**Low-Temperarue Electrolytes for Aluminium Technology.**

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**Highlights**

* Aluminium smelter technology
* High-acidic sodium and potassium cryolite melts
* Electrical conductivity
* Tube type cell, electrochemical impedance spectroscopy

**1. Introduction**

The innovation of aluminium production technology is focused on using the inert electrode materials and low temperature electrolytes. The most significant benefits are energetic, environmental, and economic aspects. The consumable carbon anodes will be replaced by inert, oxygen evolving anodes. Low-melting electrolytes (working temperature 660 °C – 900 °C) are essential due to the oxidation rate of inert electrode materials. The corrosion rate decreases strongly with decreasing temperature. Cryolite-based melts are still the best choice as electrolytes for electrolytic aluminium production, because of its unique capacities as a solvent for electrochemically active compound (alumina). The possibilities for the decreasing of TPC in cryolite-based melts are three: electrolytes based on sodium cryolite with the high excess of AlF3 (up to 45 mol %), electrolytes based on potassium cryolite, mixture electrolytes with various ratios of sodium and potassium cryolite.

The high addition of AlF3 into the sodium cryolite systems reduces markedly TPC (up to 700 °C) but also decreases the alumina solubility. The potassium system is more low melting than the sodium system (temperature less than 660 °C). The interest in potassium cryolite melts causes the fact that alumina solubility is higher than in the sodium system at the same conditions. Other properties are less favorable, for instance, the electrical conductivity is considerably lower in the potassium system. The essential physicochemical properties of these low temperature electrolytes, such as solubility of Al2O3, density, vapor pressure, viscosity or electrical conductivity were investigated only in less extent. The electrical conductivity is of great importance in the energetic aspects and it also helps with the characterisation of the melts structure. The interest in low temperature electrolytes is growing with the development of inert electrode materials.

**2. Methods**

Electrochemical impedance spectroscopy is a suitable measurement method for the investigation of electrical conductivity of new types of aluminium electrolytes. Electrical conductivity was measured using a tube-type cell with stationary electrodes applying AC-techniques with a sine wave signal in the high frequency range up to 100 kHz. Electrolytes used in this study contained high content of aluminium fluoride, up to 45 mol %. Basic binary NaF-AlF3 melt was studied at different molar ratios MR = (2.0-1.2) in the temperature range from the temperature of primary crystallization to 100 °C overheat. Basic melts KF-AlF3 and NaF-KF-AlF3 were studied at molar cryolite ratios MR = (1.5-1.2) in the temperature range defined in the same way as for previous system. The influence of the additions of Al2O3, CaF2, MgF2 and/or LiF was also investigated.

**3. Results and discussion**

The electrical conductivity of the NaF AlF3 system as a function of a temperature and composition.



**Figure 1.** The electrical conductivity of the NaF AlF3 system as a function of a temperature for compositions: ■ MR = 2.0; ● MR = 1.8; ▲ MR = 1.6; ▼ MR = 1.4; ♦ MR = 1.2. Symbols represent the experimental data; full lines non-linear regression analysis data.

**4. Conclusions**

Concentration and temperature dependences of the electrical conductivity for all the studied low-temperature multi-component systems were described by the regression equation. The mutual effect of various combinations of additives on electrical conductivity was similar than the sum of individual allowances. The decrease of electrical conductivity in multicomponent systems for melts with the lowest MR = 1.2 was up to about 13 % when compared to the binary melts. Although LiF improves the value of electrical conductivity, the addition of about 1 wt % of LiF increased the electrical conductivity only by about 1.88 % on average. Temperature and concentration dependencies of the electrical conductivity in studied multicomponent systems were described by regression equations. The summary equation precisely describes the temperature and concentration dependence of electrical conductivity in the whole studied area and can be used for practical purposes.

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**References**

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