Mechanism and Kinetics of the Anodic Reaction in Cryolite Melts. II. The Influence of AlF3 (11 wt%) at Different Al2O3 Content

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Aluminium trifluoride is the main additive to the cryolite-based electrolyte in aluminium electrolysis. By Electrochemical Impedance Spectroscopy (EIS) the influence of AlF3 upon the kinetics and mechanism of the anodic reaction in 4 cryolite–alumina melts containing 2, 4, 6 and 8 wt% of alumina and 11 wt% of AlF3 was determined at 1000°C. The addition of 11 wt% of AlF3 to a cryolite melt with a certain alumina content increases the overpotential of the anodic reaction as compared to cryolite-alumina saturated (CRAS) melt. The Tafel slope increases from around 0.12 V/dec. to 0.24 V/dec., which indicates that at low alumina content the second charge transfer step is the rds, whereas at higher alumina content this control is shifted towards the first step. The effective rate constants of both charge transfer steps are increasing with the alumina content. It can be concluded that the influence of the added AlF3 is directly related to the participation of this reagent in the first charge transfer step, in which it is a product. The diffusion coefficient of the Al2OF62– anionic species decreases as a function of the alumina content, due to the increase of the viscosity of the melts studied.

Key words: aluminium electrolysis, electrode kinetics, cryolite melts, alumina, aluminium trifluoride, electrochemical impedance spectroscopy

The molten cryolite-based electrolyte used in aluminium electrolysis contains in addition to alumina also ~5 wt% of CaF2 and ~11 wt% AlF3. In contrast to CaF2, which gets into the electrolyte as an alumina impurity, AlF3 is added to the molten electrolyte purposely to decrease its melting point and the electronic conductivity. In the first part of this paper [1] the effect of 5 wt% CaF2 on the anodic reaction with variable alumina content was evaluated. Although AlF3 is the largest additive to the cryolite melt, its influence upon the mechanism and kinetics of the electrode reactions in aluminium electrolysis is still not fully understood.

It has been found in our previous studies [2–6], that the overall mechanism of the anodic reaction in these melts can be represented by three steps:

$$\text{Al}_2\text{OF}_6^4- \rightleftharpoons k_1 \rightarrow k_2 \text{Al}_2\text{OF}_6^{2-} + 2\text{F}^-,$$  \hspace{1cm} (1)
charge transfer step with an intermediate adsorption,

$$\begin{align*}
\text{AlF}_3^{2-} + C & \overset{k_{\text{f}}}{\underset{k_{-1}}{\rightleftharpoons}} 2\text{Al}_2\text{F}_3 + C_{\text{ads}} + 2e^- \\
\text{electrochemical desorption,} & \\
\text{Al}_2\text{O}_2\text{F}_4^{2-} + C_{\text{ads}} & \overset{k_{\text{f}}}{\underset{k_{-2}}{\rightleftharpoons}} \text{CO}_2 + 2\text{Al}_2\text{OF}_4 + 2e^-
\end{align*}$$

In the above reactions, AlF$_3$ and Al$_2$OF$_4$ can be treated as intermediates, which react immediately with fluoride anions to regenerate AlF$_4^{-}$ and Al$_2$OF$_6^{2-}$ anionic species respectively. In this paper, the effect of 11 wt% of AlF$_3$ in molten cryolite melts with 2, 4, 6 and 8 wt% of alumina upon the kinetics of the anodic reaction was studied. As a method of measurements the electrochemical impedance spectroscopy (EIS) was used.

**EXPERIMENTAL**

**Apparatus.** The apparatus used was the same as that described in [1].

**Procedure.** The impedance spectra were recorded by a Solartron 1260 Frequency Response Analyzer with a Solartron 1286 Interface; the measurements were controlled by a PC through a GPIB – connection using original Solartron measuring software. All electrical connections to the Solartron instrument were made by special shielded Solartron leads. The impedance spectra were recorded at several overpotentials at 1000°C for cryolite melts containing 11 wt% of AlF$_3$ and 2, 4, 6 and 8 wt% of alumina respectively. Each spectrum for a given alumina content was recorded twice (in two separate experiments) at 200 different frequencies between 10 Hz and 100 kHz. Compared to the cryolite-alumina melts with CaF$_2$, the impedance spectra of the anodic reaction recorded in cryolite melts with AlF$_3$ were not so much scattered.

