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Electrical conductivity of low melting baths for aluminium electrolysis: the system Na_3AlF_6–Li_3AlF_6–AlF_3 and the influence of additions of Al_2O_3, CaF_2, and MgF_2

P. FELLNER*, S. MIDTLYNG‡, Å. STERTEN, J. THONSTAD

Laboratories of Industrial Electrochemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway

‡*Foundation for Scientific and Industrial Research (SINTEF) at the Norwegian Institute of Technology, N-7034 Trondheim, Norway*

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The electrical conductivity was investigated for a section of the molten ternary mixture Na_3AlF_6–Li_3AlF_6–AlF_3 with molar ratio $n(Li_3AlF_6):n(AlF_3) = 1:2$. The conductivity of this system can be described by the following equation:

$$\kappa/\mathrm{S\,cm^{-1}} = 7.22\exp(-1204.3/T(\mathrm{K})) + 0.97\,\chi(Li_3AlF_6) - 1.66\,\chi(AlF_3) - 9.42 \times 10^{-3}\chi(Li_3AlF_6)\chi(AlF_3)$$

where $\chi(i)$ represent the mole fractions of the additions. The influence of additions of CaF_2, MgF_2 and/or Al_2O_3 on the electrical conductivity of the binary system Na_3AlF_6–Li_3AlF_6 and the ternary system Na_3AlF_6–Li_3AlF_6–AlF_3 was also studied.

1. Introduction

Melts based on sodium cryolite (Na_3AlF_6) serve as solvent for alumina in the electrolytes used for the production of aluminium [1]. Cryolite is a high melting compound (1012° C), and the conventional bath consists of cryolite with 6–13% AlF_3, 3–8% CaF_2 and 2–5% Al_2O_3 (all percentages by mass); the temperature of the electrolyte is usually in the range 945 – 970° C. It might be of advantage to use an electrolyte with a lower temperature of primary crystallization [2–4]. By the introduction of low-melting baths one might expect an increase in the current efficiency, lower energy consumption and, possibly, prolonged cell life and easier adaption of inert electrode materials. The reason why the high temperature bath is prevailing is its unmatched high alumina solubility. The introduction of more efficient ways of feeding alumina to the cell by means of point feeders which can operate almost continuously, opens a possibility for use of baths with low alumina solubility. Some aspects of low-melting baths for aluminium electrolysis have been discussed in the literature [2–4]. The temperature of primary crystallization can be lowered by the use of more acid (AlF_3-rich) bath and/or by the introduction of certain additives, such as LiF, CaF_2, and MgF_2. As follows from the phase diagram of the system Na_3AlF_6–AlF_3 [1], a mixture containing an excess of about 35 mass % of AlF_3 has a temperature of primary crystallization of about 700° C. This means that the temperature of the electrolyte can in principle be lowered as much as 200° C [2] just by adding a large excess of AlF_3.

The electrical conductivity of the electrolyte, however, decreases both with increasing AlF_3 content and decreasing temperature [1]. This unfavourable effect can partly be compensated by the addition of LiF. The compositions of the melts investigated in this study were chosen in such a way that formally they corresponded to the system Na_3AlF_6–Li_3AlF_6–AlF_3, which may be considered as a promising basis for a low-melting electrolyte [4, 5].

There are no data on the electrical conductivity of these low melting systems in the literature. The objective of this work was to study the electrical conductivity of the molten mixtures Na_3AlF_6–Li_3AlF_6–AlF_3 and the influence of additions of Al_2O_3, CaF_2 and MgF_2.

2. Experimental details

The apparatus and the measuring procedure has been described in detail elsewhere [6]. The basic part of the conductivity cell consisted of a pyrolytic boron nitride tube (Boralloy, Union Carbide) of inner diameter about 4 mm and length 10 cm. The cell constant was about 45 $\mathrm{cm^{-1}}$, and it was determined by calibration with NaCl using the data for the conductivity of molten sodium chloride published by Ketelaar and Maenaut [7]. One electrode was made of a tungsten rod (diam. 2 mm), while the graphite crucible served as the

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*Permanent address: Department of Inorganic Technology, Slovak Technical University, 812 37 Bratislava, Czechoslovakia.

