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Equivalent conductivity and its activation energy of NaF-AlF_3 melts

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Abstract: Electrical conductivity of NaF-AlF_3 melts was measured by continuously varying cell constant(CVCC) technique. Relationships between equivalent conductivity at 990−1 030 ℃ 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 AlF_6^{3-}. According to the changes of molar fractions of different anions in NaF-AlF_3 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 AlF_3; there is a minimum point in the activation energy—composition curve when molar fraction of AlF_3 is 0.29.

Key words: equivalent conductivity; equivalent conductivity activation energy; continuously varying cell constant technique; NaF-AlF_3 melts

1 Introduction

NaF-AlF_3 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-AlF_3 melts as the only kind of cation, and AlF_6^{3-} which is partly decomposed also exists in the melts. But there are two main different opinions about AlF_6^{3-} decomposition mechanism. Some scholars hold that AlF_6^{3-} was decomposed as $AlF_6^{3-}=AlF_4^-+2F^-$[1−2], others thought that AlF_6^{3-} was decomposed to AlF_5^{2-} and F^-, firstly; and then AlF_5^{2-} was decomposed to AlF_4^- and F^-: $AlF_6^{3-}=AlF_5^{2-}+F^-$, $AlF_5^{2-}=AlF_4^-+F^-$[3−8]. The two-step decomposition mechanism of AlF_6^{3-} has been accepted by more scholars since 1990s.

MATIASOVSKY and DANEK[9] have researched the equivalent conductivity and its activation energy of NaF-AlF_3 melts on the basis of one-step decomposition mechanism of AlF_6^{3-}. But as mentioned above, two-step decomposition mechanism of AlF_6^{3-} 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-AlF_3 melts were restudied based on the two-step decomposition mechanism of AlF_6^{3-}. 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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$$\lambda = \frac{\kappa M_e}{\rho} \quad (1)$$

where λ is the melts equivalent conductivity in S·cm^2; ρ is the melts density in g/cm^3; κ is the melts electrical conductivity in S/cm; and M_e is the melts mean equivalent molar mass defined by the following relation:

$$M_e = \sum_i \frac{M_i x_i}{n_i} \quad (2)$$

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

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

where λ_0 is a constant in S·cm^2; E_λ 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.

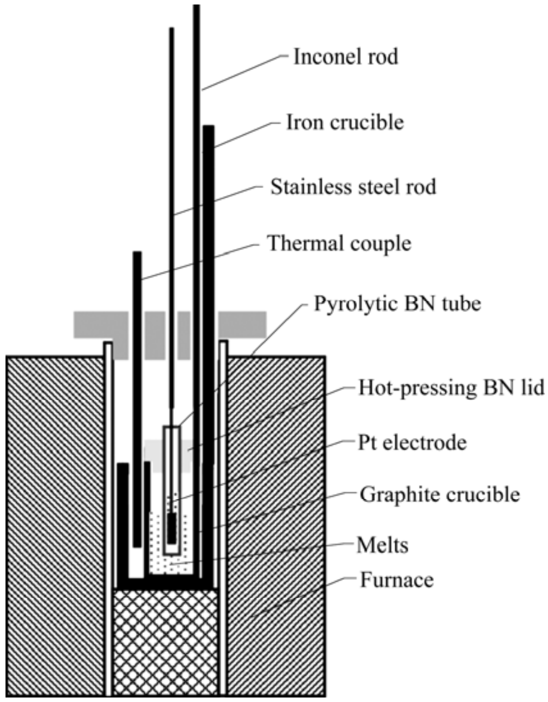

Fig.1 Schematic view of electrical conductivity measurement equipments

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 a 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 ℃ 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.

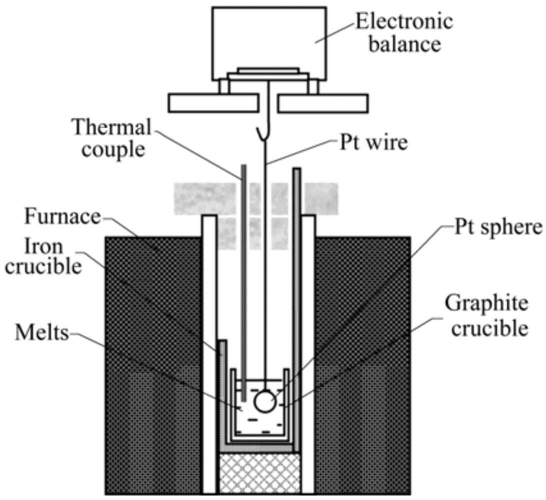

Fig.2 Schematic view of density measurement equipments

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):

$$\rho_t=(m_0-m)/V \qquad (4)$$

where ρ_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 ℃[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_3AlF_6, Na_2AlF_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):

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

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 expect 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_λ vs molar fraction of AlF_3 curve was made, as shown in Fig.6.

