

Electric Conductivity of $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ Solid Solutions

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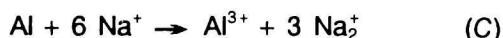
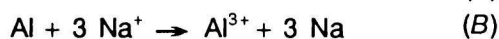
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The electric conductivity of solid solutions $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ has been measured in the temperature range 773—1123 K. It has been found that the conductivity increases with the increasing concentration of dissolved aluminium. A substantial increase in the electronic conductivity component with temperature has been observed. On the basis of the dependence of the electronic conductivity on AlF_3 concentration it has been concluded that the reaction of aluminium with cryolite results in the formation of metallic sodium which acts as an electron donor.

Investigation of the properties of metal solutions in molten salts is of practical as well as theoretical importance. In engineering practice the results of these investigations are mainly utilized in the production and electrolytic refining of metals in molten salts. Basic research, however, is carried out with the aim to obtain basic data for the description of the structure of the liquid state [1—3].

The problem which has been given recently much attention in the investigation of metal solutions in molten salts is their electric conductivity. The reason for this is the occurring change in the character of current transfer under the influence of dissolved metal — the ionic character for pure salt changes into an ionic-electronic one for a solution of salt with metal. It is also important to note that electric conductivity as a transfer property supplies much information about structural changes occurring at this occasion.

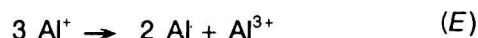
The process of aluminium dissolution in $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ electrolyte results in the decrease of the current efficiency of electrolysis. This is why this process has been the subject of studies in several laboratories [3—5]. The following reactions take place at the metal/electrolyte phase boundary



The reactions result in the formation of gaseous products such as AlF , Na , and NaF_2 [3, 6]. Apart from these processes it has also been considered that cathodic aluminium may dissolve in the metallic form and then be oxidized by the anode gases [3]



The decomposition of the reaction products formed in the processes (A—C) taking place at the electrolyte/gas phase boundary will also cause losses of the cathodic aluminium



Accordingly, the kinetics of aluminium dissolution during the electrolytic process is determined by the transport of the dissolved aluminium towards the anodic gases as well as by the pressure of the gaseous products of the reaction between aluminium and electrolyte components.

The effect of other parameters on aluminium solubility in electrolytes and the resulting current efficiency of the electrolytic processes have been discussed in Refs. [3, 7]. These papers indicate that the solubility of Al increases with both temperature and the cryolite ratio (the mole ratio NaF/AlF_3). On the other hand, solubility decreases with the increase of the concentration of AlF_3 and Al_2O_3 in the electrolyte as well as with increasing concentration of additions such as MgF_2 and CaF_2 .

It is interesting to note that the colour of the electrolyte changes from white into dark-grey while aluminium is being dissolved [8, 9]. This phenomenon is typical for nonstoichiometric ionic crystals. Then the excess of metal results in the formation defects such as the F-centres which are responsible for the nonionic charge transport. This effect suggests that the properties of liquid solutions are similar to those observed in solid ionic crystals.

It has been observed that the electric conductivity of $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ liquid solutions increases after dissolution of aluminium [10—13]. *Borisoglebskii* [11] argues that this effect is produ-

ced by the electronic component of the conductivity. Dewing and Yoshida [13] postulate that the effect of dissolved aluminium on the current efficiency is produced by its diffusion towards the oxidation area. Also changes of other electrolyte properties such as the crystallization temperature [14], vapour pressure [6], and migration of colour zone [8, 9] induced by the dissolved aluminium have been reported.

As it follows from this literature survey, the properties of the $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ liquid solution are not well determined. Difficulties in studies of this system are due to its complex composition and experimental conditions (high temperature). Therefore, it seems interesting to perform study for a model system such as the solid solutions of Al in $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$. Similarities between the liquid and the solid solutions justify such assumption.

The aim of the present work is to determine the electric conductivity of $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ solid solutions and to evaluate the electronic component of the conductivity. The results will be analyzed in terms of the formation mechanism of the electronic component in liquid solutions.

