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RESEARCH ON THE ELECTRICAL CONDUCTIVITY OF FLUORIDE ELECTROLYTES NaF - AlF$_3$ - CaF$_2$ IN LIQUID AND SOLID STATE

BADANIA PRZEWODNICTWA ELEKTRYCZNEGO ELEKTROLITÓW FLUORKOWYCH NaF-AlF$_3$-CaF$_2$ W FAZIE CIEKŁEJ ORAZ W STANIE STAŁYM

The main aim of the present work was to perform conductivity measurement of fluoride electrolytes in binary system Na$_3$AlF$_6$- CaF$_2$ and ternary system Na$_3$AlF$_6$- AlF$_3$ - CaF$_2$. The experiments were done in a wide range of temperature (580-1300 K), including the liquid and solid phase. Temperature dependencies of the conductivity of the liquid and solid cryolite mixtures with CaF$_2$ (2, 4 and 6 wt %) and ternary solution (88 wt % Na$_3$AlF$_6$ − 8 wt % AlF$_3$ -4 wt % CaF$_2$) were determined by an A.C. two-electrodes technique. The simultaneous measurements of conductivity and temperature were made in 1min steps during heating and cooling of the sample with rate 0,5 K·min^{-1}. It was confirmed, that the addition of CaF$_2$ to liquid electrolyte decreases its electrical conductivity and liquidus temperature, whereas addition of aluminium fluoride up to 4 wt % in solid state has the inverse influence on conductivity. The studied ternary system showed the highest conductivity in the solid state at temperatures up to phase transition $\alpha - \beta$ in solid cryolite (ca. 780 K). This may be due to the formation of a solid solution of NaCaAlF$_6$ in β-Na$_3$AlF$_6$ and the formation of cationic vacancies, which facilitate the transport of electrical charge.

Keywords: aluminium, electrical conductivity, cryolite electrolytes, aluminium electrolytes

Głównym celem pracy było wykonanie pomiarów przewodnictwa elektrycznego elektrolitów fluorkowych w układzie dwu-składnikowym Na$_3$AlF$_6$-CaF$_2$ oraz trójskładnikowym Na$_3$AlF$_6$-AlF$_3$-CaF$_2$. Pomiary wykonano w szerokim zakresie temperatur (580-1300K) zawierającym fazę ciekłą oraz fazę stałą. Temperaturowe zależności przewodnictwa ciekłych roztworów kriolitu z CaF$_2$ (2, 4 i 6% mas.) oraz roztworu trójskładnikowego o składzie 88% mas.Na$_3$AlF$_6$-8%mas. AlF$_3$-4%mas. CaF$_2$ określono dwuelektrodową techniką zmiennoprądową. Jednoczesne pomiary przewodnictwa i temperatury wykonywano w 1 minuto-wych odstępach czasu podczas cykli ogrzewania i chłodzenia z szybkością 0,5 K·min^{-1}. Na podstawie uzyskanych wyników potwierdzono, iż dodatek CaF$_2$ do ciekłego elektrolitu obniża jego przewodnictwo elektryczne oraz temperaturę likwidusu. Natomiast wpływ tego dodatku do kriolitu w zakresie stężeń do 4% mas. w stanie stałym jest odwrotny. Z kolei badany układ trójskładnikowy wykazał najwyższe przewodnictwo elektryczne w stanie stałym w zakresie temperatur aż do przemiany fazowej $\alpha - \beta$ w stałym kriolicie (ok. 780 K). Może to być spowodowane tworzeniem się roztworu stałego NaCaAlF$_6$ w β-Na$_3$AlF$_6$ i powstawaniem wakancji kationowych ułatwiających transport ładunku elektrycznego.

