

STUDIES ON ANODE EFFECT IN ALUMINIUM ELECTROLYSIS

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Summary

Anode effect is a characteristic phenomenon in molten salts electrolysis, especially in aluminium electrolysis. When it occurs, many small electric sparks appear on the anode, and the cell voltage increases suddenly. In this paper the anode effect was studied by means of cathode-ray oscillography. The back electromotive force of the aluminium electrolysis cell with various kinds of anode materials (carbon, graphite, platinum and other inert materials) was measured. It was clearly observed that a series of electrochemical decomposition processes took place when the anode effect occurred on carbon anodes. The values of back EMF of these processes were in the range of 1.0 - 5.5 V. These were checked with thermodynamics calculations. A direct short-circuit of current from anode to cathode was also observed during the whole process of anode effect. These phenomena were compared with those observed on microelectrolysis cells, and the mechanism of anode effect was suggested.

Wettability of Carbon Electrodes by Molten Cryolite-Alumina Electrolytes

The wettability of carbon electrodes by molten cryolite-alumina electrolytes was investigated in a laboratory micro-electrolysis cell (1,2).

When the carbon plate was given a cathodic polarization, the molten drop gradually spread on the carbon plate after several minutes of electrolysis and tended to separate from the anode. However, the molten electrolyte usually collected together and touched the anode again, then electrolysis resumed, sometimes an anode effect occurred.

When the carbon plate was given an anodic polarization, the wettability was good at the beginning of electrolysis. After several minutes of electrolysis, the electrolyte coalesced into a globe. Then the current decreased and the voltage increased suddenly, an anode effect occurred. Sometimes, most of the electrolyte adhered to the cathode and separated from the carbon plate anode. These phenomena were consistent with those mentioned above.

When platinum wire loop was used instead of carbon as an anode or a cathode, similar phenomena were observed. The wettability of platinum by the molten cryolite-alumina electrolyte was very good originally. But when it was used as an anode, after a direct current was applied, the molten electrolyte would be repulsed and separated from it. After a while the electrolyte would touch the anode again. Thus a cyclic process of electrolysis-repulsion-electrolysis appeared. When the platinum wire loop was used as a cathode, the electrolyte would climb up on it quickly, nearly all the electrolyte would be attracted by the cathode, and an anode effect was observed on the anode carbon plate.

So both carbon and platinum have the same characteristics. When anodically polarized, they would repulse the electrolyte, and when cathodically polarized they would attract the electrolyte.

The anodic repulsive force and cathodic attractive force would be increased with an increase in current intensity or a decrease in alumina content of the electrolyte.

The anode effect observed was shown in photo A.

During the anode effect, if the polarities of the electrodes were changed, the anode effect would be quenched. However, after a short period of "hesitation" the molten salts on the anode carbon plate (which was originally used as cathode) would coalesce and an anode effect occurred on it.

Critical Current Densities

In most of the previous critical current density measurements, no aluminium was added to the cryolite-alumina electrolysis cell. Hence the results obtained could not reflect the true states. In this paper the critical current densities were measured with the addition of aluminium, and the results were compared with those without addition of aluminium. The instrument used for tracing the I-V curves was X-Y recorder of LZ3-204 type. Typical I-V curves are shown in Figure 1. The values of ccd were listed in Table 1 and plotted in Figure 2. Max. values of ccd were observed in both cases at 10 - 12 % (wt.) Al_2O_3 . When Al_2O_3 concentration exceeded 12 %, the values of ccd would decrease. This was due to the presence of suspended alumina in the melts. With the addition of aluminium to the electrolysis cells, the electric arcs during AE became long and big, and the values of ccd significantly decreased. The same effect was also observed with the addition of carbon powder to melts. For carbon anodes which had undergone an anode effect for 5 minutes, the values of ccd would be greatly decreased (in comparison with new anodes).