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other electrode. The graphite crucible was placed in a vertical furnace with controlled atmosphere (argon) and heated up to the required temperature. The temperature was measured with a Pt–Pt10Rh thermocouple, and it was kept constant within 0.5 K.

A Solartron 1250 frequency response analyser was used for the measurement of the cell impedance. The ac amplitude was 10 mV. The frequency was varied from 5 to 30 kHz and the real part of the cell impedance was extrapolated to infinite frequency by plotting it as a linear function of the inverse square root of the angular frequency. A more detailed discussion of the measuring procedure can be found in our previous paper [6].

Hand-picked crystals of Greenland cryolite (Na_3AlF_6) and AlF_3 sublimed under low pressure (about 100 Pa) at 1100° C were used for the preparation of the samples. LiF, MgF_2 and Al_2O_3, and NaCl (used for the determination of the cell constant) were of analytical grade (Merck); CaF_2 was pure precip. (Merck).

3. Results and discussion

3.1. *The system Na_3AlF_6–Li_3AlF_6–AlF_3*

The mixtures used contained cryolite with up to 26.25 mass % of excess AlF_3 and 8.11 mass % of LiF. This upper concentration limit corresponded to a mixture consisting of 50.00 mol % Na_3AlF_6 + 16.67 mol % Li_3AlF_6 + 33.33 mol % AlF_3. The temperatures ranged from 820 to 1000° C. The molar ratio of Li_3AlF_6 and AlF_3 in the ternary system Na_3AlF_6–Li_3AlF_6–AlF_3 was chosen to be 1 : 2. This composition range was selected on the basis of investigations of losses of aluminium and current efficiency [4] and solubility of alumina [8] in electrolytes with temperatures of primary crystallization as low as 800° C.

The results obtained are summarized in Fig. 1. It was found that the experimental conductivity data can be described by the equation

$$\begin{aligned}\kappa/\mathrm{S\,cm^{-1}} &= 7.22\exp(-1204.3/T(\mathrm{K}))\\ &+ 0.97\,\chi(Li_3AlF_6) - 1.66\,\chi(AlF_3)\\ &- 9.42\times10^{-3}\chi(Li_3AlF_6)\chi(AlF_3) \qquad (1)\end{aligned}$$

where $\chi(i)$ represents the mole fraction of the additives Li_3AlF_6 and AlF_3. The standard deviation was found to be 0.015 S cm^{-1}. The first term in Equation 1 describes the temperature dependence of the conductivity of pure molten Na_3AlF_6. Because the melting point of this salt is 1012° C [1] this term corresponds rather to the electrical conductivity of the supercooled liquid. It follows that the activation energy of the electrical conductivity is 10.01 kJ mol^{-1}. The model used to describe the temperature and concentration dependencies of the electrical conductivity of cryolite-based melts is based on the assumption that the activation energy of the process does not depend on composition provided that the concentration of Na_3AlF_6 exceeds 50 mol %. The linear concentration terms represent the influence of the additives as it follows from the addition rule. The parameters + 0.97 for Li_3AlF_6 and − 1.66 for AlF_3 correspond to the influence of these additives on the electrical conductivity in the binary mixtures Na_3AlF_6–Li_3AlF_6 and Na_3AlF_6–AlF_3 [6]. As can be seen, the term representing the ternary interaction is rather small, and it exceeds the experimental uncertainty limit only when the product of the molar fractions of Li_3AlF_6 and AlF_3 exceeds 0.15 (see Fig. 1).

