Piotr Palimąka, Stanisław Pietrzyk

The electronic component of solid fluoride electrolytes

Składowa elektronowa stałych elektrolitów fluorkowych

Abstract

Solid electrolytes based on sodium cryolite are present in aluminium electrolysers as frozen crystals formed on the side walls of the carbon lining (side ledge). Their main task is to protect the lining from the effect of liquid electrolyte and ensure temperature stabilization during the process of electrolysis. On the other hand, being electrically conductive, they can reduce current efficiency. In this study, the value of the electronic component of the total conductivity of the solidified electrolytes of different compositions was determined. It was found that the highest electronic conductivity is exhibited by electrolytes containing both aluminium and calcium fluoride. However, the electronic component of the total conductivity is not high, as it only reaches 0.1–2.3 mS/cm. Its share in the total conductivity of the solid multi-component electrolytes varies and, depending on their composition, is within a range of 1–10%.

Keywords: aluminium electrolysis, electronic conductivity, electrical conductivity

Streszczenie

Stałe elektrolity na bazie kriolitu sodowego są obecne w elektrolizerach do produkcji aluminium jako wykrystalizowane na bocznych ścianach wyłożeniach węglowego garnisaże. Ich głównym zadaniem jest ochrona węglowego wyłożenia przed działaniem ciekłego elektrolitu i stabilizacja temperatury procesu elektrolizy. Z drugiej strony mogą być przyczyną spadku wydajności prądowej, gdyż przewodzą prąd elektryczny. W pracy wyznaczono wielkość składowej elektronowej całkowitego przewodnictwa zakrzepłych elektrolitów o różnym składzie. Stwierdzono, że najwyższe przewodnictwo elektronowe wykazują elektrolity zawierające jednocześnie fluorek glinu i wapnia. Składowa elektronowa całkowitego przewodnictwa nie jest jednak wysoka i osiąga wartości rzędu 0,1–2,3 mS/cm. Jej udział w całkowitym przewodnictwie stałych elektrolitów wieloskładnikowych waha się, w zależności od ich składów, od 1 do 10%.

Słowa kluczowe: elektroliza aluminium, przewodnictwo elektronowe, przewodnictwo elektryczne

Piotr Palimąka Ph.D. Eng., **Stanisław Pietrzyk Prof. Ph.D. Eng.:** AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Krakow, Poland; palimaka@agh.edu.pl

1. Introduction

During aluminium electrolysis, a layer of the solidified electrolyte called the side ledge is formed on the side linings of the cell. Its composition depends directly on the composition of the liquid electrolyte. This layer plays an important role during the manufacturing process, protecting the cathode lining from the corrosive effect of the electrolyte and stabilizing the operating temperature of the cell. On the other hand, it may cause current leakages from the anode to the carbon side lining, with a resulting reduction in current efficiency in the process.

The measurements of electrical conductivity carried out in [1, 2] have shown that, depending on the composition and temperature, the solidifying electrolyte can have a high electrical conductivity, especially in a temperature range involving the coexistence of liquid and solid phases. However, according to [3], the current flow through that part of the side ledge will not cause current losses since it will be "locked" back in the electrolyte. In contrast, the completely solidified electrolyte layer directly adjacent to the carbon side linings can remove a portion of the total current of the electrolysis and, thus, contribute to the reduction of current efficiency.

The opinion expressed by many authors that the side ledge can conduct electric current [4–6] has its justification in practice, since, a reduction of Na^+ ions takes place in the carbon side lining [7]. As a result of this effect, sodium forms with carbon intercalation compounds of the NaC_x type, the formation of which is accompanied by changes in the molar volume [8]. This, in turn, leads to mechanical damage of the carbon lining (delamination, flaking, and chipping pieces of the lining). In [9], Dewing states that solid cryolite (which is an essential component of the side ledge) may have significant electronic conductivity. Both the ionic and electronic nature of current conduction by the side ledge can cause a loss of current and reduce current efficiency in the process. Therefore, the aim of this study was to determine the electronic conductivity component of those solid electrolytes that showed high electrical conductivity in the previous studies of the author [1, 2].

