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## RESEARCH ON THE ELECTRICAL CONDUCTIVITY OF FLUORIDE ELECTROLYTES NaF-AlF<sub>3</sub> IN LIQUID AND SOLID STATE

### BADANIA PRZEWODNICTWA ELEKTRYCZNEGO ELEKTROLITÓW FLUORKOWYCH NaF-AlF<sub>3</sub> W FAZIE CIEKŁEJ ORAZ W STANIE STAŁYM

The main aim of the present work was to perform measurement of the conductivity of cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and its mixtures with aluminium fluoride (AlF<sub>3</sub>) 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 and its mixtures with AlF<sub>3</sub> (4, 8 and 12 wt % AlF<sub>3</sub>) 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<sup>-1</sup>. It was confirmed, that the addition of AlF<sub>3</sub> to liquid cryolite decreases of its electrical conductivity and liquidus temperature. Whereas in solid state the influence of aluminium fluoride on conductivity is inverse. It is probably due to creation of chiolite (Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>) during the peritectic transition in 1013 K, which is stable up to room temperature.

*Keywords:* aluminium; electrical conductivity; fluoride electrolytes; side ledge

Głównym celem pracy było wykonanie pomiarów przewodnictwa elektrycznego kriolitu (Na<sub>3</sub>AlF<sub>6</sub>) i jego mieszanin z fluorkiem glinowym (AlF<sub>3</sub>) w szerokim zakresie temperatur (580-1300 K), obejmującym fazę ciekłą i stałą. Temperaturowe zależności przewodnictwa ciekłego i stałego kriolitu oraz jego mieszanin z AlF<sub>3</sub> (4, 8 i 12 % mas. AlF<sub>3</sub>) określono dwuelektrodową techniką zmiennoprądową. Jednoczesne pomiary przewodnictwa i temperatury wykonywano w 1 minutowych odstępach czasu podczas cykli ogrzewania i chłodzenia z szybkością 0,5 Kmin<sup>-1</sup>. Na podstawie uzyskanych wyników potwierdzono, iż dodatek AlF<sub>3</sub> do ciekłego kriolitu obniża jego przewodnictwo elektryczne oraz temperaturę likwidusu. Natomiast w stanie stałym wpływ fluorku glinowego jest odwrotny. Jest to prawdopodobnie spowodowane tworzeniem się chiolitu (Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>) w trakcie przemiany perytektycznej w temperaturze 1013 K, związku stabilnego aż do temperatury pokojowej.

## 1. Introduction

Electrical conductivity is one of the most important physico-chemical parameters in chemical engineering as well as in the technology of many industrial processes. Especially in aluminium electrowinning, where a great amount of electrical energy is needed. Therefore the conductivity of the electrolyte has significant influence on energy consumption and current efficiency and thus directly influences the production cost of primary metal [1]. It is generally accepted that one of phenomena which decrease current efficiency is flow of current through the side ledge to the cavity walls. Side ledge (frozen electrolyte) formed on the sidewall and has an important consequence on the cell service life and the dynamic heat balance during various operational disturbances associated with the smelting operation e.g. alumina feeding, anode changing, metal tapping, anode effect

etc. On the other hand, when the current flows through a ledge to the carbon side lining, sodium is deposited and current efficiency is lost [2]. It is generally accepted that frozen electrolyte is an electrical conductor [3,4]. While freezing, the conductivity drops about one order of magnitude. The phase diagram shows that generally the material freezing on the wall is pure cryolite. If the freezing is rapid, the composition of frozen material is similar to the bulk bath, and the conductivity could be higher. Literature studies say that electrical conductivity data of cryolite and its mixtures or solutions with AlF<sub>3</sub>, CaF<sub>2</sub>, MgF<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> in the solid state are scarce and generally inaccurate. From this point of view it is interesting to conduct research on the electrical conductivity of liquid and solid cryolite melts as a function of temperature and composition.