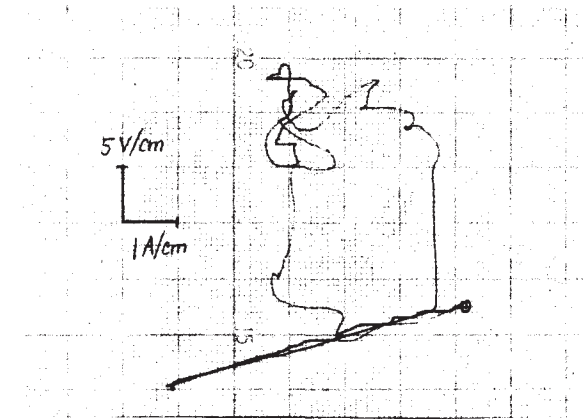


Fig. 1 I-V curve in aluminium electrolysis.
(C.R. = 2.98, Al_2O_3 8.5%, 1050°C)

Table 1. Values of ccd in cryolite-alumina melts (1050°C, carbon anode)

Al_2O_3 % (wt.)	without Al ($A \cdot cm^{-2}$)		with Al ($A \cdot cm^{-2}$)	
	new anode	anode after AE	new anode	anode after AE
0.5	3.2	2.8	2.7	1.8
2.5	6.2	5.2	4.8	3.8
4.5	8.4	7.4	5.8	5.0
6.5	10.0	8.4	6.7	5.8
8.5	11.0	9.8	7.5	6.2
10.5	11.6	10.3	7.8	6.3
12.4	11.8	10.3	7.8	6.2
15.4	10.0	9.6	7.2	5.9
20.4	7.8	7.0	2.5	2.2
2.5 % Al_2O_3 + 2 % C	3.0	2.5	2.6	1.5

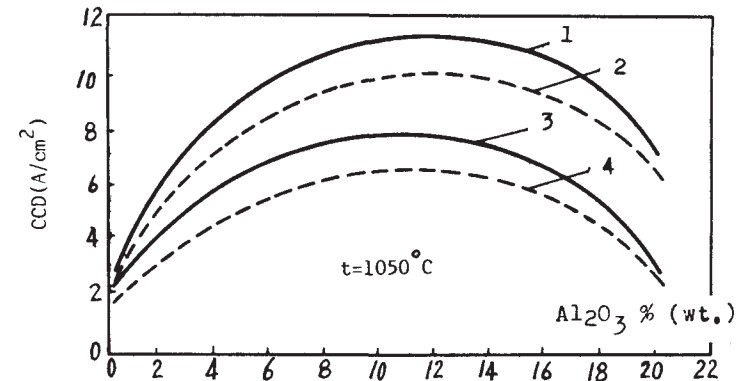


Fig. 2 Critical current densities on carbon anodes in aluminium electrolysis.
 Na_3AlF_6 (NaF/ AlF_3 mole ratio = 3.0) + Al_2O_3 (saturated), 1-new anode, 2-anode after AE, 3-new anode, with the addition of Al, 4-anode after AE, with the addition of Al.

* These values were the mean of 2 - 3 measurements. The deviation in each run did not exceed 5 %.

In the case of new carbon anode and with the addition of aluminium to the melts, a relationship of $ccd = f(Al_2O_3)$ was obtained as follows:

$$ccd = 0.25 + 2.52 \sqrt{Al_2O_3 \%} \quad A/cm^2$$

the constant $A = 0.25 A/cm^2$ was obtained by extrapolating the curves to the zero concentration of alumina.

Antipin et al (3) had measured ccd in the presence of aluminium, they also found that the values were lower than those obtained without addition of aluminium. There were several maxima and minima points on the curve. But it is rather difficult to explain.

The relationships of ccd and wetting angle (θ) to the alumina concentration were shown in Figure 3. Here the values of ccd were obtained on a new anode but with the addition of aluminium. The wetting angles (θ) were measured on carbon plate under anodic polarization ($d_a = 0.08 A/cm^2$). The curves obtained by Belyaev under different conditions were also plotted in this figure. It is clearly seen that our θ values are somewhat higher and ccd values lower, but they can reflect the true states of aluminium electrolysis in a better way.

Cathode Ray Oscillography

In the electrolysis, graphite crucible ($\emptyset 5 \times H 7$ cm) was used as cathode and carbon, platinum and other materials as anode. The graphite crucible was lined with a corundum crucible. In the bottom of the corundum crucible there was a hole of 3 cm in diameter. 120 grams of electrolyte were melted in the crucible. The electrolyte was saturated with Al_2O_3 , its bath ratio was 3.0. The temperature of electrolyte was kept constant at $1000^\circ C$. The inter-polar distance was about 2.5 cm.