1. Introduction

In the electrowinning of aluminum, part of total electrol-ysis current can be lost because of so-called current escapes. This is possible because the crystallized electrolyte (sideledge) on the carbon side lining can conduct electricity [1]. As a re-sult, this part of the current flows from the anode to the cath-ode bypassing liquid electrolyte, causing loss of current and reduced current efficiency of the electrolysis. The sideledge composition is directly dependent on the composition of the electrolyte. The current flow will depend both on the chemical composition of crystalized layer and its temperature. There-fore, it is important to know the influence of composition and temperature of the sideledge on its electrical conductivity.

In earlier work [2], the authors studied the electrical con-ductivity of cryolite – the basic component of the electrolyte and its mixtures with addition of 4, 8 and 12 wt %. AlF$_3$. The results showed that the addition of aluminum fluoride decreases the conductivity of molten cryolite. A similar effect of this additive was observed in the solid phase, in which AlF$_3$ and Na$_3$AlF$_6$ do not create solid solutions. However, in the temperature range including a mixture of liquid and solid phases (between liquidus and solidus), the aluminum fluoride strongly increased the conductivity, which is mainly caused by the presence of highly conductive liquid phase.

In the present work the effect of calcium fluoride (2, 4 and 6 wt %) on the conductivity of cryolite and the ternary system Na$_3$AlF$_6$ - AlF$_3$ (8 wt%) - CaF$_2$ (4 wt%) in a wide temperature range including the liquid and solid phase was investigated. The electrical conductivity strongly depends on the solid solutions in the studied system. The existence and range of component solubility in the cryolite are crucial for

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the value of conductivity. The theory of point defects in ionic crystals can predict the direction of conductivity changes due to introduction of metal cations into the crystal lattice. In order to determine the influence of the additives on the nature of the changes, the knowledge about the type of crystal lattice defect and the types of solution forming in the system is needed. Information in literature about the Frenkel defects in cryolite (basic material for the tests) are not fully confirmed. The data for solid solutions of CaF_2 in Na_3AlF_6 are often imprecise and in some cases contradictory. As reported by [3] and [4] it is a simple eutectic system with a minimal solubility of CaF_2 in the solid state (up to 1.76 wt %). According to others, the solubility of CaF_2 in solid cryolite may reach 8.5 wt % ([5]), and even 20 wt % ([6]). During the study of electric conductivity in these systems in the solid state, it was difficult to predict the effect of introducing a divalent metal (Ca^{2+}) into the lattice of Na_3AlF_6. The prediction of the conductivity behavior in multicomponent systems was practically impossible.

2. Experimental

The boron nitride tube, containing about 5g sample of the salt mixture, was placed on the graphite basis, which was mounted inside vertical alumina tube with controlled argon atmosphere, and heated up to required temperature. After melting and homogenization the molybdenum movable electrode was immersed into the melt. The second electrode (immovable) was graphite. When the temperature was stabilized, the resistance of the melt was measured by AC technique with sine wave signal at frequency 35kHz. Resistance measurements of the salt mixtures were performed in conductivity cells, adapted to measuring mixtures in both liquid and solid state. Heating and cooling rates did not exceed $0,5$ K·min^{-1}. The temperature was measured with Pt-PtRh10 thermocouple. More details of the experimental technique were presented in earlier work [2]. Resistance and temperature were simultaneously registered in 60 sec. steps by a computer. Figure 1 presents the scheme of the measuring system and the Table 1 shows reagents used for preparation of mixtures.
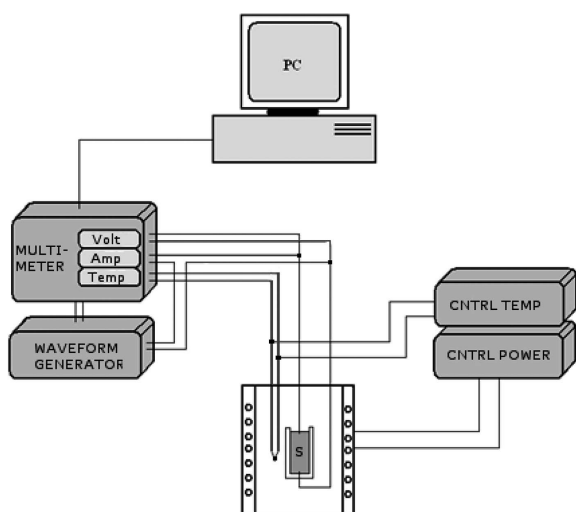
Electrical conductivity was calculated from equation (1)