2. Experimental

For the measurement of the electronic conductivity component, one can use an arrangement in which the sample of the tested electrolyte is disposed between two electrodes locking the ions movement. Recent studies, however, have shown that, for the determination of the electronic conductivity, it is better to use an unbalanced system wherein one of the electrodes is reversible with respect to the ions (particularly when its share in the total conductivity is small). This method of measurement was proposed by C. Wagner [10] and is called the Wagner asymmetric polarization technique. A Bi-Na (0.1) alloy was used since the most active ions were those of Na^+ (as a reversible electrode) in the tested

cryolite-based electrolytes. An electrode of this type allows the flow of electrons in the system due to the metallic nature of current conduction through bismuth. Molybdenum was the second electrode, and its task was to prevent the flow of Na$^+$ ions. Measurements using this method were taken in the following manner:

$$(-) \text{ Na-Bi } | \text{ solid electrolyte } | \text{ Mo } (+)$$
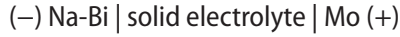
Upon application of the appropriate voltage lower than the decomposition voltage of the examined material, there is no electrolysis, and the ion current flows only in the initial moment. This current decreases to zero as the area near the blocking electrode is emptied of Na$^+$ ions (the blocking electrode is not a source of Na$^+$). In a polarized state, only the electronic current (and/or hole current) can flow. Wagner gives an equation that expresses the intensity of this current [10]:

$$I = I_e + I_h = \frac{RTS}{LF}\left\{ \kappa_e(0)\left[1 - \exp\left(\frac{-UF}{RT} \right) \right] + \kappa_h(0)\left[\exp\left(\frac{UF}{RT} \right) - 1 \right] \right\} \qquad (1)$$

where:
  I_e, I_h – electronic and hole current,
  S, L – cross-section and length of the sample,
  R, F – gas constant and Faraday constant,
    U – voltage,
    T – temperature,
  $\kappa_e(0), \kappa_h(0)$ – electronic and hole conductivity.

The Wagner equation can be written down in a rectifying system as:

$$\frac{ILF}{RTS}\left\{ \frac{1}{\exp\left(\dfrac{UF}{RT} \right) - 1} \right\} = \kappa_e(0)\exp\left(-\frac{UF}{RT} \right) + \kappa_h(0) \qquad (2)$$

Plotting the left side of equation (2) as a function $\exp\left(\dfrac{-UF}{RT} \right)$ enables the determination of $\kappa_e(0)$ from the slope of the curve and $\kappa_h(0)$ from the intersection of the graph with the axis of ordinates.

Electronic conductivity was measured with the apparatus and the vessel used for the measurement of total electrical conductivity described in [1], except that the bottom of the capillary made of boron nitride was plated with a Bi-Na alloy (which acted as a reversible electrode with respect to the sodium ions). The electrolytes were prepared for tests by mixing them in suitable proportions and placing them in the measurement vessel. For the studies, it was decided to choose pure cryolite and electrolytes that exhibited

the highest total conductivity in the solid state in [1, 2] within a temperature range of the occurrence of a high-temperature variety of β-Na$_3$AlF$_6$. For the multi-component systems, these are the electrolytes containing 4wt% of CaF$_2$ as well as the electrolyte containing 8wt% AlF$_3$ + 4wt% CaF$_2$. Additionally, using the technique described in [1], total conductivity κ was measured for the electrolytes: 94wt% Na$_3$AlF$_6$ + 4wt% CaF$_2$ and 80wt% Na$_3$AlF$_6$ + 8wt% AlF$_3$ + 4wt% Al$_2$O$_3$ + 4wt% CaF$_2$ + 4wt% MgF$_2$. For these systems, electronic conductivity was also measured.

After the application of a constant polarizing voltage of 0.1–1 V, the current flowing through the sample was recorded; this operation continued until full stabilization was reached. The time of current stabilization varied, amounting to approx. 35 minutes.