The electrical measuring system is shown in Figure 4.

It took 15 minutes to proceed pre-electrolysis. After this the current was gradually raised, and back EMF values were measured at different current densities.

Platinum and other inert anode

The back EMF values for some kinds of inert anode (such as Pt, SnO_2 , ZrO_2 , Al_2O_3) were measured. These values increased with current densities. See photo B.

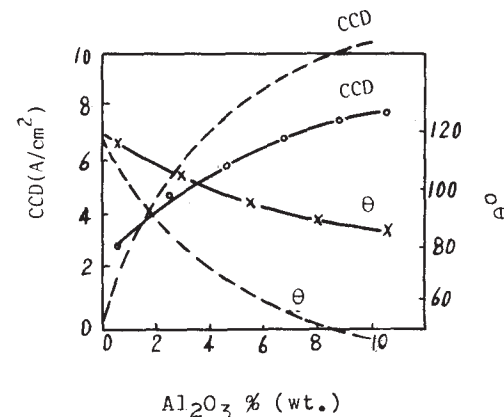


Fig. 3 $ccd = f(Al_2O_3\%)$, $\theta = f(Al_2O_3\%)$.
 curves ----- obtained by Belyaev,
 curves ——— this paper

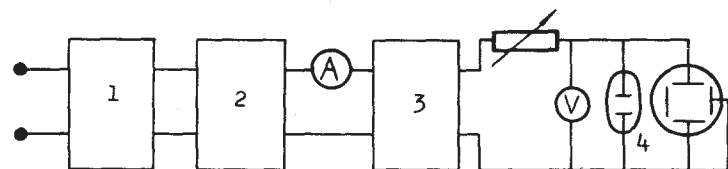


Fig. 4 Electrical measuring system.
 1--- transformer, 2--- rectifier,
 3--- commutator, 4--- electrolysis cell
 5--- oscillograph.



Photo A. Anode effect on carbon anode.

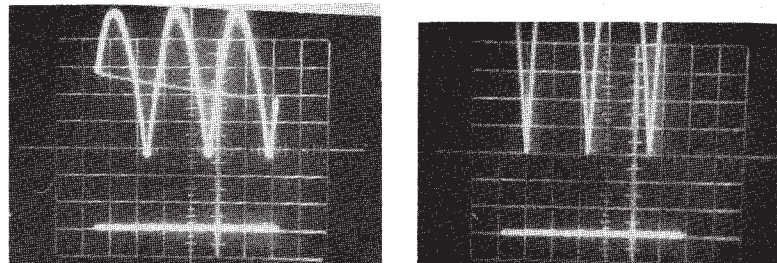


Photo B. Oscillograms in aluminium electrolysis with carbon anode.

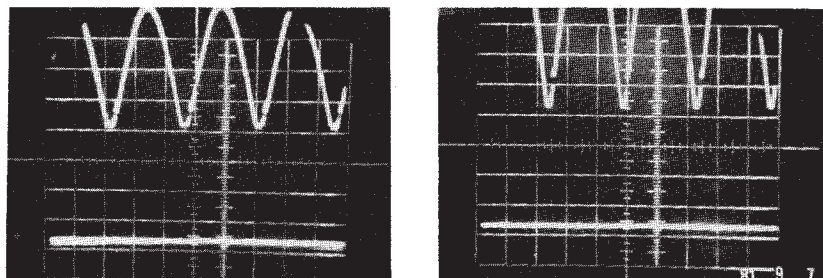


Photo C. Oscillograms in aluminium electrolysis with platinum anode.

