of F ions greater than that of Al, Si, and O ions. The small diffusion coefficients of Al, Si, and O ions are mainly due to the forming of complex ion groups between them in the melt. The large volume and strong interactions of ion groups bring resistance to the diffusion of ions.

The viscosity $\eta$ of the system is calculated using self-diffusion coefficients $D$ of ions in the system and the Einstein–Stokes formula, as shown in eq 5, where $\lambda$ is the step length of particle diffusion. $\Lambda$ is considered to be equal to the diameter of Na$^+$, Al$^{13+}$, Si$^{14+}$, O$^{2-}$, and F$^-$ ions (which is 2.04, 1.07, 0.80, 2.80, and 2.66 Å respectively). Because the published data on the viscosity of cryolite containing both silica and alumina are rare, this value is compared with data of the Na$_3$AlF$_6$–Al$_2$O$_3$ system and the Na$_3$AlF$_6$–SiO$_2$ system. The experiment data show that viscosity is 2.35 in the Na$_3$AlF$_6$–Al$_2$O$_3$ system containing 4 wt % Al$_2$O$_3$ at 1000°. In the Na$_3$AlF$_6$–SiO$_2$ system (13.3 wt % SiO$_2$) at 1030°, the viscosity is 3.75°. The deviation is mainly due to the difference between temperatures, and the addition of SiO$_2$ leads to the formation of
complex ion groups like $[\text{SiF}_3\text{O}_2]^3^-$ and $[\text{SiAlO}_3\text{F}_3]^3^-$, which increase the viscosity.

Ionic conductivity $\sigma$ is calculated using self-diffusion coefficients $D$ and the Nernst–Einstein equation, as shown in eq 6, where $n$ is the unit volume concentration of the carrier ions which equals the number of the carrier ions in a unit volume and $q$ is the charge of the ion. This value is compared with the data of Na$_3$AlF$_6–$SiO$_2$ and Na$_3$AlF$_6–$Al$_2$O$_3$ systems. The experiment data show that $\sigma$ is $2.1$ in the Na$_3$AlF$_6–$SiO$_2$ mixture (containing $84$ wt % Na$_3$AlF$_6$ and $16$ wt % SiO$_2$) at $1000^\circ$C and $2.45$ in the Na$_3$AlF$_6–$Al$_2$O$_3$ system (containing $4$ wt % Al$_2$O$_3$) at $1000^\circ$C, respectively. The main reason of an increase in ionic conductivity is that addition of both SiO$_2$ and Al$_2$O$_3$ into the melt leads to the formation of large ion groups, which increases the viscosity and restricts the motion of ions. Reduction of the number of carrier ions also causes a decrease in the melt conductivity.

It is necessary to point out that the experiment for melt systems under a strong corrosive environment at high temperatures is quite difficult and may lead to errors in the result. Korenko et al. 32 have pointed out that different experimental procedures can lead to a large-scale variation of experiment data. For instance, the viscosity of the Na$_3$AlF$_6$ melt at $1000^\circ$C measured by Brockner et al. 34 is $2.3$, while the measured result by Janz and Tomkins 35 at the same system is $1.28$. However, the first-principles molecular dynamics simulation, which requires no fitting to experimental or computed data, can get relatively accurate results. It is a useful predictive tool to expand our knowledge of the system.

# CONCLUSIONS

The first-principles molecular dynamics simulation was applied to the high SiO$_2$ content Na$_3$AlF$_6–$Al$_2$O$_3–$SiO$_2$ system to study the ion aggregation situation and transport properties for the first time. The study reveals that the main Si ions in this melt are complex ion groups of Si, O, and F ions, such as $[\text{SiF}_3\text{O}_2]^2^-$, $[\text{SiFO}_3]^3^-$, and $[\text{SiF}_2\text{O}]^3^-$. Al ions have the same tendency to form ion groups with O and F ions, and the presence of $[\text{AlF}_3\text{O}]^3^-$, $[\text{AlF}_2\text{O}]^2^-$, and $[\text{AlF}_2\text{O}]^3^-$ is also observed. The formation of intricate ion groups between Si and Al ion groups is also noticed. $[\text{AlF}_3]^2^-$ and $[\text{AlF}_4]^2^-$ ion groups, which are prevalent in the ordinary cryolite melt [20], are rare in the system. The average coordination number of Al–F is $3.21$, which indicates the widespread presence of $[\text{AlF}_3\text{O}]^3^-$ and $[\text{AlF}_2\text{O}]^2^-$ groups. The coordination number of Si–F is $2.45$, corresponding to the main forms of Si ions $[\text{SiF}_3\text{O}_2]^2^-$ and $[\text{SiF}_2\text{O}]^3^-$ groups in the melt. The O ions mainly act as bridge ions in the melt. The bonding ability of Al with O ions is stronger than that of Si with O ions. The Al–O bond is mainly covalent, while the Al–F bond is basically ionic characters. The average Bader charges of five ions are Na (+1.01e), Al (+2.47e), Si (+3.12e), O (−1.52e), and F (−0.86e). The order of diffusion ability of five ions from large to small is Na, F, Al, Si, and O. Addition of SiO$_2$ into Na$_3$AlF$_6–$Al$_2$O$_3$ molten salt causes a decrease of the viscosity and a decrease of ionic conductivity. Despite the limitations of experiments upon strong corrosive molten salt at high temperature, the first-principles molecular dynamics simulation can study the system on a microscopic perspective, which enlightens our knowledge on the high silica content aluminum electrolyte system.

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### Notes

The authors declare no competing financial interest.

Table 2. Ion Self-Diffusion Coefficients $D$ ($10^{-9}$ m$^2$/s), Viscosity $\eta$ (mPa·s), and Ionic Conduction $\sigma$ (S/cm) in the Na$_3$AlF$_6–$ Al$_2$O$_3–$SiO$_2$ System

| ions                     | self-diffusion coefficient | viscosity | ionic conductivity |
|--------------------------|----------------------------|-----------|--------------------|
|                          | Na | Al | Si | O | F |                |                   |
| computation value ref 31 | 7.3| 3.53| 2.64| 2.48| 5.52| 3.373 | 2.021 |
| (Na$_3$AlF$_6–$Al$_2$O$_3$ system) ref 30 | | | | | | 2.35 | 2.10 |
| (Na$_3$AlF$_6–$SiO$_2$ system) | | | | | | 3.75 | 2.45 |

Figure 8. MSD and linear fitting curves of Na, Al, Si, O, and F ions.
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