**RESULTS AND DISCUSSION**

**Tafel constants.** Fig. 1 presents as a Bode plot a typical impedance spectrum of the graphite anode in the cryolite melt containing 11 wt% of AlF$_3$ and 6 wt% of alumina in the medium overpotential range (0.2 < $\eta$ < 0.4 V). A pronounced influence of the two charge transfers with an intermediate adsorption is clearly seen. The impedance spectra were interpreted in terms of the equivalent circuit approach [7], as well as by the kinetic theory of Bai and Conway [8].

![Figure 1](image-url)
In the equivalent circuit approach, the equivalent circuit developed earlier [7] was used for the evaluation of the outer inductance and electrolyte resistance [10], and as seen in Fig. 1, the fit is extremely good. The electrolyte resistance together with the current reading from the Solartron 1286 display were used for the evaluation of the coefficients \( a \) and \( b \) of the Tafel equation:

\[
\eta = a + b \log j
\]

(4)

where \( \eta \) is the overpotential defined by:

\[
\eta = E - E_{rev} - IR_{el}
\]

(5)

\( E \) is the potential set by the potentiostat, \( E_{rev} \) is the reversible potential, \( I \) is the current and \( j \) (Acm\(^{-2}\)) the current density. The values of reversible potentials were calculated from the alumina activity in cryolite melts data given by Dewing and Thonstad [9]. Typical Tafel graph for the melt with 2 wt% of alumina is presented in Fig. 2.

![Figure 2. Tafel line for 2 wt% of alumina.](image)

The average values of the coefficients \( a \) and \( b \) of the Tafel equation for a given alumina content (all with 11 wt% of AlF\(_3\)) are presented in Table 1.

<table>
<thead>
<tr>
<th>Alumina content (wt %)</th>
<th>( a ) (V)</th>
<th>( b ) (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.604</td>
<td>0.120</td>
</tr>
<tr>
<td>4</td>
<td>0.647</td>
<td>0.174</td>
</tr>
<tr>
<td>6</td>
<td>0.710</td>
<td>0.197</td>
</tr>
<tr>
<td>8</td>
<td>0.734</td>
<td>0.237</td>
</tr>
</tbody>
</table>

It is seen in Table 1 that the values of \( a \) are increasing with the alumina content. Such an increase of the overpotential should be rather expected as AlF\(_3\) is a product of the first charge transfer step (reaction 2). The added AlF\(_3\) can also influence the reversible potential of the aluminium reference electrode, which is reversible against AlF\(_4^-\) anions [6]. As a result of the alumina dissolution reactions:

\[
\text{Al}_2\text{O}_3 + 4\text{AlF}^- + 2\text{F}^- \Leftrightarrow 3\text{Al}_2\text{OF}_{6}^{2-} \quad (6) \quad \text{Al}_2\text{O}_3 + \text{AlF}_4^- + 2\text{F}^- \Leftrightarrow 3/2\text{Al}_2\text{O}_2\text{F}_4^{2-} \quad (7)
\]

the concentration of the AlF\(_4^-\) anions decreases with the increase of the alumina content and this in turn decreases the reference electrode potential. However, in the pres-
The reference electrode was saturated with alumina and its potential should be thus independent of the alumina content in the melt studied. We can therefore conclude, that the addition of AlF₃ decreases the rate of the anodic reaction as compared to the influence of CaF₂ [1] at a similar alumina content and increases the overpotential.

The Tafel slope \( b \), however, is not dependent upon the reference electrode potential and as seen in Table 1 its value is increasing with the alumina content. Though its value does not reach the limiting value of 0.252 V/dec for the first step to be the rds, it increases towards this value. Increasing the alumina content shifts the equilibrium between the two main oxyfluoroaluminate complexes \( \text{Al}_2\text{OF}_6^{2-} \) and \( \text{Al}_2\text{O}_2\text{F}_4^{2-} \):

\[
2\text{Al}_2\text{OF}_6^{2-} \rightleftharpoons \text{Al}_2\text{O}_2\text{F}_4^{2-} + 2\text{AlF}_4^{-} \tag{8}
\]

to the right, towards the \( \text{Al}_2\text{O}_2\text{F}_4^{2-} \) anion, which is the reactant of the second charge transfer step (reaction 3). The relative increase of the rate of the second charge transfer step must be reflected by the increase of the Tafel slope \( b \). Such increase is clearly seen in Table 1. The conclusions from the Tafel analysis should be confirmed by the kinetic approach to the analysis of the impedance spectra in terms of the theory of Bai and Conway [8], which allows the evaluation of the so-called effective rate constants of the two charge transfer steps.