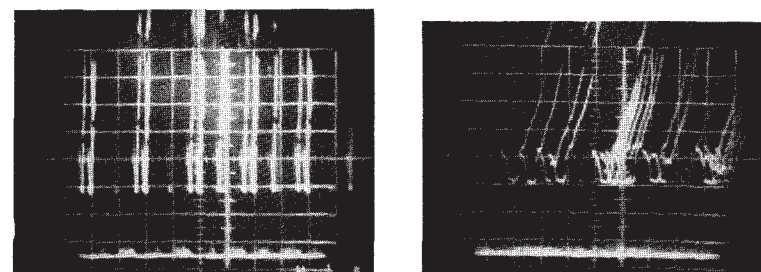
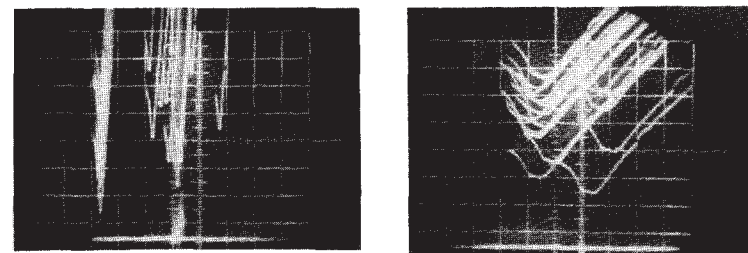
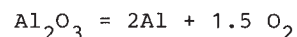


Photo D. Oscillograms during anode effect in aluminium electrolysis.

Inert Anode	Pt	SnO ₂	ZrO ₂	Al ₂ O ₃
Back EMF (V)	2.0-2.25	2.15-2.5	2.0-2.5	2.0-2.2

These values correspond to the decomposition of Al₂O₃ according to the following equation:



The standard EMF value of the above reaction at 1273 K is 2.196 V ($G_{1273}^{\circ} = -303800 \text{ cal/mol Al}_2\text{O}_3$).

Electrolysis with carbon anode

Before electrolysis the voltage drop across the cell was about 1 V. During electrolysis the values of back EMF measured were in the range of 1.2 - 1.6 V, which increased with current density, too. But after reaching 1.6 V, the back EMF value increased only a little bit until the anode effect occurred. See photo C.

The relationship between the current density and back EMF is shown in Figure 5, in which curve 1 is for platinum anode and curve 2 for carbon anode. The values obtained by Abramov et al on carbon anode are also plotted in this figure as curve 3. It is seen that curve 2 and 3 are in good agreement. In general the values of curve 1 are higher than these of curve 2 about 700 mV at different current densities.

Anode Effect

Different wave shapes during the anode effect are shown in photo D.

Before the occurrence of anode effect, the steepness of waves increased with current density. When anode effect initiated, the waves became nearly vertical. There appeared many minute electric sparks on the carbon anode, but they were unstable. The waves shown on the screen of the cathode ray oscillograph were unstable, too. From photo D we can also clearly tell the different values of the back EMF from one another. These values (1.0 - 5.5 V) indicated that various reactions were taking place during the anode effect.

We calculated the standard EMF values with data of thermodynamics for some possible reactions during the anode effect. The calculated standard EMF values and the measured back EMF values are listed in Table 2.

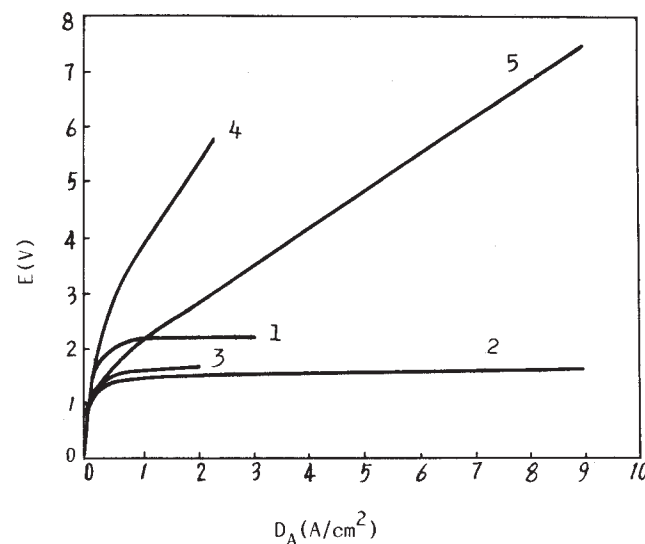


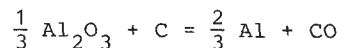
Fig. 5 Relationships between anodic current density and back EMF of aluminium electrolysis cell. 1--- back EMF of platinum anode, 2--- back EMF of carbon anode, 3--- back EMF obtained by Abramov, 4--- cell voltage of platinum anode, 5--- cell voltage of carbon anode.