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## 2. Experimental

Electrical conductivity is an intensive property and cannot be measured directly; it must be calculated from a measurement of the corresponding extensive property, resistance:

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

where:  $R_{el}$  is resistance,  $\rho$  is electrical resistivity  $\kappa$  is electrical conductivity,  $L$  is the effective length of the current path,  $S$  is the effective cross-sectional area of the current path, and  $G$  is the cell constant [5]. In most of the techniques, determination of electrical conductivity is a comparative procedure dependent on calibration of cell constant in a standard liquid. Calibration is accomplished by measuring resistance of the standard  $R_s$  and calculating the  $G$  by the relationship of  $G = k_s R_s$ , where  $k_s$  is the well known electrical conductivity of standard liquid. The conductivity of the liquid of interest  $\kappa_{el}$  is then determined by measuring its resistance and using the measure cell constant,  $\kappa_{el} = G/R_{el}$ . In this research, a molten KCl was used as a liquid standard for calibration.

A.C. technique was used with a sine wave signal with amplitude 1V and frequency 35 kHz. This value

of frequency was selected from dispersion-independent region for performing conductivity measurement.

The apparatus for measuring conductivity of molten and solid electrolytes is based on tube-type cell, as shown in Fig.1 and Fig.2. The cell consist of a boron nitride (HPBN-Hot Pressed Boron Nitride) tube of inner diameter 5mm, outer diameter 15mm and length 50mm, and graphite basis which was used as one electrode (immovable).

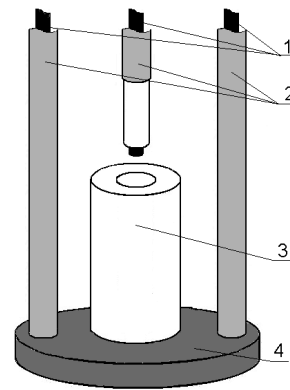


Fig. 1. Experimental cell: 1 – Mo rods, 2 – alumina tube, 3 – HPBN capillary, 4 – graphite basis

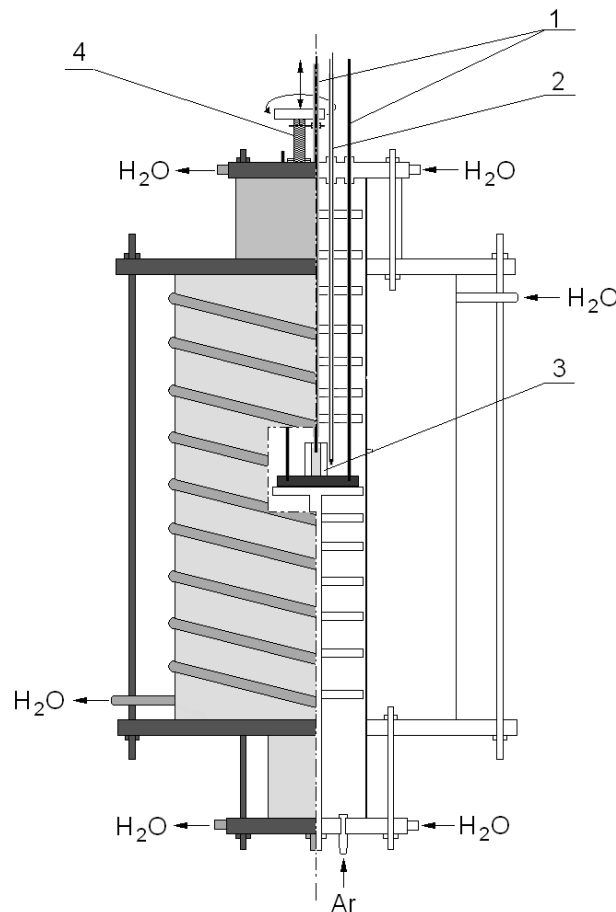


Fig. 2. Scheme of laboratory furnace with cell: 1 – electrode leads, 2 – thermocouple, 3 – measuring cell, 4 – movable electrode

The second electrode was mechanically immersed to the melt allows, the depth determination with a precision of 0,25mm. The cell allowed to measure of the conductivity of liquid as well as of solid cryolite melts.

