Effect of some electric factors on the effective oxidation level of aluminum

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In the present work, conditions were set for a study of the effect of field geometrical structure, by its transition from uniform to non-uniform field by varying the ratio of anode and cathode active areas on the effective oxidation level, assumed to be a measure for non-conformity with Faraday law by the anodic dissolution of aluminum in solutions of sodium chloride. Non-conformity with Faraday law was observed as in the range of low current densities (lower than $10-150$ $\text{Am}^{-2}$) the effective oxidation level changes in a wide interval depending on the factors studied and electric field geometry; in the range of high current densities (higher than $10-150$ $\text{Am}^{-2}$) the effective oxidation level is slightly affected by the electric field geometry and conditions used.

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Wöhler and Buff\textsuperscript{1} back in 1857 reported their observation for lack of Faraday conformity between the mass of the dissolved aluminum and the quantity of electricity passed through the solution. Other cases of such non-conformity have been often reported in the contemporary literature\textsuperscript{2-6}. Some of the authors came to the conclusion that the mass of the dissolved aluminum is smaller\textsuperscript{7-9}, while others report that it is bigger\textsuperscript{4,10-12} than the theoretical mass predicted by Faraday's laws of electrolysis (or that the anode current efficiency is not unity).

To explain the release of hydrogen on both the electrodes, Turrentine\textsuperscript{13} presumed that aluminum ions of lower or varying degree of oxidation were generated. This supposition explains well the simultaneous release of hydrogen on both electrodes, although it does not reveal the reason for the bigger release of (compared to the release without electric current) total amount of hydrogen, the so-called "negative difference effect"\textsuperscript{14} (NDE). NDE is accompanied by anomalously high rate of metal dissolution (compared with calculated by the Faraday's law on the basis of normal oxidation level of the cation passing into the electrolyte). In order to characterize the NDE, the effective oxidation level $N_e$ was introduced which formally obeys Faraday's law.

Besides the parameters current efficiency and effective oxidation level, another parameter was proposed - transition current density\textsuperscript{15} for assessment of the anomalous anodic dissolution of some metals. It determines the current density at which the difference effect transforms from positive to negative and vice versa.

There is no generally accepted mechanism of dissolution of aluminum in the scientific literature which would be not only of theoretical but also of great practical importance for the effectiveness of the use of aluminum as anode material (electrocoagulation, electroflotation, electro-M process)\textsuperscript{4,5,8}.

The data on anodic dissolution of aluminum in a number of studies are rather controversial and does not pretend to be thorough. The case becomes still more complicated if the electrolysis is carried out in non-uniform electric fields, if different types of dynamically varying currents are used or if magneto-electrolysis is studied (or electrolysis under imposed magnetic field).

The aim of the present work is to study the effect of electric field geometry (which has not been reported so far) and the type of the electric current (the law of the change of the current density with time) on the effective oxidation level of technically pure aluminum in a comparatively wide range of variation of the following factors: electric current density, distance
between the electrodes, electrolysis duration and concentration of the background electrolyte - sodium chloride.

Theoretical investigation

Effective oxidation level

Faraday's law reverberates the conformity between the quantity of electricity passed through the electrolyte and the equivalent amount of substance oxidized on the anode:

\[ Q = F n_z \]  

where \( F \) is Faraday's number representing the quantity of electricity per unit quantity of electrons, C/mol.

When Faraday's law is obeyed, the following relationships are valid:

\[ Q = F_n = F_z n_f \]

where \( z \) is the normal oxidation level of aluminum, or \( z = n_f/n_f \).

When there is a discrepancy from Faraday's law, the following relationships are valid:

\[ Q = F_{n_e} = F_{n_e} n = F_{n_e} M_f \]

where \( n_e \) is the effective oxidation level, or \( n_e = n_{n_e}/n \neq z \).

The effective oxidation level can be expressed also by:

\[ N_e = \frac{Q}{F} = \frac{Q}{A} = \frac{A}{M} = \frac{J_{x}}{\omega_{n_e}} \geq z \]

\[ Q = \frac{Q}{F} \frac{1}{n_f} = \frac{Q}{F} \frac{A}{M} = \frac{J_{x}}{\omega_{n_e}} = \text{const.} \]

Further, the discrepancy can be expressed by:

\[ \frac{z}{N_e} = \frac{n_f}{M_f} = \frac{\omega_a}{\omega_{n_e}} = \eta_a \]

which gives another meaning to current efficiency \( \eta_a \) reflecting the degree of discrepancy of the effective oxidation level \( N_e \) from the normal oxidation level \( z \) of the metal.