Table 2. Some possible reactions during AE

Reactions	Calculated Standard EMF, V (1000°C)	Measured Back EMF V(1000°C)
(1) $\frac{1}{3} \text{Al}_2\text{O}_3 + \text{C} = \frac{2}{3} \text{Al} + \text{CO}$	1.08	1.0 - 1.3
(2) $\frac{2}{3} \text{Al}_2\text{O}_3 + \text{C} = \frac{4}{3} \text{Al} + \text{CO}_2$	1.17	1.0 - 1.5
(3) $\frac{4}{3} \text{AlF}_3 + \text{C} = \frac{4}{3} \text{Al} + \text{CF}_4$	2.04	2.0 - 2.2
(4) $\frac{4}{3} \text{Na}_3\text{AlF}_6 + \text{C} = \frac{4}{3} \text{Al} + 4\text{NaF} + \text{CF}_4$	2.56	2.5 - 2.6
(5) $4 \text{NaF} + \text{C} = 4\text{Na} + \text{CF}_4$	2.57	2.5 - 2.6
(6) $\frac{2}{3} \text{Na}_3\text{AlF}_6 = \frac{2}{3} \text{Al} + 2\text{NaF} + \text{F}_2$	4.44	4.3 - 4.8

J. Thonstad et al (4) had reported the possibilities of reactions (2), (3), (4) and (6) during the anode effect. Our experiments had confirmed the results obtained by them, but there may be other possibilities:

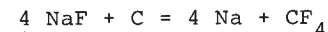
- (1) During the anode effect, a decomposition process of alumina with the formation of CO may take place:



The standard EMF (at 1273°K) of this reaction is 1.08 V. The reaction of CO formation may be proved by the following facts:

- One of the back EMF values measured is about 1.0 V.
- The CO gas concentration in the anode gases during the anode effect is about 40 - 50 %, while the CO₂ concentration is about 20 %, and the fluorine containing gas compounds amount to 30 - 40 %.
- During the anode effect the temperature is very high and the anodic current density is low, favoring the formation of Co.

- (2) The decomposition reaction of NaF may occur:



The standard EMF (at 1273°K) of this reaction is 2.57 V, the corresponding back EMF values measured are 2.5 - 2.6 V.

(3) There are various kinds of carbon fluorides, therefore during the anode effect there may be different types of electro-chemical decomposition reactions in addition to that of CF₄ formation.

(4) Some measured back EMF values are as high as 5.25 - 5.5 V. These may correspond to the direct decomposition of certain compounds.

The anode effect became more stable when the current intensity was increased. The predominant reaction during the anode effect probably was the decomposition of Al₂O₃ into CO₂ and CO, because the major back EMF values were in the range of 1.0 and 1.5 V (for cryolite saturated with Al₂O₃, or cryolite with 0.5 % Al₂O₃).

During the anode effect electric arcs appeared on the base line of the oscillography. Their positions were just opposite to the voltage peaks. The highest voltage observed was about 90 V (i.e. the effective voltage value read from the voltmeter). The voltage peaks even exceeded 130 V. Electric arcs with such a high voltage may pass through the electrolyte and attack the opposite electrode. This phenomenon had already been observed in a micro-electrolysis cell, then the voltage across the cell was only 26 V (see photo A).

Some strange phenomena were observed when we reversed the direction of current during the anode effect. At first the anode effect was quenched. After a while an anode effect appeared on the electrode, which was originally used as cathode and then as anode. This effect was vigorous with a hissing sound at high frequency. These phenomena were confirmed by direct observation in our micro-electrolysis cell mentioned above.

Aqueous Solution Electrolysis

In order to observe the anode effect more clearly, we carried out aqueous solution electrolysis in a glass beaker (volume 1 liter, 0.5 M NaCl solution). Two carbon electrodes were used, one was larger (Ø 10 mm) and the other was with a tip (Ø 6 mm).

Alternating current electrolysis

When voltage was above 20 V, some gas bubbles appeared on the electrodes. Quantities of gas evolved increased with current intensity. At 120 V, the electrodes were covered with gas bubbles and began to vibrate. At 140 V, electric arcs appeared on the small electrode. This phenomenon was something like the anode effect in aluminium electrolysis.