The salts  $\text{Na}_3\text{AlF}_6$  and  $\text{AlF}_3$  were supplied from Sigma-Aldrich (+99,99% purity) and just before the experiments were dried for 18h at 473K. The salt was introduced to the cell which was then placed in a vertical laboratory furnace (Fig.2) and heated until the salt had melted. When the electric contact was obtained, accurate measurements of resistance and temperature started. Data points were collected in the range of temperature between 1300 and 580 K. The furnace was heating/cooling with a linear rate  $0,5 \text{ K}\cdot\text{min}^{-1}$  and was controlled by a SHINCO controller/programmer instrument.

The temperature was measured with a accuracy  $\pm 0,5$

K by of a Pt/Pt-10Rh thermocouple placed at about 5mm from the sample. Both temperature and conductivity were measured in 1 min steps during heating and cooling and registered automatically by a computer.

The apparatus was tested with NaCl and NaF. The preliminary results obtained with this salts are in agreement with the literature data within less than 5%.

### 3. Results and discussion

Temperature dependencies of the electrical conductivity of cryolite in the temperature range between 580 and 1293 K are presented in Fig. 3 as a natural logarithm of specific conductivity  $\kappa$  versus reciprocal of absolute temperature  $T/\text{K}$ .

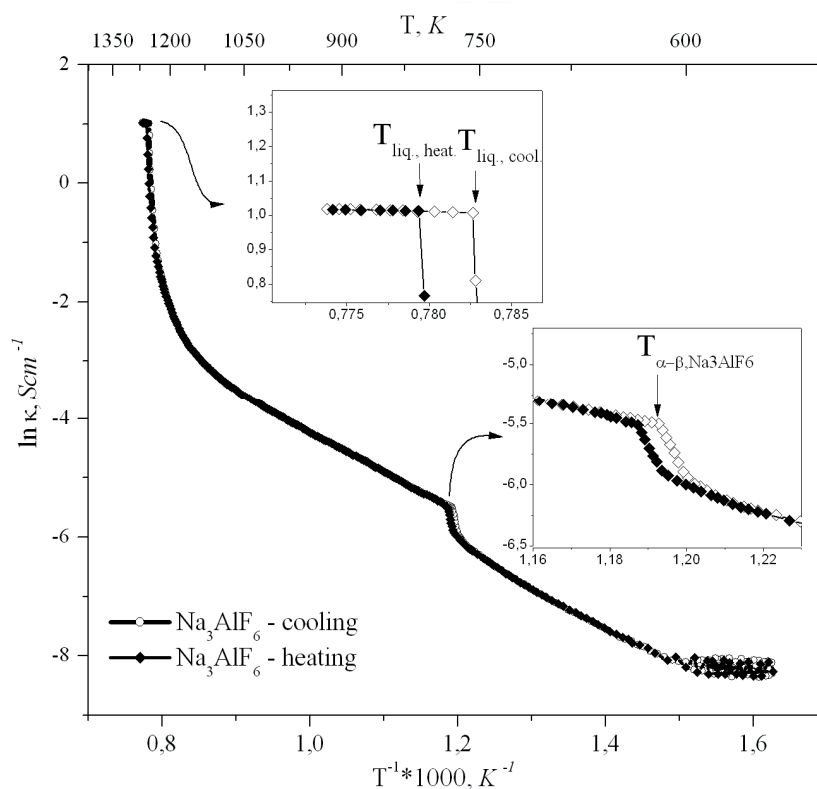


Fig. 3. Changes of the electrical conductivity of pure cryolite

In liquid state electrical conductivity decreases gradually with temperature up to  $2,765 \text{ Scm}^{-1}$  at 1283 K. At this temperature cryolite is crystallizing and a significant conductivity drop is observed. A second, much smaller effect, either a drop in electrical conductivity, takes place at approximate temperature 838 K during cooling. In this temperature cryolite undergoes a transition from a monoclinic low-temperature modification,  $\alpha - \text{Na}_3\text{AlF}_6$  (space group P21/n) to a cubic structure,  $\beta - \text{Na}_3\text{AlF}_6$

(space group Fm3m) [6,7]. The  $\alpha -$  cryolite is stable up to a room temperature. The electrical conductivity values obtained during heating as well as during cooling are similar. A little hysteresis was observed during the liquid – solid and  $\beta - \alpha$  phase transitions.