EXPERIMENTAL

Electrolyte specimens were obtained by melting of natural cryolite (from Greenland), AlF_3 , and Al_2O_3 in boron nitride crucibles. AlF_3 was purified by the sublimation process beforehand. Cryolite dried in vacuum was used for the reaction. Pre-treatment of Al_2O_3 involved its annealing at 1273 K. High purity aluminium (99.999 %) was applied for preparation of $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ solid solutions. The solutions of the required contents of AlF_3 and Al_2O_3 were prepared by dissolving the appropriate amount of aluminium fluoride in molten cryolite. Then Al_2O_3 was added up to the saturation state. In a solution prepared by that way aluminium was dissolved electrolytically. Aluminium concentration in electrolyte was determined by the volumetric method. The electrolyte was then quenched and dispersed. The powder

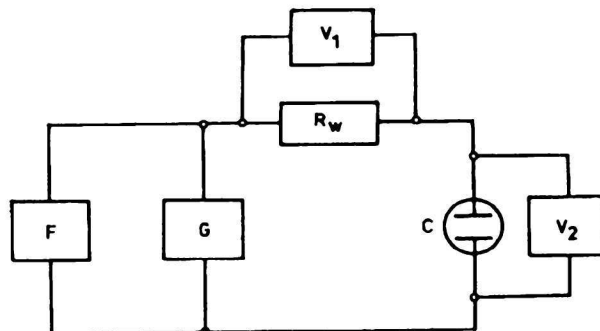


Fig. 1. Schematic representation of the measuring system for the determination of electric conductivity, V_1 , V_2 - digital voltmeters, G - generator, C - specimen, R_w - standard resistor, F - frequency meter.

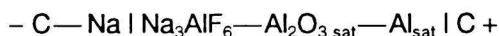
was used to form pellets of 10 mm diameter and 10–15 mm thickness. The pellets were made under a pressure of 45 MPa.

The experiments were carried out with direct current in a resistance furnace feed. The temperature was measured with a thermocouple Pt—PtRh10 in direct contact with the measured sample. The accuracy of temperature measurement was ± 1 K.

Table 1 provides the chemical composition of the prepared specimens.

The total electric conductivity was determined by measuring the resistance of samples of solid electrolyte in the system of two metallic electrodes. The circuit applied for the determination of the resistance is shown in Fig. 1 [15].

The electronic component of conductivity was determined by Wagner's method [16] based on the polarization of the following cell



The electrode reversible with respect to sodium cations was made of graphite saturated with sodium vapour. The second electrode, acting as an ionic blockade, was made of pure graphite. The measuring set-up and the sample holder are shown in Fig. 2.

Measurements of the electronic component were performed so that a voltage E , the value of which

Table 1. Chemical Composition of Samples Used in the Measurements of Electric Conductivity

Sample type	$w(\text{NaF})$	$w(\text{AlF}_3)$	$w(\text{excess AlF}_3)$	$w(\text{Al}_2\text{O}_3)$	$w(\text{Al})$
	%	%	%	%	%
3 NaF · AlF ₃	60.00	40.00	—	—	—
3 NaF · AlF ₃ — Al ₂ O _{3 sat}	51.54	34.36	—	14.10	—
3 NaF · AlF ₃ — Al ₂ O _{3 sat} — Al _{sat}	51.49	34.33	—	14.09	0.098
2.8 NaF · AlF ₃ — Al ₂ O _{3 sat} — Al _{sat}	50.05	33.36	2.77	13.72	0.099
2.6 NaF · AlF ₃ — Al ₂ O _{3 sat} — Al _{sat}	48.37	32.18	5.79	13.57	0.100
2.4 NaF · AlF ₃ — Al ₂ O _{3 sat} — Al _{sat}	46.21	30.62	9.09	13.99	0.098

was lower than the reduction potentials for both aluminium and sodium ions, was applied until the moment at which a constant current value I was established. This was an indication that the polarized cell reached the equilibrium state. In that way current—voltage characteristics were determined. These characteristics were then used for the determination of the electronic conductivity.

RESULTS AND DISCUSSION

The changes of electric conductivity with temperature for solid state electrolytes are illustrated in Fig. 3. For comparison the obtained dependences are shown along with available literature data [15, 17—19]. A good agreement can be observed. As it is seen the addition of Al_2O_3 results in a strong decrease of the conductivity. This conductivity change is partially compensated by aluminium dissolved in the electrolyte.

Phase analysis of the studied system did not reveal any precipitates of metallic aluminium. The presence of metallic aluminium in the solutions was determined only by volumetric analysis [4, 5]. It is claimed that this form of aluminium only slightly affects electric conductivity.