Variation interval of the effective oxidation level \( N_e \)

The hypothesis of stepwise mechanism of the anodic oxidation of metals presents one of the possible explanations of the Faraday non-conformity between the mass of the dissolved aluminum and the quantity of electricity transferred through the solution. Heyrovsky\(^{15}\) proved the impossibility of exchange of more than one electron in a single act of oxidation, thus providing a theoretical possibility for formation of ions of low oxidation level when multi-charge ions are obtained. Then, Conway and Bockris\(^{16}\) proved theoretically that metals (except for alkali ones) precipitate as a result of a stepwise reaction involving chemical and electrochemical stages.

The cations of lower oxidation level obtained have high reactivity (and, therefore, are quite unstable) and show affinity to oxidation. They can take part in a purely electrochemical chain of reactions to give an electron, as it is illustrated in Fig. 1 (A). The hypothesis of stepwise mechanism of dissolution limits the minimum value of \( N_e \geq 1 \) (Fig. 1). The process includes a possibility for a part of the ions with medium oxidation level to participate in chemical reactions with components of the solution (particularly with hydrogen ions or water molecules) [Fig. 1 (D)]. These reactions can lead to release of hydrogen and formation of ions of maximum oxidation level without consumption of electric power, thus increasing the apparent current efficiency and diverging the effective from the normal oxidation level. Naturally, different combinations of these two processes would give non-integer values of the effective oxidation level. Defenders of this hypothesis produced data on analogous oxidation processes for Al\(^{23,41,17}\), Be\(^{2,18}\), Mg\(^{19,20}\), Cu\(^{21}\), Ni\(^{22-25}\), Ga and TI\(^{17,26}\), In\(^{17,28}\), Ta\(^{27}\), Cd\(^{28}\),
Formation of singly oxidized magnesium\textsuperscript{19}, beryllium\textsuperscript{18}, aluminum\textsuperscript{29,30}, cuprous\textsuperscript{21,31} and nickel\textsuperscript{24} ions was experimentally established. Opponents of the hypothesis of stepwise mechanism of metal dissolution explain the anomalies observed by local chemical corrosion (negative difference effect)\textsuperscript{12,14,32,33} or by non-uniform disintegration of the metal lattice (effect Chunk) followed by chemical dissolution of the particles with release of hydrogen\textsuperscript{34}. These processes can take place simultaneously with the stepwise electrochemical dissolution and their occurrence allows a minimum effective oxidation level of $N_e<1$ [Fig. 1 (E,F)]. Schmidt \textit{et al.}\textsuperscript{35} measured 400\% current efficiency with silicon anode. Robinson and King\textsuperscript{36} determined the effective oxidation level of magnesium to be 0.8; Rausch \textit{et al.}\textsuperscript{37} 0.27; Garreau\textsuperscript{2} 0.998 for aluminum and Johnson and Liu\textsuperscript{38} 0.4 for antimonium. According to Straumanis and Wang\textsuperscript{14,32,35}, ions of unusual oxidation level (often lower than 1) would always be present in processes of anodic dissolution, if difference effects affecting the rate of self-dissolution are neglected. The theory of the negative difference effect\textsuperscript{32} states that the active metals (Mg, Al, Ti) react with the electrolyte (self-dissolution) at places where the protecting film is detached from their surface. The problem of the mechanism of formation and destruction of the oxide films on the anodic surface of "valve" metals (such as aluminum), the influence of different factors on these processes and their role in the anodic dissolution has been studied by many authors\textsuperscript{39-44}. Nevertheless, no one has so far proved whether the existence of an oxide film in metal surface is necessary and sufficient condition for the negative difference effect. For example, March and Schaschl\textsuperscript{34} suggested that the release of agglomerates of several atoms into the solution could be sufficient reason for the effect to take place.

The anode-anion activation (AAA) of passive metals (which takes place in the defects of the oxide layer formed before the anode polarization) also plays a significant role in the anodic dissolution of aluminum [Fig. 1(G)].