**Effective rate constants.** The use of this theory [8] has already been presented in our earlier papers [5,6]. The simulated impedance spectra were fitted by our special FORTRAN program to give the values of the Tafel slopes \( b_1 \) and \( b_2 \), the effective rate constants \( k_{1e}^{\text{eff}}, k_{2e}^{\text{eff}}, k_{1e}^{\text{eff}}, k_{2e}^{\text{eff}} \), the charge \( q \) needed for full coverage of the electrode by a monolayer, the double layer capacitance \( C_{dl} \) and the electrode coverage \( \theta \) at a given constant overpotential \( \eta \) [1]. The values of the effective rate constants \( k_{1e}^{\text{eff}} \) and \( k_{2e}^{\text{eff}} \) are then plotted as a function of overpotential and the values \( k_{1e}^{\text{eff}} \) and \( k_{2e}^{\text{eff}} \) extrapolated to zero overpotential were evaluated by LSFit. These effective rate constants are effective in the sense that they contain the respective concentration terms. The values of \( k_{1e}^{\text{eff}} \) and \( k_{2e}^{\text{eff}} \) for different alumina content are plotted in Figs. 3 and 4.

![Figure 3. The dependence of the effective rate constant of the first charge transfer step on alumina content.](image-url)
In agreement with the Tafel analysis, the effective rate constants in Figs. 3 and 4 for melts with AlF₃ are smaller, almost by one order of magnitude, than the corresponding values for the melts with CaF₂ [1]. Contrary to CaF₂, the added AlF₃ can directly influence the rate of the first charge transfer step in our mechanism, in which AlF₃ is the product. The decrease of the rate of the first charge transfer step automatically drops down also the rate of the second charge transfer step through the decrease of the electrode coverage, which plays an important role for the second charge transfer step. As expected, both effective rate constants increase with alumina content as they contain the respective concentration terms. \( k_{1e}^{0} \) contains the concentration of \( \text{Al}_2\text{OF}_6^{2-} \) and \( k_{2e}^{0} \) the concentration of \( \text{Al}_2\text{O}_2\text{F}_4^{2-} \).

**The Warburg diffusion impedance.** The fit of the experimentally recorded impedance spectra, using the equivalent circuit developed earlier [7] with added Warburg element [1] by the Boucamp [10] program, yields also the Warburg admittance \( W \), which is the reciprocal of the Warburg diffusion impedance \( Z_d \):

\[
Z_d = \frac{RT}{n^2F^2A} \left( \frac{1}{c_x \sqrt{D_x}} + \frac{1}{c_o \sqrt{D_o}} \right)
\]  

Eq. (9) can be only approximate as we hardly know the concentration of the reactant (\( \text{Al}_2\text{OF}_6^{2-} \)) and we have no information about the concentration of AlF₃, which is the product of the first step and undergoes adsorption on the graphite anode. At first we shall adopt the common practice and put \( c_o = c_R \). (9) will thus take the form:

\[
Z_d = \frac{RT}{n^2F^2A} \left( \frac{2}{c \sqrt{D}} \right)
\]  

where \( c \) and \( D \) refer to alumina. Due to vigorous evolution of gaseous CO₂ in the high overpotential range, where the Warburg diffusion impedance is seen, one can expect an additional convectional contribution to the diffusion transport. The diffusion impedance, as evaluated by the Boucamp program [10], is presented in Fig. 5 for different alumina contents.
As seen in Fig. 5, the diffusion impedance, as expected, decreases with the increase of the concentration of alumina. Converting the wt% into \( c \) (mole/cm\(^3\)) of alumina allows for making a graph in which, according to (10), the diffusion impedance can be plotted against \( 1/c \) (Fig. 6).