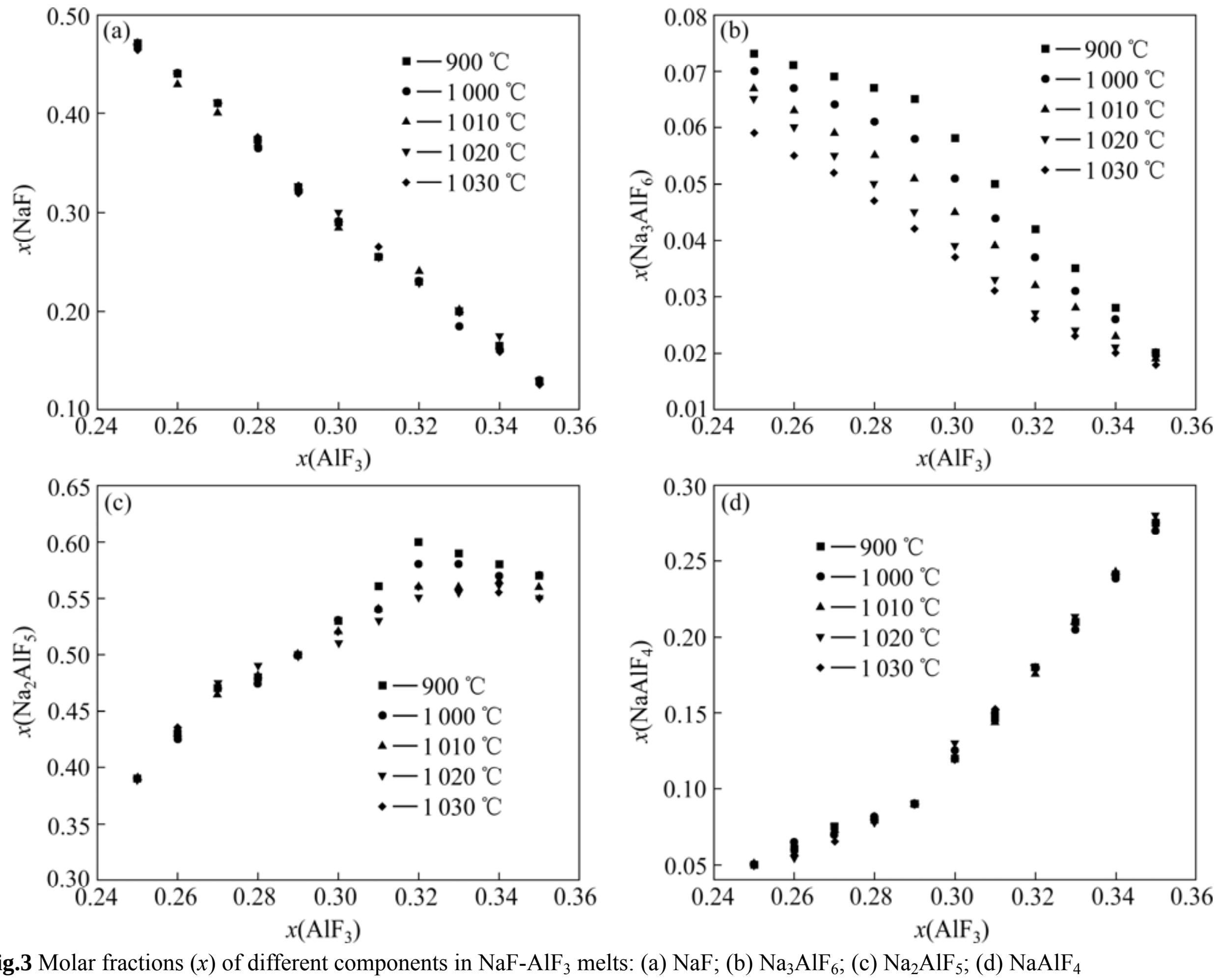

Fig.3 Molar fractions (x) of different components in NaF-AlF_3 melts: (a) NaF; (b) Na_3AlF_6; (c) Na_2AlF_5; (d) $NaAlF_4$

Table 1 Measured values of density and electrical conductivity of NaF-AlF_3 melts

Temperature/℃	Molar fraction of AlF_3	Density/(g·cm^{-3})	Electrical conductivity/(S·cm^{-1})
990	0.25	2.099 9	2.78
990	0.27	2.093 9	2.61
990	0.29	2.076 8	2.52
990	0.32	2.032 4	2.38
990	0.35	1.968 3	2.16
1 000	0.25	2.091 4	2.80
1 000	0.27	2.085 5	2.63
1 000	0.29	2.068 3	2.54
1 000	0.32	2.023 9	2.40
1 000	0.35	1.959 8	2.18
1 010	0.25	2.082 9	2.82
1 010	0.27	2.077 0	2.65
1 010	0.29	2.059 9	2.56
1 010	0.32	2.015 5	2.42
1 010	0.35	1.951 3	2.20
1 020	0.25	2.074 5	2.85
1 020	0.27	2.068 5	2.67
1 020	0.29	2.051 4	2.58
1 020	0.32	2.007 0	2.44
1 020	0.35	1.942 9	2.21
1 030	0.25	2.066 0	2.87
1 030	0.27	2.060 0	2.61
1 030	0.29	2.042 9	2.52
1 030	0.32	1.998 5	2.38
1 030	0.35	1.934 4	2.16