$$R_{el} = \rho\left(\frac{L}{S}\right) = \left(\frac{1}{\kappa}\right)\left(\frac{L}{S}\right) = \frac{G}{\kappa_{el}} \quad (1)$$

where: R_{el} – measured resistance, ρ – electrical resistivity κ – electrical conductivity, L – the effective length of the current path, S – the effective cross-sectional area of the current path, and G – the cell constant.

In this experiment, a molten KCl was used as a liquid standard for calibration and determination of cell constant G.

TABLE 1

Reagents using for the preparation of mixtures

Reagent	Purity	Source
Cryolite Na_3AlF_6	99,98%	Sigma-Aldrich
Calcium fluoride CaF_2	99,95%	Merck
Aluminium oxide Al_2O_3	98,5	P.O.CH

3. Results and discussion

The system Na_3AlF_6 – CaF_2

Temperature dependences on the electrical conductivity of cryolite with 2, 4 and 6 wt. % of CaF_2 in the temperature range between 580 and 1291 K are presented in Fig. 2 as a natural logarithm of the specific conductivity κ versus reciprocal of absolute temperature T/K. For comparison, figure also contains data obtained for pure cryolite in the earlier work [2].

Curves obtained during cooling of the sample indicates the existence of several temperature ranges, separated by discontinuous, abrupt changes of electrical conductivity. The first of these changes corresponds with the liquidus temperature of the electrolyte, the second to the solidus temperature, while the third refers to the alpha – beta phase transition in solid Na_3AlF_6. The temperatures of these transitions determined from the conductivity curves are shown in Table 2.
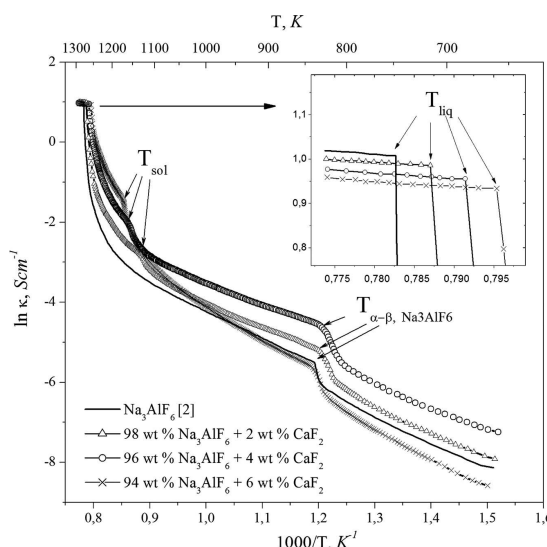

Fig. 1. Scheme of the measuring system. S – sample of the electrolyte, CNTRL TEMP – temperature controller, CTRL POWER – heating power controller

Fig. 2. Electrical conductivity of cryolite with different contents of CaF_2

Temperatures of phase transitions in the system Na_3AlF_6 - CaF_2 obtained from the conductivity curves during cooling

System Na_3AlF_6- CaF_2 / wt %	T_{liq} /K	T_{sol} /K	$T_{\alpha-\beta Na3AlF6}$ / K
98 - 2	1270	1132	831
96 - 4	1263	1158	831
94 - 6	1256	1171	843

The described transformations separate areas where the effect of CaF_2 on conductivity of studied electrolytes is different. At the highest temperatures, calcium fluoride which is dissolved in cryolite strongly decreases the conductivity, and temperature effect is slight.