The least squares straight line for the melts with 11 wt% of AlF\(_3\) crosses the \( Z_d \) axis much closer to zero as compared to the cryolite-alumina melt containing 5 wt% of CaF\(_2\) [1], which shows, that the contribution of the convectional transport, although present, is here much less pronounced. The slope of this straight line can be used for an approximate evaluation of the apparent diffusion coefficient of alumina according to (10). The so obtained apparent alumina diffusion coefficient \( D \) is \( 2.0 \times 10^{-6} \) cm\(^2\) s\(^{-1}\), which is much smaller than \( D = 1.67 \times 10^{-5} \) cm\(^2\) s\(^{-1}\), obtained by a similar procedure in melts with 5 wt% of CaF\(_2\) [1]. In view of [11], this value of the apparent diffusion coefficient of alumina is definitely not correct. It follows that in the melt containing 11 wt% of AlF\(_3\) and variable content of alumina the assumption made in (10) \( (c_0 = c_R) \) is not valid and we have a different situation as that which exists in the previously studied melt with 5 wt% of CaF\(_2\) [1]. The diffusion coefficient can, thus, be only evaluated by the analysis of the impedance spectra in terms of the preceding chemical step, which allows the splitting of the total recorded Warburg diffusion impedance into two parts, related to the Warburg coefficients of the reduced (\( \sigma_R \)) and oxidised (\( \sigma_O \)) species. The theory of impedance of a charge transfer process preceded by a chemical reaction was presented in [1] and it can be found elsewhere [12].
The preceding chemical step. The preceding chemical step in the electrode process studied is represented by (1), which was studied by several authors [11,13,14]. The impedance equilibrium constant \( K \) of the reaction (1) is simply the ratio of the concentration of \( \text{Al}_2\text{OF}_6^{2-} \) and \( \text{Al}_2\text{OF}_8^{4-} \):

\[
K = \frac{[\text{Al}_2\text{OF}_6^{2-}]}{[\text{Al}_2\text{OF}_8^{4-}]} \quad (11)
\]

In cryolite-alumina saturated melt with no additives, as given by Kvande [14], is between 0.5 and 1. With the procedure described earlier [1], the kinetic parameters \( (\sigma_R, K, k) \) at several alumina content were evaluated and are presented in Table 2. The splitting of the total Warburg coefficient \( \sigma \) into oxidised \( \sigma_O \) and reduced \( \sigma_R \) parts allows for the calculation of the diffusion coefficient of the \( \text{Al}_2\text{OF}_6^{2-} \) anionic species, which is presented in the last column of Table 2. It is seen that this diffusion coefficient value is now similar to the previously evaluated values. This value in cryolite-alumina melt with \( \text{CaF}_2 \), studied in [1], decreases with the alumina content as a result of increasing viscosity of these melts [11,15]. In the melt with 11 wt% of \( \text{AlF}_3 \) the diffusion coefficient also decreases with alumina content, but not to that extent as in cryolite-alumina melts containing \( \text{CaF}_2 \).

<table>
<thead>
<tr>
<th>Alumina content (wt %)</th>
<th>( K )</th>
<th>( k ) s(^{-1})</th>
<th>( \sigma_R ) ( \Omega) s(^{-1/2})</th>
<th>( D ) cm(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.745</td>
<td>561000</td>
<td>0.0323</td>
<td>1.49 \times 10^{-5}</td>
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<tr>
<td>4</td>
<td>0.753</td>
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<td>1.46 \times 10^{-5}</td>
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<tr>
<td>6</td>
<td>0.762</td>
<td>570000</td>
<td>0.01091</td>
<td>1.42 \times 10^{-5}</td>
</tr>
<tr>
<td>8</td>
<td>0.770</td>
<td>560000</td>
<td>0.00822</td>
<td>1.39 \times 10^{-5}</td>
</tr>
</tbody>
</table>

It is interesting to see that the impedance equilibrium constant presented in Table 2 agrees well with the literature [13,14]. As expected, the preceding chemical step, as follows from the relatively large value of the sum of rate constants \( k \), is also relatively fast.

REFERENCES