Direct current electrolysis

Some gas bubbles appeared on the electrodes at 2 V (back EMF). At 140 V an anode effect occurred on the anode (the small electrode).

When the small electrode was used as cathode and the large one as anode, at 90 V, a "cathode effect" (just like the anode effect mentioned above) was observed on the small electrode, too.

In these two cases an "electrode effect" would occur when the electrode was covered with a thick layer of gas bubbles (i.e. the electrode was with high gas density) at high voltage, whether it be an anode or a cathode.

In these experiments we did not observe an arc short-circuit between electrodes. And on the base line of the oscillography electric arcs did not appear. It may be due to the fact that such a high voltage (100 - 180 V) is not sufficient for arcs to "break through" the electrolyte yet.

Mechanism of Anode Effectin Aluminium Electrolysis (Discussion)Anode effect due to increasing current density

Once the electrolysis process started, the electrolyte would be repelled away partly from the anode due to the evolution of gases. Hence the effective current density was decreased. When the current density was lower than the critical one, normal electrolysis proceeded yet. But when the current density was increasing, either due to increasing current intensity or decreasing penetration depth of the anode in the electrolyte, the gas density on the anode would be increased. The electrolyte was repelled by the anode to a greater extent, i.e., the wettability of the anode by the electrolyte would become worse. After reaching its critical current density, the anode would be nearly covered with gas bubbles, and it was only partly keeping in contact with the molten electrolyte. Most of the current passages were blocked. The electric current then was compelled

to pass through the gas layer at a high voltage with many small arcs, i.e., the gases were ionized, and an anode effect occurred.

The initiation of this type of anode effect (AE-I) was not necessarily related to the formation of CF_4 or other fluorides, because on the oscillography we had not observed any significant change in the back EMF value right before its initiation. Moreover, the formation of these compounds probably may be considered chiefly as a result of an anode effect. We agree with the opinion of K. Grjotheim (5).

Anode effect due to decrease in Al_2O_3 concentration

During the normal electrolysis process, compounds CxO and $CxO \cdot O$ formed on the anode, and part of CO_2 was adsorbed there. The de-adsorption of CO_2 was a slow process. Then the anode became less active, and the anodic overvoltage increased.

When the Al_2O_3 concentration in the molten electrolyte decreased to 1 % or less, F ions would discharge together with O^{2-} ions to form compounds $COFx$ on the anode. Then there were much adsorbed compounds and gases at the boundary of anode-electrolyte. The anode surface became more inert. The electrolyte would be repelled by the anode to a greater extent and the effective current density was increased. Of course, it was a gradually developing process. When the anode surface was covered with a thick layer of gas bubbles, a critical current density was reached and an anode effect occurred.

Therefore the initiation of this type of anode effect (AE-II) may be related to the formation of surface compounds and high gas density.

Gas network

W.E. Haupin (6) had made very interesting experiments in cells with windows made of sapphire and of quartz. The visual observations reported that when the anode effect occurred, the gas bubbles tended to coalesce.

Our observations (both in industrial cells and in laboratory cells) were in agreement with Haupin's.

This film of gases was in the shape of a network. Among the gas bubbles there was some electrolyte. When the electric charges of gases at certain localities of the anode were neutralized, the electric arcs would be extinguished there and reappeared at some other places. Therefore it seemed that the electric arcs are glimmering on the anode.

The gas film network stuck coherently to the anode surface and penetrated into the pores and fissures of the anode. This may be due to an electrostatic attraction force of the anode as gas bubbles were ionized. The electrostatic attraction force obviously is the result of anode effect and not the cause.

In industrial aluminium electrolysis pots, for quenching the anode effects, we usually caused the anode and cathode to be short circuited at some places, i.e., by splashing the negatively charged liquid aluminium to the anode or by moving the anode downward to contact the cathode liquid aluminium, or even by adopting critical measures to decrease the line current intensities, so that the strength of the electric field may be weakened.

Conclusion

1. During the anode effect there are various electro-chemical reactions, such as decomposition of Al_2O_3 into CO_2 and CO , decomposition of AlF_3 , NaF and Na_3AlF_6 . In addition, there may be some other unknown reactions.
2. During the anode effect a direct short circuit of electric arcs happens between the anode and cathode.
3. The mechanism of anode effect is discussed.

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