3. Test results

Figure 1 shows a sample polarization curve plotted for pure cryolite at a temperature of 1073 K.
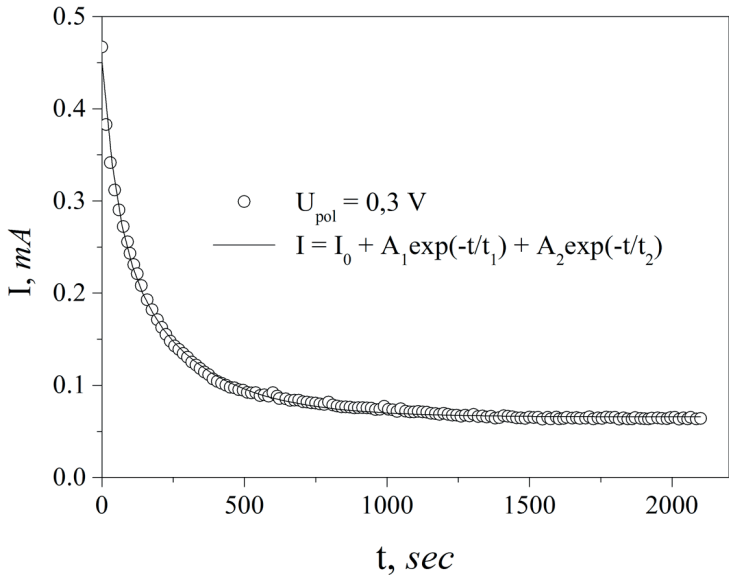

Fig. 1. The polarization curve plotted for cryolite at a temperature of 1073 K and a voltage of 0.3 V

As shown in Figure 1, the final values of the current flowing in the system after a period of about 30 minutes take the form of a plateau and correspond to residual non-ionic current I_0. The values of I_0 were determined from the fitted to experimental data, second

degree exponential functions (R^2 for all > 0.98). The general form of this function is indicated in the drawing. Thus, the obtained values of I_0 were used for further calculations of the electronic component. An example of the determination of this component is shown in Figure 2.
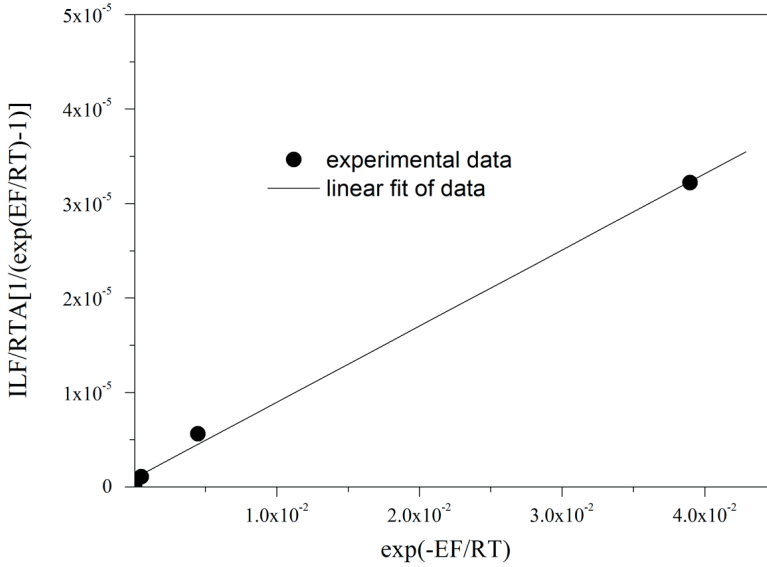

Fig. 2. Example of the determination of the electronic component for cryolite at a temperature of 1073 K

For pure cryolite, the obtained value of electronic component κ_e at a temperature of 1073 K was $8.062 \cdot 10^{-4}$ S·cm^{-1}. In turn, the value of the ordinate of the linear equation shown in Figure 2 (corresponding to the hole conductivity) was a thousand times lower than the electronic component (and, therefore, negligible). The same calculations were performed for all of the tested electrolytes in a solid state. Similar to the case of cryolite, the component of hole conductivity was assuming the values by three orders lower than the electronic component. Table 1 summarizes, the values obtained in [1] and [2] of total conductivity (κ), electronic component (κ_e), ionic component (κ_j) calculated from equation (3), and the percent share of κ_e in κ ($U_{\kappa e}$ calculated from equation (4).

$$\kappa_j = \kappa - \kappa_e, \text{ S·cm}^{-1} \tag{3}$$

$$U_{\kappa e} = \frac{\kappa_e}{\kappa} \cdot 100 , \% \tag{4}$$

151

Table 1. Summary of the obtained results of the total, electronic, and ionic conductivity of the tested solid electrolytes