Further experiments based on the Wagner's method have led to the determination of the electronic conductivity components. These components were determined from the behaviour of the current—voltage characteristics of the used cell. The Wagner equation can be written in the following form [16, 20, 21]

$$J = \frac{RT}{F\ell} \left\{ \sigma_{e^-}^{\circ} \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] + \sigma_{h^+}^{\circ} \left[\exp\left(\frac{EF}{RT}\right) - 1 \right] \right\} \quad (1)$$

where J is electric current density at equilibrium state, E applied voltage, R gas constant, T temperature, F Faraday constant, $\sigma_{e^-}^{\circ}$ specific electronic conductivity, $\sigma_{h^+}^{\circ}$ specific electron—hole conductivity, ℓ thickness of sample. When assuming

$$y = \frac{J\ell F}{RT \left[\exp\left(\frac{EF}{RT}\right) - 1 \right]} \quad (2)$$

and

$$x = \exp\left(-\frac{EF}{RT}\right) \quad (3)$$

eqn (1) takes the form

$$y = \sigma_{e^-}^{\circ} x + \sigma_{h^+}^{\circ} \quad (4)$$

Fig. 4 shows, as an example, the experimental current—voltage characteristics for Na_3AlF_6 — Al_2O_3 —Al electrolyte determined at various temperatures. Values of the electronic conductivity components ($\sigma_{e^-}^{\circ}$, $\sigma_{h^+}^{\circ}$) determined from eqn (4) for examined solutions are listed in Table 2 in the temperature range 725—1126 K. As evident from Table 2 the following relationship can be written for the studied electrolyte solutions

$$\sigma_{e^-}^{\circ} \gg \sigma_{h^+}^{\circ} \quad (5)$$

This means that the electron component predominates in the electronic conductivity. As seen from Table 2 its value is by four orders higher than the electron—hole conductivity.

Fig. 5 shows the change in both total electric conductivity and the electronic conductivity component as a function of temperature. Table 3 contains the calculated values of the ionic and

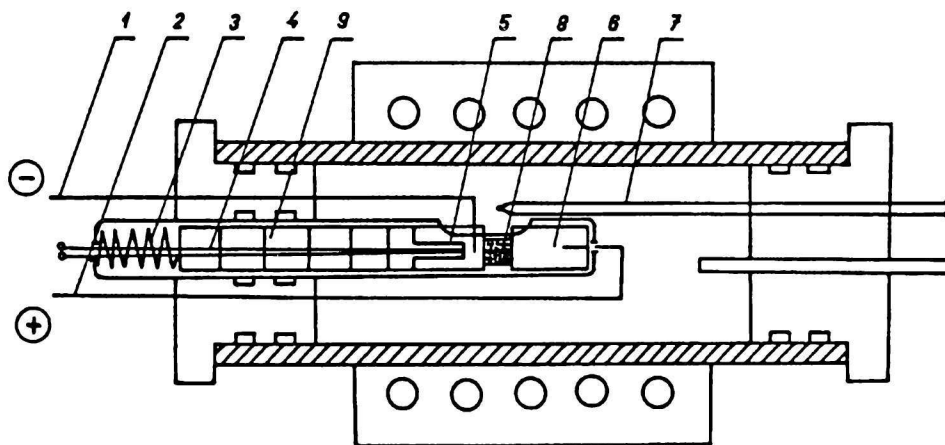


Fig. 2. Measuring system for the determination of electric conductivity. 1, 2. Current leads (Mo wire), 3. pressure spring, 4. Pt—PtRh10 thermocouple, 5. C—Na electrode, 6. graphite electrode, 7. Pt—PtRh thermocouple (controller and regulator), 8. electrolyte specimen, 9. rings distance (quartz).

