Equivalent conductivity and its activation energy of NaF-AlF₃ melts

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Abstract: Electrical conductivity of NaF-AlF₃ melts was measured by continuously varying cell constant(CVCC) technique. Relationships between equivalent conductivity at 990−1030 °C and temperature and composition, and relationship between equivalent conductivity activation energy and composition of the melts were then studied on the basis of two-step decomposition mechanism of AlF₆³⁻. According to the changes of molar fractions of different anions in NaF-AlF₃ melts, courses of dependence of equivalent conductivity and its activation energy on composition were analyzed. The results show that the influence of temperature on equivalent conductivity of the melts is small in the researched temperature range, and equivalent conductivity increases with increasing the molar fraction of AlF₃; there is a minimum point in the activation energy—composition curve when molar fraction of AlF₃ is 0.29.

Key words: equivalent conductivity; equivalent conductivity activation energy; continuously varying cell constant technique; NaF-AlF₃ melts

1 Introduction

NaF-AlF₃ melts with different compositions are used as solvent in modern aluminium electrolysis industry. So, it is of most importance to study their physicochemical properties. Electrical conductivity is an important property for aluminium electrolyte from theoretical and technological viewpoints. The theoretical significance for melts electrical conductivity research lies in its close relation with structural entity species in melts and their transfer mechanism. Research on equivalent conductivity of melts would contribute to understanding the contribution of different entities to conductance. So, melts equivalent conductivity research is the bridge between researches on its electrical conductivity and ionic structure.

The viewpoint is generally accepted that Na⁺ exists in NaF-AlF₃ melts as the only kind of cation, and AlF₆³⁻ which is partly decomposed also exists in the melts. But there are two main different opinions about AlF₆³⁻ decomposition mechanism. Some scholars hold that AlF₆³⁻ was decomposed as AlF₆³⁻=AlF₄⁻+2F⁻[1−2], others thought that AlF₆³⁻ was decomposed to AlF₃²⁻ and F⁻, firstly; and then AlF₃²⁻ was decomposed to AlF₄⁻ and F⁻: AlF₆³⁻=AlF₃²⁻+F⁻, AlF₃²⁻=AlF₄⁻+F⁻[3−8]. The two-step decomposition mechanism of AlF₆³⁻ has been accepted by more scholars since 1990s.

MATIASOVSKY and DANEK[9] have researched the equivalent conductivity and its activation energy of NaF-AlF₃ melts on the basis of one-step decomposition mechanism of AlF₆³⁻. But as mentioned above, two-step decomposition mechanism of AlF₆³⁻ is more reasonable by recent research. In this work, relationships between equivalent conductivity and temperature and composition and between equivalent conductivity activation energy and composition of NaF-AlF₃ melts were restudied based on the two-step decomposition mechanism of AlF₆³⁻. And then reasons for equivalent conductivity and its activation energy change were analyzed through the investigation of molar fraction change of different anions.

2 Experimental

Equivalent conductivity of molten mixture could be calculated by Eq.(1)[9]:

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\[
\lambda = \frac{\kappa M_e}{\rho}
\]  
(1)

where \(\lambda\) is the melts equivalent conductivity in S·cm\(^2\); \(\rho\) is the melts density in g/cm\(^3\); \(\kappa\) is the melts electrical conductivity in S/cm; and \(M_e\) is the melts mean equivalent molar mass defined by the following relation:

\[
M_e = \sum \frac{M_i x_i}{n_i}
\]  
(2)

where \(M_i\) is the molar mass of component \(i\) in g/mol; \(x_i\) is the molar fraction of component \(i\); and \(n_i\) is the number of positive or negative charges of the cation or anion of component \(i\).

Relationship between melts equivalent conductivity and temperature conforms to Arrhenius equation, that is

\[
\lambda = \lambda_0 \exp \left( \frac{-E_\lambda}{RT} \right)
\]  
(3)

where \(\lambda_0\) is a constant in S·cm\(^2\); \(E_\lambda\) is the equivalent conductivity activation energy in J/mol; \(R\) is the universal gas constant, and its value is 8.314 J/(mol·K); \(T\) is the thermodynamic temperature in K.

So, equivalent conductivity of molten mixture could be obtained based on its electrical conductivity and density.

### 2.1 Electrical conductivity measurements

Continuously varying cell constant (CVCC) technique was used to measure NaF-AlF\(_3\) melts electrical conductivity. This technique has been reported before\[10−15\]. Measuring principle of the technique was reported in Ref.[13]. A schematic drawing of measuring apparatus is shown in Fig.1.

Two-electrode measuring system was used. A Pt column in a BN tube connected with a Pt wire was used as the work electrode, and was immovable. The electrolyte-holding graphite crucible connected with an inconel rod was used as both counter electrode and reference electrode. The graphite could move vertically accurately together with the furnace, so, the distance between the graphite and the Pt electrode could be varied and then the conductivity cell length was varied. Temperature was measured by a Pt-PtRh\(_{10}\) type thermal couple.

AC impedance method was used for resistance measurement. Electrodes were connected to Autolab PGSTAT30 POTENTIOSTAT/GALVANOSTAT (BOOSTER 20 A). Frequency signal application and AC impedance data recording were controlled by computer. The AC amplitude was 10 mV, and circle resistance value at 10 kHz AC frequency was read.