Electrolyte	T [K]	$\kappa \cdot 10^{-3}$ [S·cm^{-1}]	$\kappa_e \cdot 10^{-3}$ [S·cm^{-1}]	$\kappa_j \cdot 10^{-3}$ [S·cm^{-1}]	$U_{\kappa e}$ [%]
Na$_3$AlF$_6$	773	1.07 [1]	0.25	0.83	22.9
	873	5.30 [1]	0.24	5.06	4.6
	973	11.10 [1]	0.38	10.72	3.4
	1073	23.00 [1]	0.81	22.19	3.5
Na$_3$AlF$_6$ + 4 wt% CaF$_2$	773	2.54 [2]	0.26	2.28	10.3
	873	13.90 [2]	0.30	13.61	2.1
	973	25.10 [2]	0.52	24.58	2.1
	1073	46.10 [2]	1.16	44.94	2.5
Na$_3$AlF$_6$ + 6 wt% MgF$_2$	773	2.73	0.27	2.46	10.0
	873	24.70	0.31	24.39	1.3
	973	41.00	0.47	40.53	1.1
	1073	63.60	1.08	62.52	1.7
Na$_3$AlF$_6$ + 8 wt% AlF$_3$ + 4 wt% CaF$_2$	773	27.70 [2]	1.30	26.40	4.7
	823	43.80 [2]	1.51	42.29	3.4
	873	57.70 [2]	1.84	55.86	3.2
	923	89.80 [2]	2.30	87.50	2.6
Na$_3$AlF$_6$ + 8 wt% AlF$_3$ + 4 wt% Al$_2$O$_3$ + 4 wt% CaF$_2$ + 4 wt% MgF$_2$	773	10.31	0.99	9.32	9.6
	823	23.21	1.15	22.06	4.9
	873	33.45	1.37	32.08	4,1
	923	50.25	1.7	48.55	3,4

The values of the electronic component obtained for the tested electrolytes and their comparison with the values obtained previously for total conductivity are shown in Figures 3–5.
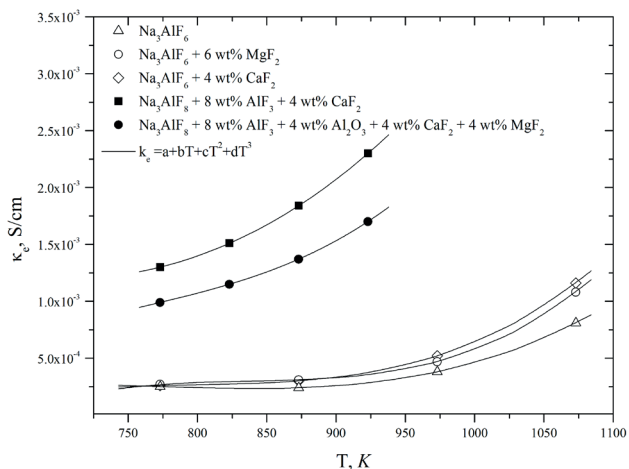