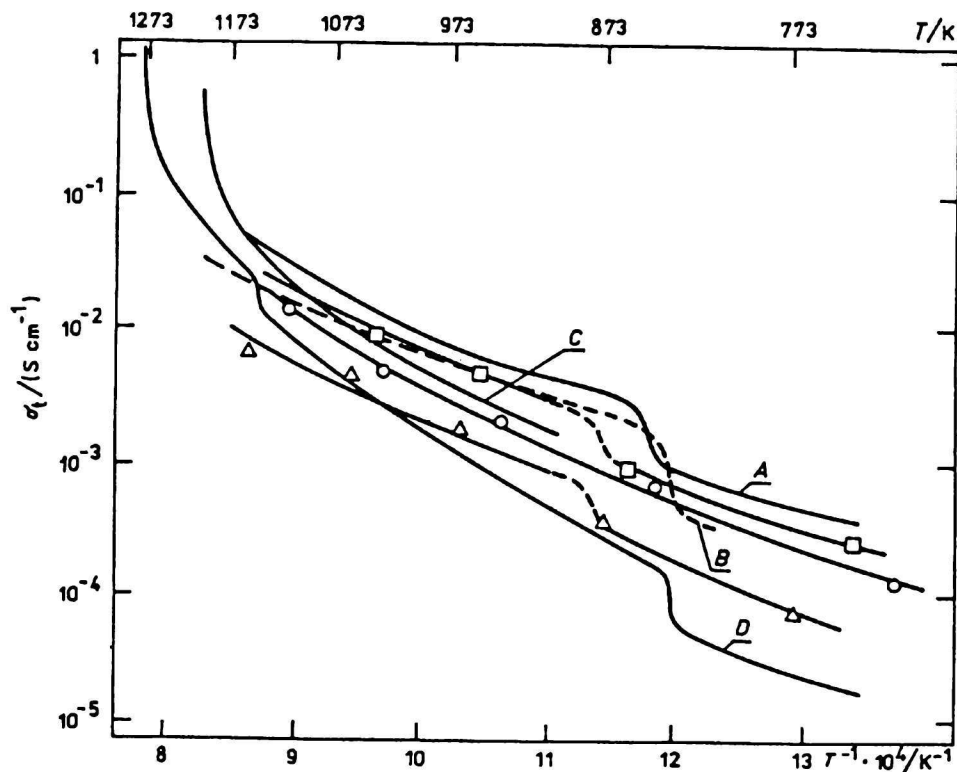


Fig. 3. Dependence of electric conductivity of stable electrolytes vs. temperature. \square Na_3AlF_6 , \triangle $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{sat}$, \circ $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{sat—Al}_{\text{sat}}$, Na_3AlF_6 : A [19], B [18], C [17], D [15].

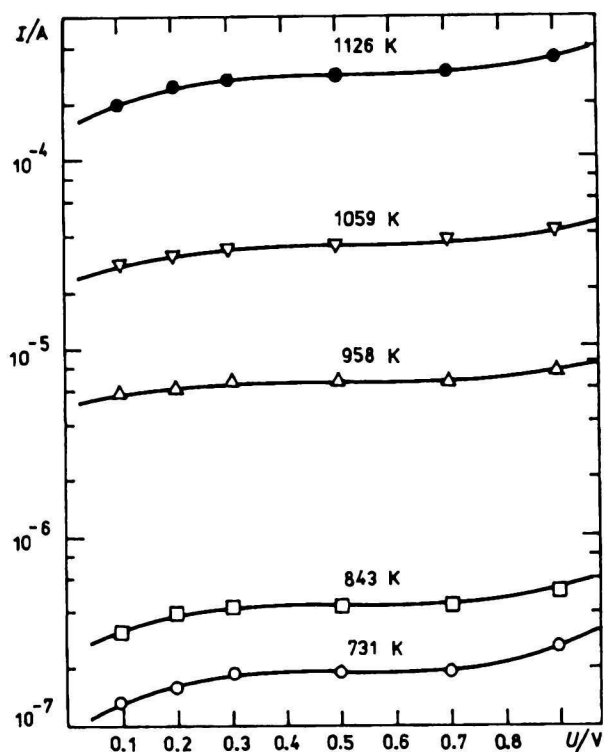


Fig. 4. Current—voltage characteristics for the electrolyte $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{sat—Al}_{\text{sat}}$ in a solid state.

the electronic transport numbers. These results clearly indicate that the electric conductivity of the $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ solid solutions increases with the increasing concentration of Al. This increase, in the temperature range 773—1123 K, varies from 2.40×10^{-4} to 1.38×10^{-2} S cm^{-1} , respectively, *i.e.* by the factor of 50. On the other hand, in the same conditions the electronic component increases by the factor of 300 (from 3.98×10^{-6} to 1.14×10^{-3} S cm^{-1}).