\textbf{Geometrical structure of the field}

In linear medium with specific electric resistance $\rho$, there is a correlation between the two basic characteristics of the electric field:

$$
\vec{E} = \rho \vec{J}, \quad \text{or} \quad \vec{E} = \rho \vec{J}.
$$

(7)

or the electric field can be described structurally by either vectors $\vec{E}$ or $\vec{J}$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Hypotheses of anodic oxidation of aluminum. Variation of the minimum values of the effective oxidation level of aluminum $N_e$ and current efficiency $\eta_e$ according to different hypotheses.}
\end{figure}
The geometrical structure of the electric field of conductivity changes with the transition from uniform to non-uniform electric field. The change can be provoked in two ways:

- by varying the ratio of the active areas of both electrodes \( S_a:S_e \), thus changing the degree of non-uniformity \( \beta (\beta = 1 \text{ for uniform field}) \):
  \[
  \beta = \frac{S_a}{S_e} \geq 1
  \] (8)
  where \( S \) is electrode area for uniform field (\( S = S_a = S_e \)). Electrode polarity may be straight (SP) \( S = S_a \) or reverse (RP) \( S = S_e \);

- by varying the apparent length of the current vector tube \( \alpha (\alpha = 1 \text{ for uniform field}) \):
  \[
  \alpha = \frac{d}{L} \geq 1
  \] (9)

where \( d \) is the minimum possible length of the current vector tube \( (d = d_a, \alpha = 1 \text{ for uniform field}) \).

The electric resistance in non-uniform field \( R_e \) is expressed in terms of the electric resistance in uniform field \( R_e^u \):

\[
R_e = \frac{\rho}{d} = \frac{\rho \alpha \beta d S}{s} = \alpha \beta R_e^u
\] (10)

or the ratio between both voltages represents the change of geometry,

\[
G = \frac{u}{u^u} = \frac{R_e^u i}{R_e i} = \frac{R_e^u}{R_e} = \alpha \beta
\] (11)

The change of the geometrical structure of the field can be realized by:

- varying the ratio of active areas \( S_a:S_e \) while keeping \( \sqrt{S_a/S_e} = \text{const} \) (through \( \alpha \) and \( \beta \));
- using dynamically varying electric current interacting with its own magnetic field (through \( \alpha \));
- interaction of the electric current with external magnetic field (magnetoelectrolysis) (through \( \alpha \));
- using inhomogeneous conducting medium, \( \rho(x, y, z) \neq \text{const} \) (through \( \alpha \));
- varying the specific electric resistance of the medium, e.g. \( \rho(T) \) or \( \rho(C) \) (through \( \alpha \));

- varying the distance \( d \) between the electrodes (through \( \alpha \)).

**Investigation modes**

The degree of non-uniformity \( \beta \) is an independent factor of the electrolysis which can be modified by varying the ratio \( S_a:S_e \). The apparent length of the current vector tube \( \alpha \) depends on a number of factors: degree of non-uniformity \( \beta \), distance between the electrodes \( d \), concentration of the background electrolyte \( C \), temperature \( T \) and influence of external magnetic fields.

By galvanostatic \((i = \text{const}) \) regime \( \beta = \text{const} \), while \( \alpha \) follows the changes of the voltage \( u \) over the electrolysis cell, depending on the specific electric resistance \( \rho \) of the electrolyte at constant geometrical factor \( \lambda = d/s \):

\[
i = \frac{u}{\rho \lambda \beta \alpha} = \text{const}, \quad \text{or} \quad \frac{u}{\alpha \rho} = \text{const}
\] (12)

The effects of \( \alpha \) and \( \beta \) of the geometrical factor \( G \), on the anodic dissolution of aluminum were studied with variation of \( \beta \) at levels of \( \beta = 1 \) (practically uniform field, \( \alpha = 1.54 \); \( \beta = \sqrt{2} (\alpha = 1.71) \) and \( \beta = 2 (\alpha = 1.75) \) and \( G = 1.54, 2.42 \) and 3.50.

The effect of the intensive factors (anodic current density \( J_p \), distance between electrodes \( d \), electrolysis time \( t \) and concentration of the background electrolyte \( C_{NaCl} \)) was studied under the conditions shown in Tables 1 and 1.1.

The experimental data reported on the effects of various factors on the effective oxidation level of aluminum (anodic current density, concentration and ion composition of the electrolyte, temperature, anodic potential, convective diffusion, pH, electrolysis duration, type of the current, electric field uniformity) are rather controversial, which supports the investigation in this direction by a comparatively complex experiment.