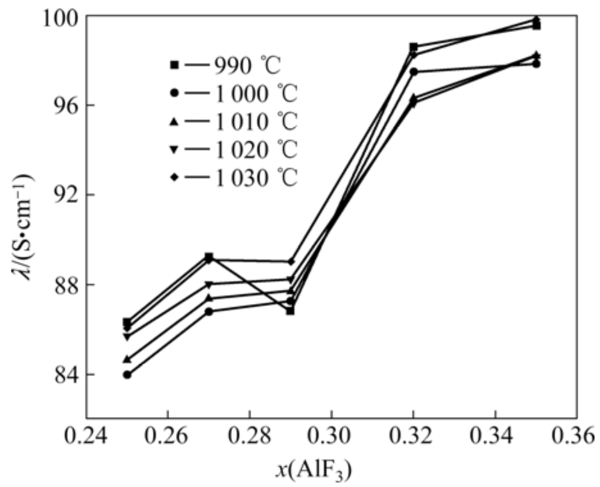

Fig.4 Equivalent conductivity of NaF-AlF_3 melts

Isotherms of equivalent conductivity with different compositions and curve of equivalent conductivity activation energy vs composition of NaF-AlF_3 melts should be analyzed together with relative content change of different components in the melts.

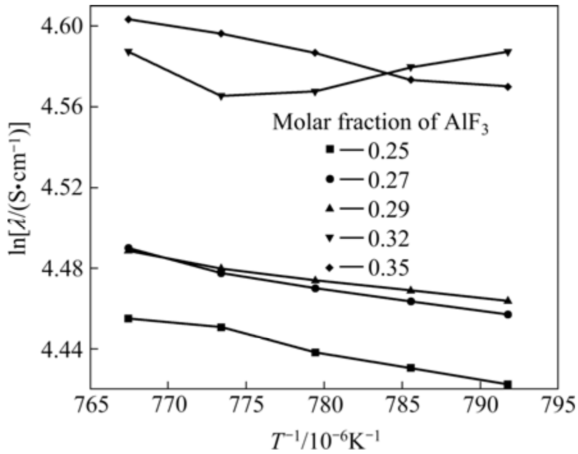

Fig.5 lnλ—1/T of NaF-AlF_3 melts

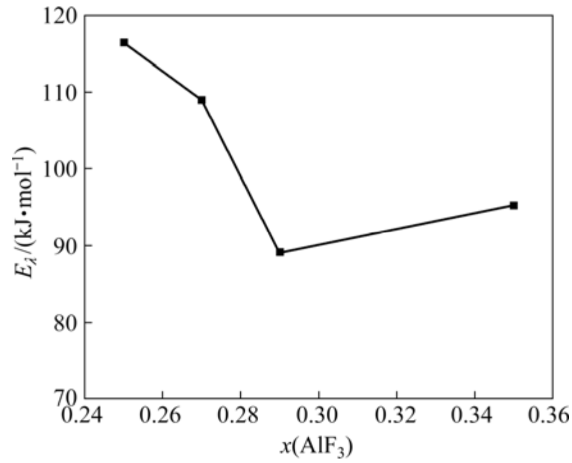

Fig.6 Equivalent conductivity activation energy of NaF-AlF_3 melts

Fig.3 shows that, in the researched molar fraction range of AlF_3, molar fraction of Na_3AlF_6 is small compared with the other components in the melts. It is so thought that it has little influence on the change of melts equivalent conductivity. From Fig.4, it can be seen that change trends of the five curves are similar, indicating that the temperature effect on melts equivalent conductivity is small in the researched temperature range. That is proved by the fact that molar fractions of components in the melts only have a little change with temperature changing. It can be found in Fig.3 that in NaF-AlF_3 melts, Na_2AlF_5 has the maximum content among the four components, and its equivalent molar mass is higher than $NaAlF_4$ or NaF, which is thought as the reason that equivalent conductivity is increased when molar fraction of AlF_3 increases, as shown in Fig.4. Slopes of different curves in Fig.4 are higher when molar fraction of AlF_3 in the range of 0.29−0.32 is more than that for lower or higher AlF_3 molar fraction, which is ascribed to the sharp increase of $NaAlF_4$ content when the molar fraction of AlF_3 is between 0.29 to 0.32 in Fig.3. Another expression of the sharp increase is that the 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 ℃ and 1 000 ℃ 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_2AlF_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 ℃ were worked out on the basis of two-step decomposition mechanism of AlF_6^{3-}. 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.

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