The results of the measurement were fitted to an Arrhenius type equation:

$$\kappa = \kappa_o \exp(\frac{-E_a}{RT}) \qquad (2)$$

where: κ_o – pre-exponential factor, Scm^{-1}

E_a – the activation energy, $Jmol^{-1}$

R – the gas constant (R = 8.3145 $Jmol^{-1}K^{-1}$)

T – absolute temperature, K

The pre-exponential factor κ_o and the activation energy E_a were determined for each mixture using the last squares method. Respective values are shown in the Table 3.

The activation energy of electrical conductivity in liquid phase

System Na_3AlF_6- CaF_2 / wt %	Temp. range / K	K_o /$S \cdot cm^{-1}$	E_a / $kJ \cdot mol^{-1}$
98 - 2	1270-1291	6,215 ±0,013	8,88±0,08
96 - 4	1263-1291	7,001 ±0,011	10,42 ±0,08
94 - 6	1256-1291	6,234 ±0,029	9,40 ±0,06

Calculated, low activation energy of conductivity is typical for the molten salt.

In the Figure 3 the influence of CaF_2 in the examined range of concentrations on the conductivity of cryolite in the liquid phase are presented. For comparison, the figure also contains results of similar studies conducted by Wang et all. [7]. In the investigated temperature range, decrease of conductivity obtained in this work is 0.03 Scm^{-1} for 1% of addition, whereas Wang is three times smaller (0.01 Scm^{-1} for 1% added). The differences in the values and a stronger influence of CaF_2 on the conductivity obtained in this study can be the result of the applied measuring system, the purity of the reagents but also the methodology of measurement (in the present work measurements were carried out continuously with temperature changes).

Decrease of the electrical conductivity with the temperature is the result of lowering the viscosity of molten salts and lessening ion mobility of charge carriers. Calcium fluoride which is dissolved in Na_3AlF_6 causes formation of complex ions according to reaction (3) [8]:

$$CaF_2 + (3-n)\, AlF_5^{2-} = CaF_n(AlF_5)_{3-n}^{(4-n)-} + (2-n)\, F^- \qquad (3)$$
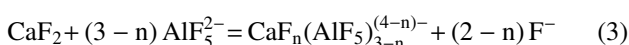
The expanded structure of the ions causes their low mobility. Furthermore, they may hinder the movement of migration of Na^+ ions, which have the biggest participation in the total charge transfer. Therefore, the higher content of CaF_2 dissolved in liquid cryolite is, the less its electrical conductivity might be.
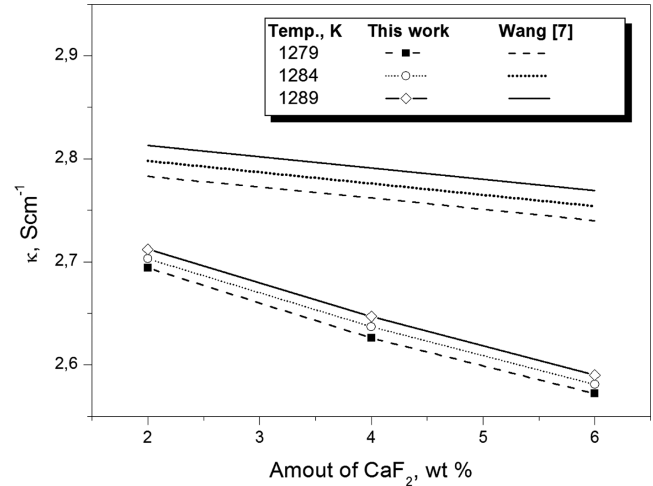

Fig. 3. The influence of CaF_2 on the conductivity of cryolite in the liquid phase. Results obtained in this work and by Wang at all. [7]

At the beginning of crystallization (liquidus) for each of the compositions sudden, discontinuous decrease in conductivity was observed. It is due to the appearance of the first crystals of β-Na_3AlF_6 in liquid phase. With decreasing temperature the content of solid phase increases and the liquid decreases. Because of significant differences in the conduction of electric current through these two phases, the decrease of the conductivity with temperature is observed.