The cross-sectional area of the conductivity cell was calibrated by measuring the electrical conductivity of molten cryolite at 1 000 \(^\circ\)C according to the published data (2.80 S/cm)[16]. To avoid the influence of the BN tube deforming caused by high temperature, the cross-sectional area was calibrated at intervals, and this procedure was done when the BN tube was changed.

### 2.2 Density measurements

Density measurement was based on Archimedes law. A schematic drawing of measuring apparatus is shown in Fig.2.

A Pt sphere was connected to electronic balance through a Pt wire. The furnace could move vertically accurately. Melts was held in a graphite crucible. Temperature was measured by a Pt-PtRh\(_{10}\) type thermal
couple.

Melts density was calculated by Eq.(4):

$$\rho_t = \frac{(m_0 - m)}{V}$$ (4)

where $\rho_t$ is the melts density in g/cm$^3$; $m_0$ is Pt sphere mass in the air in g; $m$ is the Pt sphere mass in melts in g; $V$ is the Pt sphere volume in cm$^3$. Value of $V$ was calibrated by measuring the density of molten NaCl at 800 °C[17] and then corrected to the value at measuring temperature according to the thermal expansion coefficient of Pt[18].

3 Results and discussion

As mentioned above, calculation of NaF-AlF$_3$ melts equivalent conductivity was based on two-step decomposition mechanism of AlF$_6^{3-}$. Molar fractions of Na$_3$AlF$_6$, Na$_2$AlF$_5$, NaAlF$_4$, and NaF from Raman spectrum research results of GILBERT[4] were used in the present calculation, as shown in Fig.3, with some data calculated through relationship between component molar fraction and temperature.

Measured values of density and electrical conductivity of NaF-AlF$_3$ melts of different compositions at different temperatures are listed in Table 1.

So, the equivalent conductivity of NaF-AlF$_3$ melts could be calculated by using Eq.(2). Relationships between equivalent conductivity and composition of NaF-AlF$_3$ melts at different temperatures are shown in Fig.4.

Eq.(5) could be deduced by taking natural logarithm on both sides of Eq.(4):

$$\ln \lambda = \left(\frac{-E_\lambda}{R} \right) \frac{1}{T} + \ln \lambda_0$$ (5)

It is clear that $\ln \lambda$ is linear with $1/T$, so, the value of the slope of $\ln \lambda-1/T$ curve equals $-E_\lambda/R$. Relationships between $\ln \lambda$ and $1/T$ of NaF-AlF$_3$ melts with different compositions are shown in Fig.5.

It can be seen from Fig.5 that linear relationship between $\ln \lambda$ and $1/T$ is satisfied for all of the researched compositions of NaF-AlF$_3$ melts except for the one with AlF$_3$ molar fraction of 0.32. It is thought that the exception was originated from experimental error. $\ln \lambda-1/T$ curves of the four reasonable compositions were linearly fitted by the least square method and then equivalent conductivity activation energy could be obtained by calculation of slope value fitted multiplied by $-R$. Calculated value of $E_\lambda$ vs molar fraction of AlF$_3$ curve was made, as shown in Fig.6.
Table 1 Measured values of density and electrical conductivity of NaF-AlF₃ melts

<table>
<thead>
<tr>
<th>Temperature/℃</th>
<th>Molar fraction of AlF₃</th>
<th>Density/(g·cm⁻³)</th>
<th>Electrical conductivity/(S·cm⁻¹)</th>
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<tr>
<td>990</td>
<td>0.25</td>
<td>2.0999</td>
<td>2.78</td>
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<td>2.61</td>
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</table>

Fig.4 Equivalent conductivity of NaF-AlF₃ melts

Isotherms of equivalent conductivity with different compositions and curve of equivalent conductivity activation energy vs composition of NaF-AlF₃ melts should be analyzed together with relative content change of different components in the melts.
minimum value of the equivalent conductivity activation energy appear when molar fraction of AlF$_3$ is 0.29 in Fig.6, which is attributed to the lower energy barrier of AlF$_4$ movement. When AlF$_3$ molar fraction is more than 0.32, curves in Fig.4 increase more and more gently, especially for 990 °C and 1 000 °C isotherms, in which equivalent conductivity is even decreased with AlF$_3$ molar fraction increasing. As seen from Fig.3, in this AlF$_3$ molar fraction range, there is little change of NaAlF$_4$ molar fraction change rate, and Na$_2$AlF$_5$ molar fraction increases more gently, even shows a decrease trend. That is responsible for the slope change of equivalent conductivity isotherm in Fig.4.

4 Conclusions

1) Equivalent conductivity vs composition curves of NaF-AlF$_3$ melts at 990, 1 000, 1 010, 1 020 and 1 030 °C were worked out on the basis of two-step decomposition mechanism of AlF$_4$$^{−}$.$^{−}$. It was thought that temperature had little effect on melts equivalent conductivity in the researched temperature range, and equivalent conductivity was increased with increasing AlF$_3$ molar fraction, in general. When molar fraction of AlF$_3$ was between 0.29 to 0.32, melts equivalent conductivity change rate was higher than that for lower or higher AlF$_3$ molar fraction.

2) Linear relationship between ln$\lambda$ and 1/$T$ of NaF-AlF$_3$ melts was proved. Equivalent conductivity activation energy vs composition curve of NaF-AlF$_3$ melts was worked out. It was found that the curve had a minimum value when AlF$_3$ molar fraction was 0.29.

3) It was thought that change of equivalent conductivity and its activation energy of NaF-AlF$_3$ melts was caused by anions content change, and then the changing reason was analyzed.

References


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