Table 2. Components of the Nonionic (σ_e^0 , electronic, σ_h^0 , hole) Conductivity of Electrolytes in the Solid State

Sample	T	σ_e^0	σ_h^0
	K	S cm^{-1}	S cm^{-1}
Na_3AlF_6	725	7.22×10^{-7}	3.81×10^{-11}
	837	4.55×10^{-6}	2.34×10^{-10}
	951	1.98×10^{-5}	3.92×10^{-9}
	1042	5.75×10^{-5}	7.11×10^{-9}
	1123	1.25×10^{-4}	2.46×10^{-8}
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{sat}$	727	6.31×10^{-7}	3.62×10^{-11}
	833	4.70×10^{-6}	2.21×10^{-10}
	946	1.90×10^{-5}	3.76×10^{-9}
	1030	4.79×10^{-5}	6.87×10^{-9}
	1118	1.15×10^{-4}	2.25×10^{-8}
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{sat—Al}_{\text{sat}}$	731	2.38×10^{-6}	5.56×10^{-10}
	843	2.15×10^{-5}	3.45×10^{-9}
	958	1.81×10^{-4}	1.60×10^{-8}
	1054	6.00×10^{-4}	4.97×10^{-7}
	1126	1.41×10^{-3}	1.67×10^{-6}

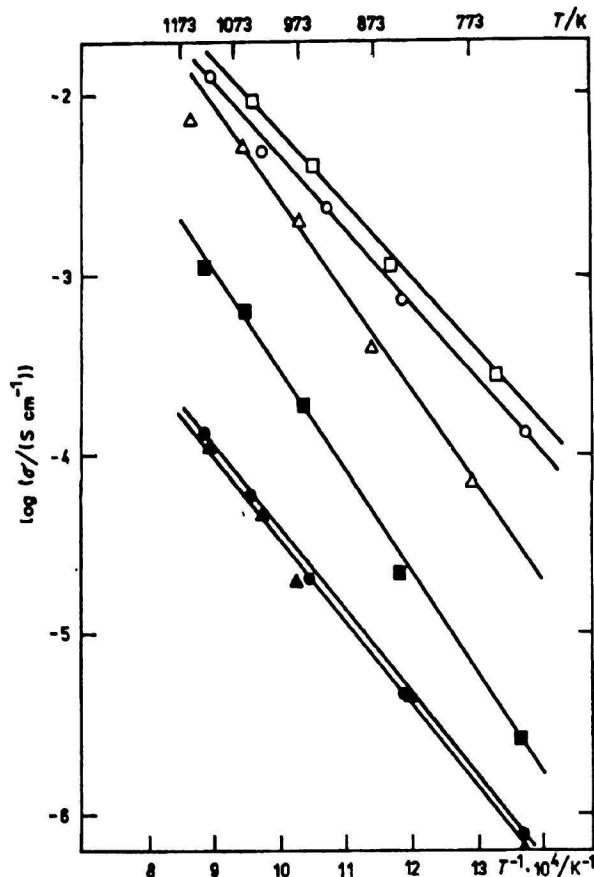


Fig. 5. Changes in total electric conductivity σ_t (\square Na_3AlF_6 , \triangle $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{ sat}$, \circ $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{ sat—Al}_{\text{sat}}$) and its electronic component σ_e^- (\bullet Na_3AlF_6 , \blacktriangle $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{ sat}$, \blacksquare $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{ sat—Al}_{\text{sat}}$) as a function of temperature.

A great increase of the electronic component in comparison with the total conductivity indicates that the electronic transport numbers are responsible for this effect (Table 3). A more detailed analysis of the effect of aluminium dissolution on the electric conductivity could be performed only

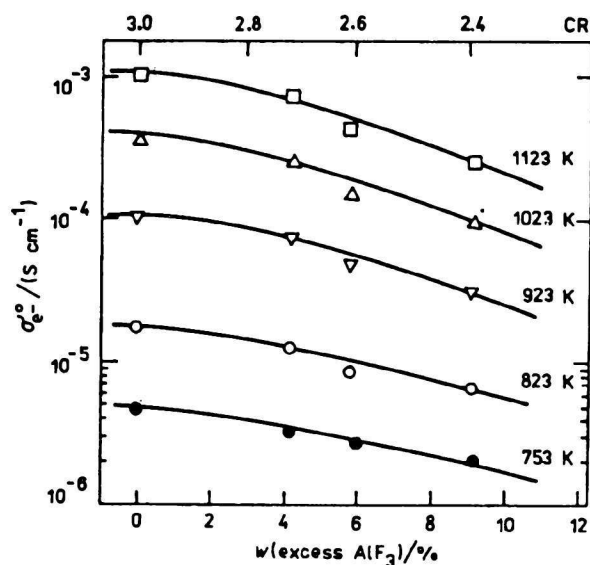


Fig. 6. Changes in the electronic conductivity component as depending on the composition of the solution $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ in a solid state. CR - cryolite ratio.

by the determination of the concentration and the mobility of electronic charge carriers.