**Experimental Procedure**

The dissolution of aluminum electrodes (99.5%, with main alloys, mass%: Fe - 0.26, Si - 0.14, Cu - 0.1, Mg - 0.001) was studied in solutions of chemically pure NaCl in distilled water. The electrodes were vertical. The electrolyte was actively agitated during all the experiments. Prior to each experiment the electrodes were mechanically polished, cleaned with ethyl alcohol, washed with distilled water and dried. The mass of the
Table I — Changes in the geometrical structure of the field

<table>
<thead>
<tr>
<th>Degree of non-uniformity $\beta$</th>
<th>2</th>
<th>$\sqrt{2}$</th>
<th>1</th>
<th>$\sqrt{2}$</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarity</td>
<td>Reverse</td>
<td>Straight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$, cm$^2$</td>
<td>4</td>
<td>8</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$S_2$, cm$^2$</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>$S_3$, cm$^2$</td>
<td>8</td>
<td>8</td>
<td>$\sqrt{2}$</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>$I_x$, A/m$^2$</td>
<td>41</td>
<td>21</td>
<td>$I^*$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$I_y$, A/m$^2$</td>
<td>4:1</td>
<td>4:2</td>
<td>4:4</td>
<td>2:4</td>
<td>4:1</td>
</tr>
<tr>
<td>$I_z$, A/m$^2$</td>
<td>2:1</td>
<td>$\sqrt{2}$</td>
<td>1</td>
<td>$\sqrt{2}$</td>
<td>1</td>
</tr>
</tbody>
</table>

*The correlation between current density $J$ and the other parameters in the experimental plan selected is shown in Table 1.*

Table 1.1 — Parameters of the electrical regimes.

<table>
<thead>
<tr>
<th>No.</th>
<th>$d$, Am$^{-2}$</th>
<th>$\tau$, mm</th>
<th>$C_{NaCl}$, g/l</th>
<th>$Q_{calc}$, g/dm$^3$</th>
<th>No.</th>
<th>$J_x$, A/m$^2$</th>
<th>$\tau$, mm</th>
<th>$C_{NaCl}$, g/l</th>
<th>$Q_{calc}$, g/dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>60</td>
<td>20</td>
<td>900</td>
<td>5</td>
<td>5</td>
<td>83</td>
<td>13</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>2.</td>
<td>600</td>
<td>5</td>
<td>900</td>
<td>5</td>
<td>5</td>
<td>832</td>
<td>14</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>3.</td>
<td>600</td>
<td>20</td>
<td>150</td>
<td>5</td>
<td>5</td>
<td>139</td>
<td>15</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>4.</td>
<td>600</td>
<td>20</td>
<td>150</td>
<td>5</td>
<td>5</td>
<td>139</td>
<td>16</td>
<td>600</td>
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</tr>
<tr>
<td>5.</td>
<td>600</td>
<td>5</td>
<td>900</td>
<td>1</td>
<td>5</td>
<td>832</td>
<td>17</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>6.</td>
<td>600</td>
<td>5</td>
<td>150</td>
<td>5</td>
<td>14</td>
<td>18</td>
<td>18</td>
<td>600</td>
<td>12.5</td>
</tr>
<tr>
<td>7.</td>
<td>600</td>
<td>20</td>
<td>150</td>
<td>5</td>
<td>5</td>
<td>14</td>
<td>19</td>
<td>330</td>
<td>5</td>
</tr>
<tr>
<td>8.</td>
<td>330</td>
<td>20</td>
<td>900</td>
<td>1</td>
<td>5</td>
<td>457</td>
<td>20</td>
<td>600</td>
<td>5</td>
</tr>
<tr>
<td>9.</td>
<td>600</td>
<td>12.5</td>
<td>900</td>
<td>1</td>
<td>5</td>
<td>83</td>
<td>21</td>
<td>600</td>
<td>12.5</td>
</tr>
<tr>
<td>10.</td>
<td>600</td>
<td>20</td>
<td>525</td>
<td>1</td>
<td>48</td>
<td>22</td>
<td>60</td>
<td>525</td>
<td>5</td>
</tr>
<tr>
<td>11.</td>
<td>600</td>
<td>5</td>
<td>150</td>
<td>3</td>
<td>139</td>
<td>23</td>
<td>530</td>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>12.</td>
<td>600</td>
<td>20</td>
<td>150</td>
<td>3</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Dissolved aluminum was determined gravimetrically after appropriate washing and drying, in two parallel experiments. pH was measured before and after the electrolysis.

