

## **A new type of Aluminium Smelting Baths Electrical Conductivity**

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### **Abstract**

The electrical conductivity of low-melting electrolytes (AlF<sub>3</sub>-rich, e.g. n(NaF)/n(AlF<sub>3</sub>) = 1.4, with additives Al<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub>) was determined using a pyrolytic BN tube type cell. AC - techniques with a sine wave signal with 10 mV amplitude in the high frequency range were applied. Basic melt contained 58.33 mol % NaF and 41.67 mol % AlF<sub>3</sub>. To this melt 2 wt % alumina and/or 5 wt % calcium fluoride were added. The electrical conductivity data in the molten system can be described by a simple equation of the Arrhenius type:

$$\kappa = A e^{-B/T}$$

where  $\kappa$  represents the electrical conductivity ( $\Omega^{-1} \text{ cm}^{-1}$ ),  $T$  is the temperature (K), A and B are constants for the measured system.

**Keywords:** acid melts, aluminium, cryolite-based melts, electrical conductivity, low temperature

### **Introduction**

Aluminium occupies a special place in extractive metallurgy because it can be produced as a high-purity product, enabling its special properties to be utilised (Thonstad et al. 2001). It has many economically attractive applications in the construction sectors, in the transportation sector, in numerous industrial products, packaging, and containers. The substitution of aluminium for common materials such as steel, copper, and certain composites can generate large energy savings over the net life of various products. It also reduces the production of the greenhouse gas, carbon dioxide, particularly in transportation applications because lightweight aluminium-intensive vehicles will use less fuel than conventional vehicles.

Industrial production of primary aluminium is carried out in alumina reduction cells (Hall-Héroult process) adopted in the late nineteenth century, and continues as the process in commercial use today. The Hall-Héroult process involves the electrolytic decomposition of aluminium oxide dissolved in a molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) bath operating at temperatures about 960 °C. Carbon anode is consumed in the reaction that makes CO and  $\text{CO}_2$ . Molten aluminium is reduced at the cathode.

Producing aluminium by the Hall-Héroult electrolytic cell process requires a large amount of energy and produces significant emissions of greenhouse and other detrimental gases. However, scientists and engineers have sought alternative methods for producing aluminium for years in an attempt to reduce the energy intensity and capital investments required for aluminium production by this method. Moreover, world-wide concern about effects of certain air emissions on global warming has more encouraged governmental, environmental, and industrial leaders to find ways to cost-effectively mitigate this potentially serious long-term problem.

Progress in material science is producing new “inert” materials for anodes and cathodes in the electrolysis cell (Thonstad et al. 2001). Titanium diboride ( $\text{TiB}_2$ ) is used as the main component of most cathode concepts, either in pure form or as composites. The anode material is inert in the sense that it is not consumed in the cell reaction, as the carbon anode is. A large number of inert anode materials have been tested, mostly coming from two groups of materials - cermet and metal. For inert anodes a low electrolyte temperature should be advantageous because the solubility of the oxide material that makes up the active anode surface decreases with decreasing temperature. If a metal substrate is used, a low temperature is even more compelling, because the rate of oxidation of metals drops sharply with temperature, i.e. as much as an order of magnitude per 100 °C.

To minimize corrosion during electrolysis process of assumed inert anode materials, it is necessary that dissolved alumina should be maintained close to saturation in the molten electrolyte and/or that the cell temperature should be lowered. A lower-temperature bath means that the electrolyte composition will probably have to be changed by addition of  $\text{AlF}_3$  to keep molar ratio  $n(\text{NaF})/n(\text{AlF}_3)$  in the melt lower than 1.5.

The purpose of this work was to measure the electrical conductivity of sodium cryolite ( $n(\text{NaF})/n(\text{AlF}_3) = 1.4$ ) in a temperature range (780 – 870) °C and to study the effect of alumina and calcium fluoride additions on the electrical conductivity of these systems.

## Experimental

### Apparatus and Experimental Procedure

The apparatus for measuring the electrical conductivity of molten salts is based on a tube-type