The increase of CaF_2 content causes rise of the electrical conductivity. It is due to the presence of larger part of the liquid phase at a given temperature. Conduction in this region possibly takes place only by liquid phase through the connected capillary vessels.

Other sudden changes in the electrical conductivity during cooling of the samples occur at the solidus temperature (T_{sol}) and during the phase transition in solid cryolite ($T_{\alpha-\beta Na3AlF6}$). Conduction of electric current below T_{sol} is performed with using defects in the crystal structure. Their concentration decreases with temperature, which ultimately leads to a decrease in electrical conductivity. As it can be seen in Fig. 2 for a content of 2 and 4 wt % CaF_2 conductivity curves are located above the curve obtained for pure cryolite in the whole temperatures range including the solid phase. It might be caused by the existence of solid solution in this range of calcium fluoride contents.

Different shape of the curve is observed for the electrolyte containing 6 wt % CaF_2. In comparison to other electrolytes, from the solidus, electrical conductivity decreases rapidly with temperature. In the temperature range (843-1053 K) where the dependence of $\ln k = f(1/T)$ is approximately linear to all three additives of CaF_2, calculated activation energy of conductivity is 49 and 44 $kJmol^{-1}$, respectively for 2 and 4% CaF_2, while for 6% of CaF_2 is much higher, about 69 $kJmol^{-1}$.

The system Na₃AlF₆ - AlF₃ - CaF₂

Figure 4 shows the results obtained for the ternary system containing 88 wt % Na_3AlF_6, 8 wt. % of AlF_3 and 4 wt.% of CaF_2. For comparison, the results of earlier tested electrolytes are also plotted – pure cryolite, binary electrolyte Na_3AlF_6-AlF_3 and Na_3AlF_6-CaF_2.
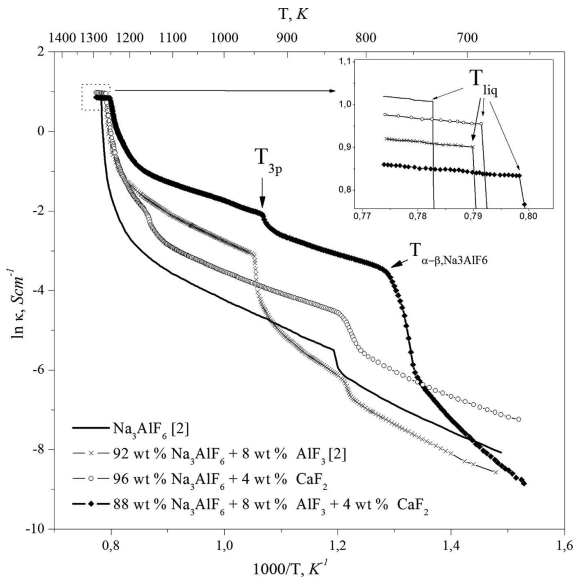

Fig. 4. Electrical conductivity of pure cryolite and with content of AlF_3 and CaF_2

The results show that introducing to the liquid electrolyte Na_3AlF_6 - AlF_3 another component, which is calcium fluoride, cause further reduction of its electrical conductivity. The structure of liquid becomes more and more complicated as an outcome of the formation of a new group of complex ions. Therefore the solution becomes less conductive. What is more, the liquidus temperature of this electrolyte is lower than binary system (determined from the curve T_{liq} is 1253 K). Below this temperature, the conductivity decrease faster than in the liquid phase.