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

$$\kappa = \kappa_0 \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

in the ranges of temperature where the dependence  $\ln\kappa=f(T^{-1})$  could be approximated with a linear function. In equation (2)  $\kappa_0$  is the pre-exponential factor,  $E_a$  – the activation energy,  $R$  – the gas constant ( $R=8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) and  $T$  is absolute temperature. The activation energy was calculated by the method of least squares. The  $E_a$  value for  $\alpha$  – cryolite is higher ( $57,47 \pm 0,07 \text{ kJ}\cdot\text{mol}^{-1}$ ) than for  $\beta$  –  $\text{Na}_3\text{AlF}_6$  ( $56,01 \pm 0,08 \text{ kJ}\cdot\text{mol}^{-1}$ ).

Obtained results for pure cryolite show that in a wide range of temperature, in solid state the electrical conductivity follows an Arrhenius behaviour which is characteristic of a thermally activated transport. Obtained results of temperature dependences of the electrical conductivity (where  $d\kappa/dT > 0$ ) and calculated values of energy activation for  $\alpha$  –  $\text{Na}_3\text{AlF}_6$  and  $\beta$  –  $\text{Na}_3\text{AlF}_6$  confirm the cationic mechanism of conduction in solid cryolite.

It indicates that cryolite belongs to a group of sodium ionic semiconductors, although low value of conductivity doesn't allow to classify this compound to a group of superionic conductors.

Next, cryolite melts with addition 4, 8 and 12 wt. % of  $\text{AlF}_3$  was examined. In this range of composition and temperature (580-1300 K) literature studies [8] show that in high temperatures only liquid phase exists, in lower (below liquidus) – mixture of solid cryolite and liquid and below peritectic temperature only mixture of solid chiolite ( $\text{Na}_5\text{Al}_3\text{F}_{14}$ ) and solid cryolite.

Temperature dependencies of the electrical conductivity of  $\text{Na}_3\text{AlF}_6 - \text{AlF}_3$  melts and cryolite (for comparison) in the temperature range between 580 and 1293 K are presented in Fig.4. Conductivity values obtained on heating as well as on cooling are close to each other. A little hysteresis was observed during the phase transitions. For clarity, Fig.4 presents only results obtained during the cooling cycle.