From the determined temperature dependence of the electric conductivity it is impossible to determine the participation of the particular structural units in the charge transport. On the other hand, it is known that Na^+ ion predominates in the charge transport in $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ liquid solutions ($t_{\text{Na}^+} = 0.99$) [22—24]. Accordingly the increase in the activity of the sodium ions should lead to the increase of the electric conductivity of the solution.

Fig. 6 shows changes of the electronic conductivity components vs. the composition of the $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ solution. As evident the increase in the activity of sodium ions results in the increase of the electronic conductivity component in the whole examined range of temperature.

Table 3. Electric Conductivity σ_t , Electronic Conductivity Component σ_e^- , Ionic t_i and Electronic t_{e^-} Transport Numbers

Sample	T K	σ_t S cm^{-1}	σ_e^- S cm^{-1}	t_i	t_{e^-}
Na_3AlF_6	773	3.98×10^{-4}	1.58×10^{-6}	0.996	0.004
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$	773	7.24×10^{-5}	1.14×10^{-6}	0.984	0.016
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$	773	2.40×10^{-4}	3.98×10^{-6}	0.983	0.017
Na_3AlF_6	923	3.46×10^{-3}	1.86×10^{-5}	0.995	0.005
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$	923	1.01×10^{-3}	1.44×10^{-5}	0.986	0.014
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$	923	2.29×10^{-3}	9.54×10^{-5}	0.958	0.042
Na_3AlF_6	1073	1.15×10^{-2}	8.32×10^{-5}	0.992	0.008
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$	1073	5.25×10^{-3}	6.92×10^{-5}	0.988	0.012
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$	1073	9.55×10^{-3}	6.61×10^{-4}	0.931	0.069
Na_3AlF_6	1123	1.65×10^{-2}	1.28×10^{-4}	0.992	0.008
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$	1123	7.41×10^{-3}	1.17×10^{-4}	0.984	0.016
$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$	1123	1.38×10^{-2}	1.14×10^{-3}	0.917	0.083

When analyzing the reported experimental data one may conclude that the electronic component is associated with both Al and Na. Accordingly, the shortage of cathode aluminium during the electrolysis may be caused either by chemical reactions of sodium with the electrolyte components and anodic gases or the electron transport in the electrolyte.

The mechanism of aluminium solubility in the $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ electrolyte assumed above is in agreement with the model presented in this work. However, the facts reported above do not explain the origin of the electronic component of the electric conductivity. It may be assumed that both Al and Na may interact with the quasi-crystalline lattice of the liquid salt leading to nonstoichiometric disorder such as M_{1+y}X or MX_{1-y} . This consideration may be based on the controlled valency theory [25].

The question may be also raised which of the two metals, Al or Na, acts as the donor of electrons and in which sublattice these defects are formed. This question cannot be answered on the basis of the experimental data obtained in this work. Nevertheless, the analysis of the results carried out on the basis of the theory of defects in crystals allows to make the following hypotheses:

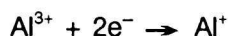
1. The electronic charge carriers in $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ solutions are similar to those in doped n-type semiconductors;

2. The effect of doping with Al or Na leads to the formation of defects in the cation sublattice;

3. Na acts as donor of electrons as a result of its ionization in the electrolyte



4. Aluminium ions behave as acceptors of free electrons



The above hypotheses are confirmed in technological processes. The current efficiency caused by the dissolution of aluminium increases with the content of multivalent ions in the electrolyte such as Al^{3+} , Ca^{2+} , and Mg^{2+} . On the contrary, the current efficiency decreases with increasing activity of Na^+ ions in the electrolyte. The influence of Li^+ ions on electric conductivity of the examined solid solutions is, so far, not clear [26, 27].

The presence of nonionic current carriers in an ionic liquid is a justification of the statement that in the liquid state the current is being transported

by structural units similar to those occurring in ionic crystals with disturbed stoichiometry resulting from doping.

Thus, when determining the magnitudes of changes in the ionic and electronic conductivities as depending on temperature and electrolyte composition for $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3\text{—Al}$ solutions in the solid state it can be assumed that also in the liquid state the character of changes of the given quantities will be analogous.

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