In the temperature indicated in the Figure 4 as T_p (938 K) the sudden and significant decrease of conductivity value was observed. It may be due to the peritectic transformation and disappearance of the liquid phase. Finally, sudden change of conductivity was observed during the alpha-beta phase transition in solid cryolite at temperature about 780 K. It was discovered, that at temperatures from the solid phase until the phase transition in solid cryolite, ternary system shows the highest conductivity of all the previously studied ones. The reason for such high values of κ can be compound $NaCaAlF_6$ which is formed in this system, and which according to [9] has a high solubility in the β - Na_3AlF_6. However, at lower temperatures the solubility of $NaCaAlF_6$ in Na_3AlF_6 decreases rapidly. As a result, rapid decrease of conductivity values during the rebuilding of the lattice Na_3AlF_6 was observed. It is worth mentioning that the conductivity of the cryolite with aluminium and calcium fluorides at 923 K is 0.0847 Scm^{-1} is comparable to the value of superionic conductors such as NASICON (sodium conductor), sodium β " – alumina and LISICON (Lithium Conductor). Mentioned above superionic conductors achieve similar values of conductivity at much lower temperatures, and their transport properties are the re-

sult of the laminated skeletal structure (characteristic for the superionic conductors) and called a fast ion conductors. In the ternary system Na_3AlF_6 - AlF_3 - CaF_2 during cooling of the electrolyte, the $NaCaAlF_6$ can create solid solution with the cryolite [9]. As a result, it can be expected that Ca^{2+} cations will go in normal Na^+ sites with consequent introduction of vacancies. The raised concentration of calcium fluoride in the electrolyte can, therefore, result in an increase of formed vacancies causing the solution to have a higher electrical conductivity at a given temperature than pure cryolite. In the fact of absence of a solid solution in the system cryolite – AlF_3 conductivity in the solid state is lower than in pure cryolite.

By introducing these two additions (AlF_3 and CaF_2) to the cryolite it was not expected that the conductivity of such system will be intermediate between the two binaries. It is because the conductivity of electrolytes with different compositions (including the areas of the liquid phase and two phases: liquid + solid) does not have an additive property. In multicomponent systems may occur:

– the appearance of additional compound with a higher or lower conductivity
– change the solubility of the components with the temperature
– formation of uncontrolled structure defects and their freezing during liquid – solid phase transition
– partial association defects with decreasing temperature, and their distribution with the heating.

During the aluminum electrolysis, crystallized on the side lining layer of the electrolyte – sideledge, which temperature depends on its distance from the molten electrolyte (400-950°C), can conduct electricity. According to [11] part of sideledge directly adjacent to the liquid electrolyte, containing a quantity of the liquid phase, will not cause loss of current, because current will be "locked" back into the electrolyte. Current losses to the carbon side lining can occur only by completely crystalized layer of the sideledge. Such opinion, expressed by many authors ([10-13]), has confirmation in practice, because on the carbon lining there is a reduction of Na^+ [11]. As an outcome, sodium creates with carbon intercalated compounds (NaC_x). This is accompanied by a change in molar volume and, consequently leads to mechanical damage of carbon linings (delamination, scaling and cracking) [8].

4. Conclusions

– Obtained results confirmed that the addition of CaF_2 to liquid cryolite decreases its electrical conductivity and liquidus temperature.
– In temperature range between liquidus and solidus, the addition of CaF_2 to cryolite increases the electrical conductivity.
– In solid state only additions of 2 and 4 wt % of CaF_2 increase the electrical conductivity. It may be due to the formation of solid solution and insertions of vacancies, which are additional charge carriers.
– At temperatures including the solid phase until the phase transition in solid cryolite, ternary system Na_3AlF_6 - AlF_3 - CaF_2 shows the highest conductivity of all previously

studied. This may be due to the formation of $NaCaAlF_6$ and high solubility of this compound in the β-Na_3AlF_6.

– Crystallized ledge on the side lining cell , consisting mainly cryolite and small amounts of CaF_2 and AlF_3 can conduct electricity. Consequently, this may cause flow of current from the anode to the cathode bypassing the liquid electrolyte and lead to loss of current efficiency.

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