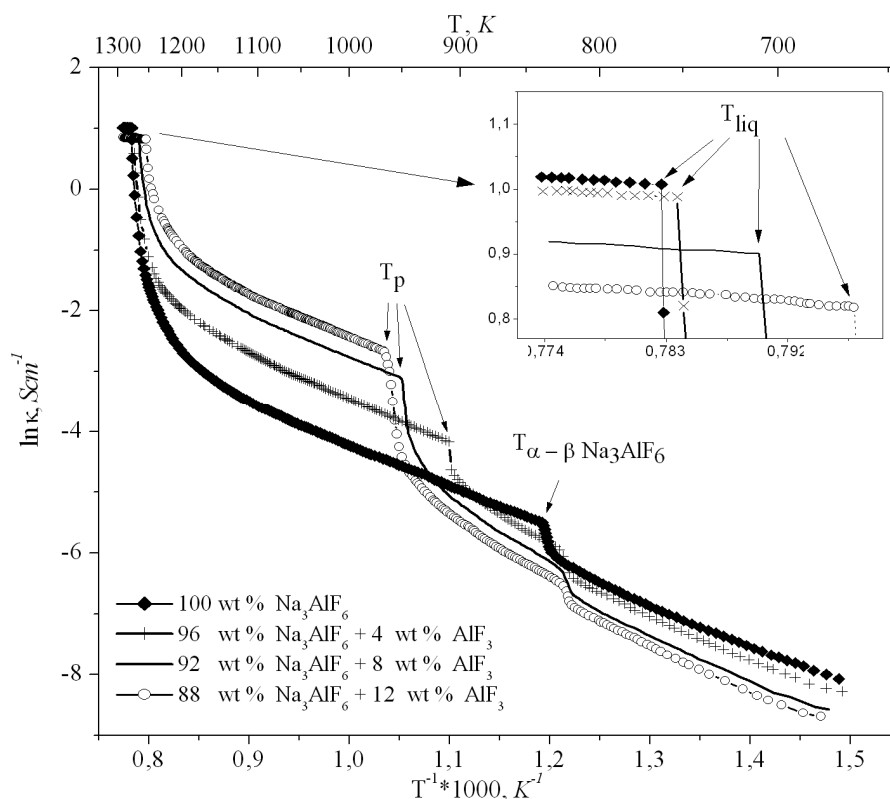


Fig. 4. Changes of the electrical conductivity of pure cryolite and its melts

In liquid state electrical conductivity of melts decreases slowly with temperature close to liquidus. In this range, addition of aluminium fluoride to cryolite decreases its electrical conductivity. In liquidus temperature ( $T_{\text{liq}}$ ) first appear crystals of solid cryolite and a

significant conductivity drop is observed. It was confirmed that addition of  $\text{AlF}_3$  to liquid cryolite decreases of liquidus temperature. The value obtained from cooling cycles are: 1276, 1266 and 1255 K for additions 4, 8 and 12 wt. % of  $\text{AlF}_3$  respectively.

The electrolytes between  $T_{liq}$  and peritectic temperature ( $T_p$ ) are characterized by coexistence of liquid and solid phase. Obtained results show that electrical conductivity decrease along with temperature as well as addition of  $AlF_3$ . It is due to decrease of the amount of liquid and increase of solid phase. It is believed that mobility of ions  $Na^+$  is much greater in liquid than in solid phase so the electrical conductivity is higher when the amount of liquid is higher. Conduction of current in this region most likely takes place only by liquid phase through the connected capillary vessels.

A second much smaller effect, either a drop in electrical conductivity, takes place during peritectic transition. It was found that this transition is strong overcooled, up to 100 K for electrolyte contains 4 wt. % of  $AlF_3$ . During cooling, after peritectic transition, in system exists only solid chiolite ( $Na_5Al_3F_{14}$ ) and  $\beta$  - cryolite, according to the reaction [8]:  $(\beta)Na_3AlF_6(s) + liq = Na_5Al_3F_{14(s)} + (\beta)Na_3AlF_6(s)$ . The third conductivity drop occurs in  $\alpha$  -  $\beta$  phase transition in solid cryolite. The presence of chiolite in studied mixtures moves the temperature of  $\alpha$  -  $\beta$  phase transition in direction of lower temperatures (826, 824, 821 K for 4, 8 and 12 wt. % of  $AlF_3$  respectively).

In solid state, all the electrolytes containing mixtures of  $Na_5Al_3F_{14}$  and low-temperature modification  $\alpha$  -  $Na_3AlF_6$  indicate lower conductivity than pure cryolite. It may suggest that chiolite is lower conduction compound than cryolite.

In the range of temperature where the dependence  $\ln\kappa=f(T^{-1})$  could be approximated with a linear function, the activation energy of conductivity was calculated and the  $E_a$  value are presented in tab.1.