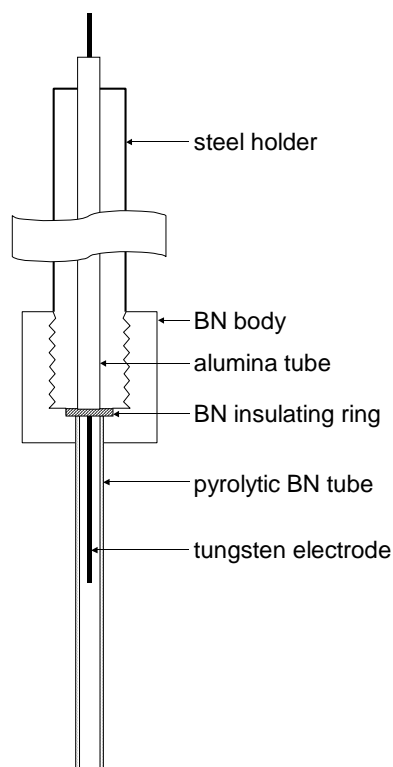


Fig.1 Conductivity probe

cell, as shown in Fig. 1. The cell consists of a pyrolytic boron nitride tube (Sintec Keramik, UK) of inner diameter 5 mm, outer diameter 6 mm and length 100 mm, a graphite crucible of outer diameter 53 mm and height 120 mm, which is used as one electrode. A tungsten rod with a stainless steel ring placed in a BN tube is used as the other electrode. The crucible, containing 13 g sample of the salt mixture, is placed in a vertical laboratory furnace with controlled atmosphere (argon 99.996 %). The temperature is measured with a Pt-Pt10Rh thermocouple. AC - techniques are being used with a sine wave signal with small amplitude in the high frequency range. The AUTOLAB FRA2 module is used for the measurements of the cell impedance. The *ac* amplitude was 10 mV, the frequency was varied from 10 Hz to 100 kHz, and 61 readings are taken within this range. A personal computer was used for controlling the AUTOLAB, and for collection of the data. The value of the electrolyte resistance obtained was used for the evaluation of the electrical conductivity of the melt, using eqn.(1),

$$\kappa = \frac{C}{R_{el}} \quad (1)$$

where  $\kappa$  is the electrical conductivity of the melt ( $\Omega^{-1} \text{ cm}^{-1}$ ),  $C$  is the cell constant ( $20.1 \text{ cm}^{-1}$ ), and  $R_{el}$  is the true electrolyte resistance ( $\Omega$ ). More details can be found in our previous papers (Híveš and Thonstad 2004, Híveš et al. 1996, Híveš et al. 1994, Híveš et al. 1993).

### Chemicals

Aluminium fluoride was purified by sublimation in a platinum crucible (inner diameter 75 mm, height 270 mm). The temperature at the bottom of the crucible was 1250 °C; the Pt lid covering the crucible was cooled in an argon atmosphere. In each run, 100 g of sublimated  $\text{AlF}_3$  was prepared. Sodium fluoride, calcium fluoride and alumina were of analytical grade,

and prior to use they were heated to remove any moisture. A NaF-AlF<sub>3</sub> mixture was prepared for each run,  $n(\text{NaF})/n(\text{AlF}_3) = 1.4$ , with or without additives Al<sub>2</sub>O<sub>3</sub> and/or CaF<sub>2</sub>.

## Results and Discussion

Investigations of the electrical conductivity of low-temperature cryolite-based systems have been an area of active research in recent years. Experimental investigations of the electrical conductivity of molten sodium cryolite systems mostly focus on highly acidic melt e.g. melts with high content of AlF<sub>3</sub> and/or molten potassium cryolite melts with high content of AlF<sub>3</sub>. Equations proposed by several investigators are summarised in the paper by Redkin et al. (Redkin et al. 2007). The model they offered for calculation of electrical conductivity of potassium cryolite-based melts exceed experimental values about 10-30 %. Data for sodium cryolite-based systems with high content of AlF<sub>3</sub> were not published yet. The melt was composed of 58.33 mol % NaF and 41.67 mol % AlF<sub>3</sub>. Addition of 2 wt % of alumina and/or 5 wt % of calcium fluoride to the melt was also used. The operating temperature ranged from 780 °C to 870 °C. The electrical conductivity data in the molten system can be described by a simple equation of the Arrhenius type:

$$\kappa = A e^{-B/T} \quad (2)$$

where  $A$  ( $\Omega^{-1} \text{ cm}^{-1}$ ) and  $B$  (K) are constants for the measured system,  $T$  represents absolute temperature (K). Figure 2 shows the experimental conductivity data as a function of temperature for the NaF - AlF<sub>3</sub> system (1), the NaF - AlF<sub>3</sub> - CaF<sub>2</sub> system (2), the NaF - AlF<sub>3</sub> - Al<sub>2</sub>O<sub>3</sub> system (3) and the NaF - AlF<sub>3</sub> - Al<sub>2</sub>O<sub>3</sub> - CaF<sub>2</sub> system (4). The solid lines in Fig. 2 represent the equation (2), the parameters  $A$  and  $B$  of this equation are given in Table 1.