Fig. 3. Temperature dependence of the electronic conductivity component in solid electrolytes
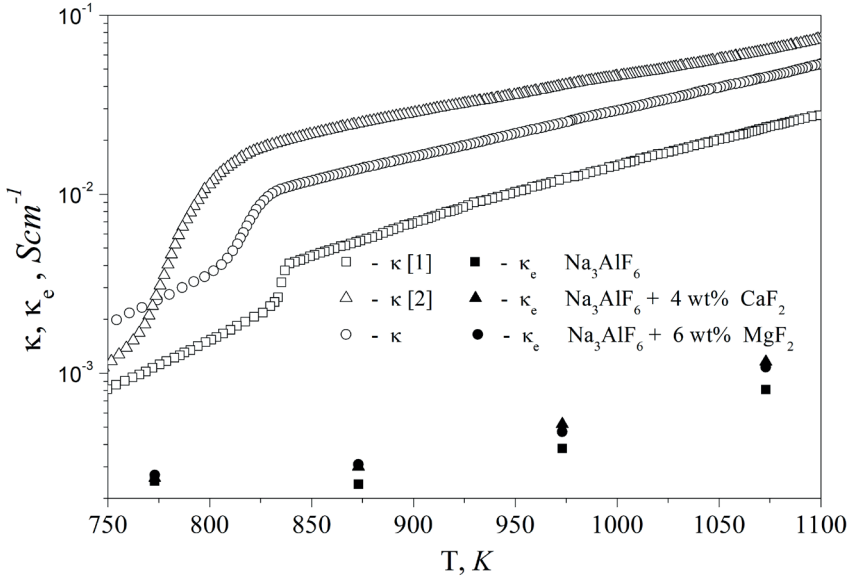
Fig. 4. The electronic conductivity component of cryolite and two-component electrolytes in a solid state plotted against total conductivity
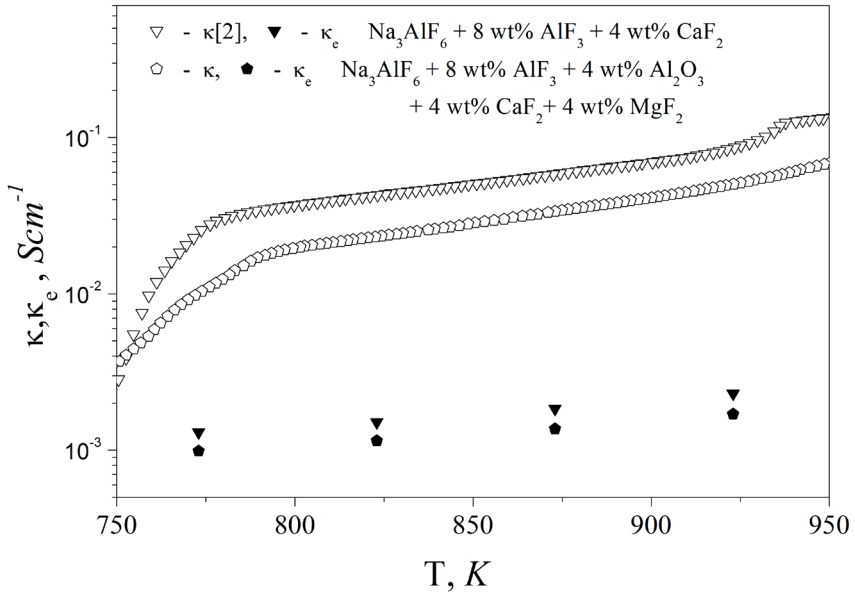

Fig. 5. The electronic conductivity component of multi-component electrolytes plotted against total conductivity

The temperature dependence of the electronic conductivity component obtained in this study can be described as a polynomial of the third degree, assuming the general form of $\kappa_e = a + bT + cT^2$. The parameters of equations derived for the tested electrolytes are summarized in Table 2.

Table 2. Parameters of equation $\kappa_e = a + bT + cT^2$ describing the dependence of electronic conductivity on temperature

Electrolyte	Temperature [K]	$\kappa_e = a + bT + cT^2$		
		a	b	c
Na_3AlF_6		0,00797	−1,848E-5	1,1E-8
$Na_3AlF_6 + 4$ wt% CaF_2	773–1073	0,01010	−2,371E-5	1,4E-8
$Na_3AlF_6 + 6$ wt% MgF_2		0,01046	−2,477E-5	1,5E-8
$Na_3AlF_6 + 8$ wt% $AlF_3 + 4$ wt% CaF_2	773–923	0,01399	−3,574E-5	2,5E-8
$Na_3AlF_6 + 8$ wt% $AlF_3 + 4$ wt% $Al_2O_3 + + 4$ wt% $CaF_2 + 4$ wt% MgF_2		0,00949	−2,413E-5	1,7E-8

The results of our measurements show that the electronic component of the tested solid electrolytes assumes the lowest values for pure cryolite and two-component systems of Na_3AlF_6-CaF_2 and Na_3AlF_6-MgF_2. Much higher electronic conductivity was observed after the introduction of aluminium fluoride to the electrolyte. Analyzing the results obtained for total conductivity in earlier works of the author [1, 2], it has been found that the differences in the total conductivity of electrolytes are not consistent with the same differences in the electronic conductivity. Hence, one can conclude that the observed changes in total conductivity accomplished through the introduction of foreign metal ions to the crystal lattice of cryolite are mainly due to a change in the ionic conductivity component.