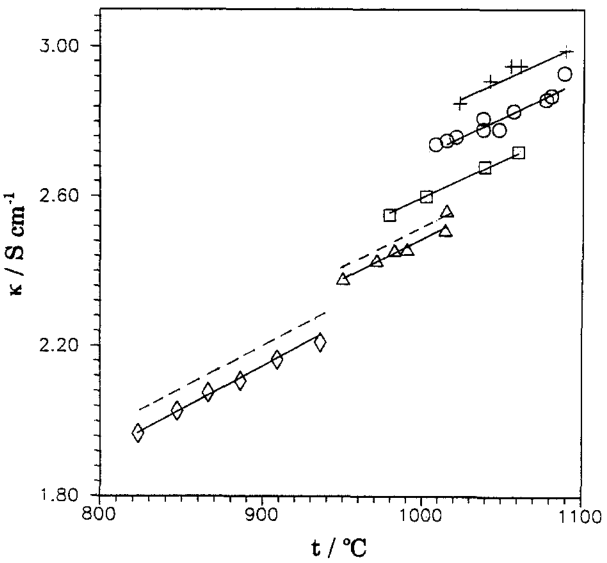

Fig. 1. The electrical conductivity of Na_3AlF_6–Li_3AlF_6–AlF_3 mixtures as function of temperature (compositions in mol %): (+) 100% Na_3AlF_6; (○) 8.35% AlF_3 + 4.15% Li_3AlF_6; (□) 16.65% AlF_3 + 8.35% Li_3AlF_6; (△) 25.0% AlF_3 + 12.5% Li_3AlF_6; (◇) 33.33% AlF_3 + 16.67% Li_3AlF_6. (——) Equation 1; (– – –) Equation 2.

Good agreement between the experimental and the calculated conductivity data justifies the use of this model. It is believed that Equation 1 can be used for estimation of the electrical conductivity for all compositions of the ternary system Na_3AlF_6–Li_3AlF_6–AlF_3 up to 40 mol % Li_3AlF_3 and 50 mol % AlF_3 under the restriction that the content of Na_3AlF_6 in the mixture should be larger than 50 mol %. These limits follow from the concentration range in which the electrical conductivity of the binary and ternary systems was investigated.

3.2. *Influence of the additions of MgF_2 and CaF_2*

Modified baths for electrowinning of aluminium may contain MgF_2 and CaF_2 in addition to LiF and to excess AlF_3 [3]. A certain concentration of CaF_2(3–6 mass %) always builds up due to the content of calcium in the alumina feed. The melting points of these mixtures can be calculated according to the equations published in [8, 9]. The electrical conductivity measurements were carried out at temperatures corresponding to a minimum superheat (temperature above the liquidus) of about 10° C. Conductivity data for the compositions investigated in this work are summarized in Table 1. In Fig. 2 the experimental data obtained are compared with calculated values. The calculations were based on similar assumptions as discussed above, that is on the insensitivity of the

Table 1. Experimental and calculated values of the electrical conductivity of cryolite-based melts related to the temperature of 1000° C

$\chi(i)$*/mol %					κ/S cm^{-1}	
AlF_3	Li_3AlF_6	MgF_2	CaF_2	Al_2O_3	Experiment	Equation 2
8.34	4.16	12.0	–	–	2.62	2.58
16.67	8.34	12.0	–	–	2.48	2.48
–	12.50	12.0	–	–	2.84	2.80
–	25.00	12.0	–	–	2.95	2.92
25.00	–	–	6.0	–	2.40	2.34
–	25.00	12.0	–	–	3.00	2.92
–	25.00	12.0	12.0	–	2.73	2.83
–	25.20	11.0	12.0	4.0	2.75	2.74
24.57	12.28	–	–	3.3	2.40	2.43

*$\chi(i)$ represents the molar fraction additions.

temperature dependence of conductivity on composition and furthermore on the assumption of additivity for contributions of the components to the electrical conductivity. The data for the binary systems were taken from our previous work [6].