Table 1 The parameters  $A$  and  $B$  of the equation (2) for the measured systems

System	1	2	3	4
molar ratio	1.4	1.4	1.4	1.4
$n(\text{NaF}) / n(\text{AlF}_3)$				
Al <sub>2</sub> O <sub>3</sub> / wt %	0	0	2	2
CaF <sub>2</sub> / wt %	0	5	0	5
Temp. range/ °C	790 - 870	790 - 870	780 - 840	800 - 860
$A / \Omega^{-1} \text{ cm}^{-1}$	$9.066 \pm 0.009$	$8.876 \pm 0.010$	$8.781 \pm 0.009$	$8.390 \pm 0.009$
$B / \text{K}$		$1929 \pm 27$		

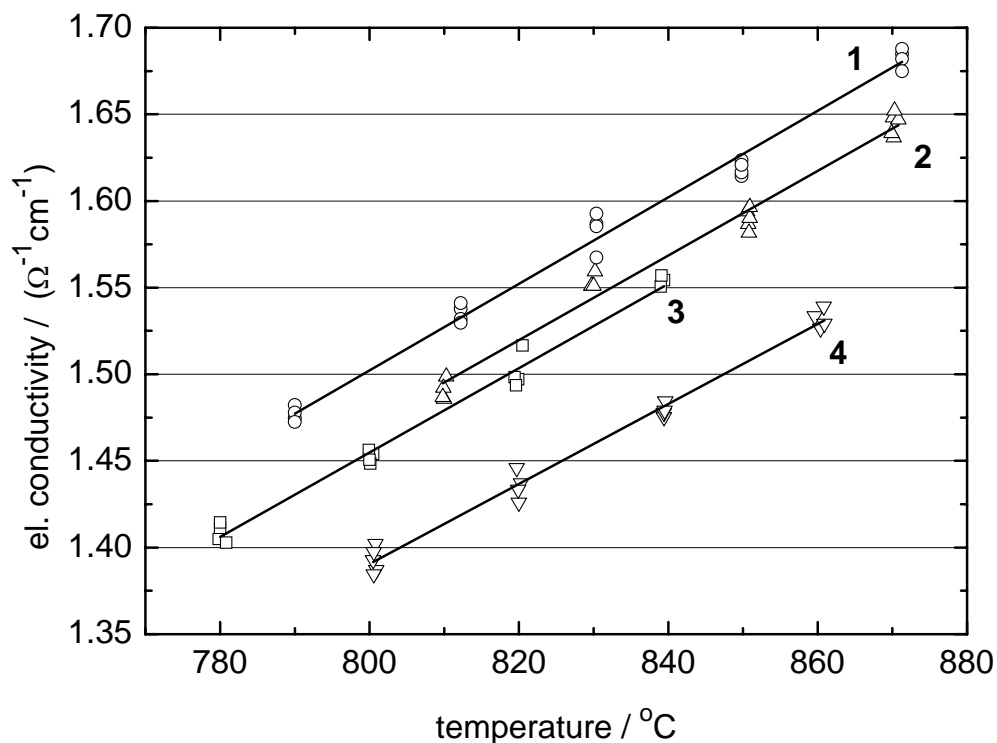


Fig. 2 The electrical conductivity of the NaF – AlF<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub> – CaF<sub>2</sub> system as a function of temperature for the compositions: (1) - 58.33 mol % NaF and 41.67 mol % AlF<sub>3</sub> - basic melt, (2) - basic melt plus 5 wt % of CaF<sub>2</sub>, (3) - basic melt plus 2 wt % of alumina, (4) - basic melt plus 2 wt % of alumina and 5 wt % of CaF<sub>2</sub>, symbols – experimental data, full lines – equation (2)

The second term in the equation (2) describes the temperature dependence of the electrical conductivity of basic melt. The model used to describe the temperature and concentration dependencies of the electrical conductivity of high acidic melts is based on assumption that the activation energy of the process does not depend on composition in our concentration range of additives. Multi-regression analysis of all obtained experimental data show us a very small variation on the temperature coefficient B for each measured composition. The effect of additives Al<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub> can be seen in Fig. 2. The addition of both additives into acidic melt causes decrease of the electrical conductivity. This effect is stronger in the case of alumina than calcium fluoride.

## **Conclusion**

The investigation of the electrical conductivity of the low-melting cryolite-based melts ( $n(\text{NaF}) / n(\text{AlF}_3) = 1.4$ ) with alumina and calcium fluoride additions in the temperature range of (780 – 870) °C showed that conductivity is substantially lower than that of conventional electrolyte which is about  $2.13 \Omega^{-1} \text{cm}^{-1}$  at 950 °C (Híveš and Thonstad 2004). A higher electrolyte voltage drop might be expected in the case of low-melting electrolyte. This can be compensated by running electrolysis at shorter interpolar distance or by using lower current density. The low electrical conductivity of such melts can be eliminated by the addition of LiF only partially.

## *Acknowledgement*

*This work was supported by courtesy of the Slovak Grant Agency (VEGA 1/0535/08)*

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