**Results and Discussion**

For all the regimes (or 230 tested samples), the mass of the dissolved aluminum is higher than expected according to Faraday's law, which determines $N_\varepsilon < 3$. In most of the experiments it was found that $2 < N_\varepsilon < 3$ (ca. 70% of all), followed by the experiments where $1 < N_\varepsilon < 2$ (ca. 30%). All the samples showed non-integral value of $N_\varepsilon$ in all the range of expected variation, or Al ions with different level of oxidation pass into the electrolyte. Figures 2-5 show the average values of the calculated effective oxidation level $N_\varepsilon$ for each of the regimes used. The factors studied, affect (within the factor space investigated) the anodic dissolution of aluminum in different ways. The least effect (measure by the variation interval of the effective oxidation level) was found at uniform electric field; the variation interval was $N_\varepsilon = 1.82 \pm 2.72$. A shift of the values to the lower boundary of the interval was observed at current density of 60 Am$^{-2}$, electrolysis time 900 s, distance between
the electrodes- 20 mm and NaCl concentration- 5 g. dm$^{-3}$. The shift to the higher boundary was observed at 300 Am$^{-2}$, 900 s, 20 mm and 1 g.dm$^{-3}$ (Figs 2-5).

Effect of current density

The increase of anodic current density at uniform electric field (Fig. 2) leads to overall shift of the interval of variation of the effective oxidation level to higher values. According to the theory of disintegration, the increase of the anodic current density produces greater difference between the effective and normal oxidation level. The stepwise mechanism acts in just the opposite direction: the increase of the current density $J_a$ (or field intensity, or anode potential) changes the ratio between the rates of electrochemical and chemical transformation of the ions with a medium oxidation level. Only the electrochemical reaction depends on anodic potential. The increase of the potential increases the effective oxidation level, i.e. the electrochemical transformations become predominant and the effective oxidation level tends to the normal one: $N_e \rightarrow 3$.

The observed way by which current density affects effective oxidation level proves experimentally the stepwise character of the process of oxidation of aluminum in sodium chloride solutions. It should be mentioned, however, that some authors$^{3,11}$ reported data rejecting the effect of current density on effective oxidation level.

Effect of electric field non-uniformity

The increase of degree of non-uniformity of the electric field by varying the ratio between the active areas of both the electrodes $(S_a:S_c)$ or $\beta$ enhances the effect of the current density on the effective oxidation level. This dependence (supporting the stepwise mechanism of oxidation) can most clearly be observed by straight polarity and $S_a:S_c=4:2$ ($\beta=\sqrt{2}$) (Fig. 2). In all the cases with non-uniform field studied, stronger characteristic effect (in favour of the stepwise mechanism) of current density on effective oxidation...
level was observed, compared with the case with uniform electric field. Thus, it can be concluded that the non-uniform electric field is characterized by specific increase of the effective oxidation level with the increase of current density $J_a$. The maximum discrepancy from Faraday's law was observed at low current densities (60 Am$^2$).

**Effect of electrolysis time**

The increase of electrolysis time $t_e$ causes a clear increase of the effective oxidation level by non-uniform electric field. The influence of this factor on the change of effective oxidation level by uniform electric field is much weaker (Fig. 4). Molodov$^{26}$ proved that, in non-stationary regime, the effective oxidation level differs from the normal one, provided the intermediate particles are oxidized to the normal oxidation level in an electrode (but not in chemical) reaction. This effect was related to the accelerated diffusion of particles with medium oxidation level to the solution due to their increased concentration on electrode surface. Similarly, Garreau$^{2}$ used the data for the initial oxidation level to prove the formation of intermediate Be$^{+}$ ions by anodic dissolution of beryllium in water-ethanol solutions of lithium perchlorate. The increase of effective oxidation level with electrolysis time ascertains also the formation of intermediate ions with low oxidation level and the stepwise mechanism of oxidation. The ions with low oxidation level interact with solution components (hydrogen ions or water molecules)$^{26}$. The low values of effective oxidation level were observed only when chemical reactions take part in the stepwise transformation of ions with low charge. The low effective oxidation level or anomalously high current efficiency exhibit the stepwise mechanism. Naturally, this mechanism can take place in purely Faraday chain of electrochemical processes but then it cannot be distinguished from the direct generation of multi-charge ion. The increased current efficiency and the formation of multi-charge ions with lower effective oxidation level indicate the stepwise mechanism of oxidation.