TABLE 1

Activation energy of conductivity of liquid and solid cryolite salts

Phase	Amount of $AlF_3$ , wt. %	Range of temperature, K	$E_a$ , $kJ\cdot mol^{-1}$
Liquid	4	1276-1292	$8,71 \pm 0,08$
	8	1266-1292	$10,12 \pm 0,03$
	12	1255-1293	$12,00 \pm 0,04$
Liquid and solid	4	910-1113	$61,12 \pm 0,02$
	8	950-1113	$56,65 \pm 0,02$
	12	964-1113	$56,99 \pm 0,01$
solid ( $Na_5Al_3F_{14}$ + $(\beta)Na_3AlF_6$ )	4	826-864	$81,39 \pm 0,09$
	8	824-882	$82,00 \pm 0,07$
	12	821-886	$78,92 \pm 0,09$
solid ( $Na_5Al_3F_{14}$ + $(\alpha)Na_3AlF_6$ )	4	683-813	$59,31 \pm 0,08$
	8	683-813	$61,92 \pm 0,07$
	12	683-813	$62,70 \pm 0,08$

The lowest activation of energy of conductivity indicates liquid phase ( $8,71 \div 12 kJ\cdot mol^{-1}$ ) instead of the

highest - solid phase, contains chiolite and  $\beta$  - cryolite ( $78,92 \div 81,39 kJ\cdot mol^{-1}$ ). In liquid state, addition of  $AlF_3$  increases the energy activation of conductivity. The same dependence is observed in solid state (contains  $Na_5Al_3F_{14} + (\alpha)Na_3AlF_6$ ), however in mixed phase (liquid and solid) the dependences is inverse. In solid state electrolyte contains chiolite and  $\beta$  - cryolite there is no evident dependence.

#### 4. Conclusions

Based on the results presented in this study and the discussion the following conclusions have been formulated:

- Obtained results confirmed that the addition of  $AlF_3$  to liquid cryolite decreases its conductivity and liquidus temperature
- During the liquid-solid phase transition the conductivity decreases by about 97 % for pure cryolite and 96, 95 and 93 % for 4, 8, 12 wt. % of  $AlF_3$  respectively
- In the range of temperature between liquidus and solidus, the addition of  $AlF_3$  increases of electrical conductivity whereas in solid state decreases of conductivity
- Obtained results confirmed that  $\alpha$  -  $\beta$  phase transition in cryolite occurs at 838 K, not at 890 K [9]
- The presence of chiolite in studied mixtures in solid state moves the temperature of  $\alpha$  -  $\beta$  phase transition in cryolite in direction of lower temperatures
- The positive temperature coefficient of conductivity ( $d\kappa/dT > 0$ ) and calculated values of energy activation of conductivity for solid phase indicate that cryolite is ionic semiconductor.

#### REFERENCES

- [1] J. J. Chen, B. J. Welch, Light Metals, 309-316 (1997).
- [2] W. Hauptin, Journal of the Minerals, Metals and Materials Society, 28-34 (1991).
- [3] R. Obłąkowski, S. Pietrzyk, J. Thonstad, G. M. Haarberrg, 1<sup>st</sup> Conference on Ionic Liquids and Solid Electrolytes, Szklarska Poręba (1997).
- [4] S. Pietrzyk, R. Obłąkowski, TMS-AIME, 1083-1089 (2002).
- [5] S. Schiefelbein, N. Fried, K. Rhoads, D. Sadoway, Review of scientific instruments **69** (9), 3308-3313 (1998).
- [6] D. Spearin, J. F. Stebbins, I. Farnan, Physics and Chemistry of Minerals **21**, 373-3861 (1994).
- [7] M. Bruno, O. Herstad, J. L. Holm, Journal of Thermal Analysis and Calorimetry **56**, 51-57 (1999).

- [8] J. Thonstad, P. Fellner, G. M. Haarberg, J. Híveš, H. Kvande, A. Sterten, Aluminium Electrolysis. Fundamentals of the Hall-Héroult Process. 3<sup>rd</sup> Edition, Aluminium Verlag, Düsseldorf (2001).
- [9] H. Yang, S. Ghose, D. M. Hatch, Physics and Chemistry of Minerals **19**, 528-544 (1993).

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