According to the proposed model the conductivity of a multicomponent system can be described by an equation of the type

$$\kappa/\mathrm{S\,cm}^{-1} = 7.22 \exp(-1204.3/T(K)) + \sum \chi_i b_i \tag{2}$$

The meaning of the first term was discussed above. The second term represents the influence of the additives to the electrical conductivity as follows from the additivity rule. The values of $b(i)$ are as follows [6]:

$$b(Li_3AlF_6) = +0.97 \qquad b(AlF_3) = -1.66$$
$$b(Al_2O_3) = -2.53 \qquad b(CaF_2) = -0.76$$
$$b(MgF_2) = -1.07$$

It was found that the experimental conductivity data obtained for mixtures containing MgF_2 and/or CaF_2 were less precise than the data obtained for the system Na_3AlF_6–Li_3AlF_6–AlF_3. The standard deviation of these data was 0.04 S cm^{-1}. The same behaviour was observed in the investigation of the binary mixtures [6]. This may be caused by gas bubbles being trapped in the tube due to poorer wetting of the boron nitride tube or by the influence of the additives on the electrode reactions taking place at the electrodes. Because of a higher standard deviation for these measurements it cannot be decided whether the deviations from the additivity rule were caused by the uncertainty in the experimental conductivity data or by ternary interactions.

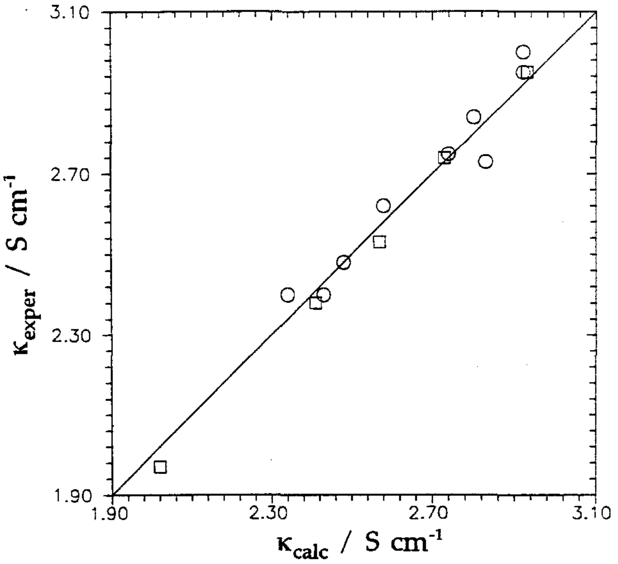

Fig. 2. The experimental conductivity data plotted against Equation 2. (□) Conductivites of the system Na_3AlF_6–Li_3AlF_6–AlF_3 at the lowest temperature from the investigated temperature range (see Fig. 1), (○) the system with additions of MgF_2 and CaF_2, and Al_2O_3 (see Table 1).

Oblakowski [10] published electrical conductivities for five cryolite based melts having constant excess of 9.1 mass % AlF_3 and additions of Al_2O_3(2 and 4 mass %), CaF_2(4 and 6 mass %), MgF_2(2 and 4 mass %), and LiF (2 mass %). These data are lower by 0.1 S cm^{-1} in comparison with Equation 2. As this deviation is constant one may assume that it may be caused by a systematic error, probably by impurities in the chemicals used (technically pure) and/or by using a conductivity cell made of hot pressed boron-nitride which is not sufficiently stable in cryolitic melts.

Recently Wang *et al.* [11] reported an extensive set of conductivity data for multicomponent molten cryolitic systems. In most cases there is a good agreement between the data by Wang *et al.* [11] and the conductivities predicted by Equation 2. Unfortunately, most of the data are given as plots in figures where the temperatures are defined to be at 30° C superheat, i.e. 30° C above the liquidus temperature. This makes a direct comparison with Equation 2 rather difficult. It seems, however, that there are some differences concerning the influences of MgF_2 and of temperature on the electrical conductivity. This may be explained partly by the neglect of nonlinear terms in Equation 2 and partly by uncertainty in the experimental data. To give a definite answer to this question, further experimental data of the electrical conductivity of ternary and quaternary mixtures are needed.

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