**Effect of the distance between the electrodes and concentration of the background electrolyte**

The non-uniform electric field gives low values of effective oxidation level and, furthermore, the small ($d=5$ mm) and big ($d=20$ mm) distance determine the maximum interval of variation and low values of
effective oxidation level (Fig. 3). At a distance of 12.5 mm, a narrow variation interval was observed and, except for the cases with straight and reverse electrode polarity at $\beta = \sqrt{2}$, the values of effective oxidation level are $N_e > 2$. The concentration of background electrolyte (sodium chloride), as well as the distance between the electrodes, affect the structure of the electric field (through $\alpha$) and the diffusion processes in the electrolyte. The increase of electric field non-uniformity leads to a decrease of the effective oxidation level or to higher discrepancy from Faraday's law (Fig. 5).

Effect of the basic factors

Thus, the effect of the basic factors on the process of electrochemical oxidation of aluminum in solutions of sodium chloride - current density, electrolysis time, distance between the electrodes and concentration of background electrolyte - is enhanced in non-uniform electric field and, besides, the variation interval is extended to the lower values of effective oxidation level. The weakest effect was found with uniform field of direct current - narrow variation interval and values of effective oxidation level close to the normal oxidation level. Some values of effective oxidation level observed during the present studies are quite different from those reported earlier by Rajjola et al. at almost the same current densities and concentrations of sodium chloride. It should be noted, however, that at NaCl concentration of 0.052 M, electrolysis time 900 s and anodic current density, depending on the electric field non-uniformity, 600, 1200 and 2400 Am$^{-2}$, the values of effective oxidation level calculated are close to theirs, although electrolysis time was 9000 s (2.5 h), i.e. 10 times longer. According to Dikusar, the reason for the anomalously high dissolution rate should be assumed to be the chemical oxidation of particles with medium oxidation level by oxidizing anions adsorbed on electrode surface. The change of $N_e$ with the increase of oxidizer concentration substantiates that the reason for the anomalously high dissolution rate is the reaction of chemical oxidation. If the particle is adsorbed, a necessary condition for decrease of $N_e$ is the specific adsorption of the oxidizer. Otherwise, exceeding of the theoretical dissolution rate and occurrence of non-Faraday dissolution of the metal is possible only if the particle with low oxidation level is stable enough and exists in the solution for a certain period.

Conclusion

The experimental study performed proved the significant effect of electric field geometry on Faraday's non-conformity by anodic dissolution of aluminum in sodium chloride solutions. The effect is specific for low and high current density even under uniform field of the direct electric current. The non-uniform electric field enhances this effect and shift the boundary between the two intervals. Low effective oxidation levels (even below unity) were found at low current density.

The effective oxidation level can be used as an integral value representing the changes in the anodic dissolution of aluminum when the specific effect of the electric field geometry is studied.

Nomenclature

$A$ - atomic mass of the aluminum;
$F$ - Faraday's number;
$I$ - current through the electrolytic cell, A;
$I_a$ - anodic current density, Am$^{-2}$;
$M$ - mass of the aluminum dissolved from anode, g;
$M_a$ - mass of the aluminum dissolved from anode in accordance with Faraday's law, g;
$n$ - quantity of dissolved aluminum $n = MA$;
$N_e$ - effective oxidation level;
$n_{eq}$ - chemical equivalent: $n_{eq} = N_e n$;
$n_i$ - theoretical amount of dissolved aluminum: $n_i = M_i/A$;
$n_p$ - chemical equivalent: $n_p = M_p/A$;
$Q$ - quantity of electricity, C;
$S$ - active geometrical area of the anode, m$^2$;
$S_N$ - active geometrical area of the cathode, m$^2$;
$\delta$ - ratio of the anodic and cathodic active areas;
$w_a$ - anodic dissolution rate, gs$^{-1}$m$^{-2}$;
$w\_d$ - anodic dissolution rate according to Faraday's law, gs$^{-1}$m$^{-2}$;
$z$ - normal oxidation level of aluminum;
$\beta$ - degree of electric field non-uniformity;
$\eta$ - current efficiency.

References