The largest share of the electronic component in total conductivity had pure cryolite ($U_{\kappa e} = 23\%$) at 773 K. At higher temperatures, this share decreased quite significantly. The same decreasing trend was observed in all of the tested electrolytes. The highest values of electronic conductivity were obtained for the three-component electrolyte, which also had the highest total conductivity. However, the share of κ_e in κ was small, and with values of 2.6–4.7% it changed as a function of temperature. The obtained results have indicated the absence of electronic conductivity depending on the phase variety of cryolite. This means that the observed rapid changes in the value of the total conductivity near the α → β phase transition temperature of cryolite (838 K) were related to

the reconstruction of the crystal structure of cryolite and changes in the ionic and not electronic conductivity.

The values of κ and κ_e measured for the tested electrolytes clearly indicate that the observed increase in the total conductivity of electrolytes in a solid state under the influence of the metal ions of Ca^{2+} and Mg^{2+} introduced to the crystal lattice of cryolite was mainly due to an increase in the ionic component. Modification of the cryolite structure with those metals first of all leads to an increase in the concentration of ionic defects, and this accounts for the observed increase in total conductivity. The low value of the electronic component may be due to intrinsic electronic conduction; i.e., the presence of thermally-generated electronic defects.

4. Conclusions

1. The electronic conductivity determined in this study assumes the lowest values for pure cryolite ($0.25 \cdot 10^{-3}$ S·cm^{-1} at 773 K) and shows little dependence on temperature or the presence of MgF_2 and CaF_2 within the examined range of temperatures.
2. Similar to the total conductivity, the greatest influence on the electronic conduction has the additions of AlF_3 and CaF_2. The electronic component of an electrolyte containing these additives increases to $1.51 \cdot 10^{-3}$ S·cm^{-1} at 773 K and to $2.3 \cdot 10^{-3}$ S·cm^{-1} at 932 K.
3. The increased total conductivity of the solid electrolyte in both the two- and multi-component systems is mainly due to an increase in the ionic component.
4. The trend in aluminium metallurgy to enrich liquid electrolytes with AlF_3 and CaF_2 in order to lower the temperature of electrolysis and increase current efficiency can have negative consequences for the process of electrolysis, mainly due to higher current leakages through the layer of the side ledge.

References

[1] Palimąka P., Pietrzyk S.: Research on the Electrical Conductivity of Fluoride Electrolytes NaF-AlF3 in Liquid and Solid State. Archives of Metallurgy and Materials, 55, 2 (2010), 533–538
[2] Palimąka P., Pietrzyk S.: Research on the Electrical Conductivity of Fluoride Electrolytes NaF-AlF3-CaF2 in Liquid and Solid State. Archives of Metallurgy and Materials, 59, 1 (2014), 71–75
[3] Grjotheim K., Krohn C., Malinovský M., Matiašovský K., Thonstad J.: Aluminium Electrolysis. The Chemistry of the Hall- Hérolut Process. Aluminium Verlag, Düsseldorf 1977
[4] Obłąkowski R., Pietrzyk S., Thonstad J., Haarberg G.M.: The electrical conductivity of cryolite electrolytes during the liquid-solid phase transition. 1st Conference on Ionic Liquids and Solid Electrolytes, Szklarska Poręba 1997
[5] Pietrzyk S., Obłąkowski R.: Electrical conductivity of cryolite electrolytes during the liquid-solid phase transition. TMS-AIME, (2002), 1083–1089
[6] Wei C.C., Chen J.J., Welch B.J.: Modeling of Dynamic Ledge Heat Transfer. Light Metals: Proceedings of Sessions. TMS Annual Meeting, Warrendale, PA, 1997, 309–316

[7] Haupin W.: The influence of additives on Hall-Héroult bath properties. Journal of the Minerals, Metals and Materials Society, 43, 11 (1991), 28–34

[8] Grjotheim K., Krohn C., Malinovský M., Matiašovský K., Thonstad J.: Aluminium Electrolysis. Fundamentals of the Hall-Hérolut Process. 2nd Edition, Aluminium Verlag, Düsseldorf 1982

[9] Dewing E.W.: Thermodynamics of the system NaF-AlF$_3$: Activities in liquid mixtures, Metallurgical Transactions 3, (1972), 495–501

[10] Wagner C.: International Committee of Electrochemical Thermodynamics and Kinetics, Butterworth Scientific Publication 7, 1956