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On the cathode reaction in aluminium electrolysis

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The cathode reaction in the aluminium electrolysis has been studied both in laboratory and industrial cells. At normal current densities the cathodic overvoltage on aluminium in cryolite range from 0.09 to 0.15 V. The overvoltage decreases with incrasing CR (mol NaF/ mol AlF_3), being only 0.03 V at CR = 8. Straight Tafel lines are obtained, the slope decreasing from 0.22 V/decade in cryolite to 0.07 V/decade at CR = 8. Double pulse and impedance measurements showed that the charge transfer overvoltage is negligible, but these methods did not reveal the nature of the overvoltage.

The slowness of the potential rise at current switch-on and of the potential decay at switch-off indicates that the overvoltage is mainly transport controlled. Since the sodium ion is the carrier of current, an accumulation of NaF will occur in a layer near the cathode.

The effect of such a shift in concentration on the emf of an aluminium electrode was studied using the galvanic cell $Al \mid NaF + Na_3AlF_6,\ Al_2O_3 \mid\mid Na_3AlF_6,\ Al_2O_3 \mid Al$. Calculations based on the resulting emf curve and the diffusion laws show that the overvoltage can largely be ascribed to the concentration shift at the cathode surface.

However, there are indications that subvalent metal formation plays a part in the reaction. Formation of sodium gas at 1 atm. pressure is excluded except at very high current densities, but intermediate products, consisting partly of sodium, may be formed at the cathode. These processes probably play an important part in the reactions determining the current efficiency.

1. INTRODUCTION

The principal questions concerning the cathode reaction in cryolite-alumina melts are

1) Is the reaction accompanied by overvoltage, and if so, what type of overvoltage?
2) Does sodium discharge play any part in the reaction?
3) Has the reaction any influence on the current efficiency of the process?

The answers to these questions have been a matter of some controversy; partly due to actual differences in opinion, but also partly because of different nomenclature. The ambiguity is connected with the word overvoltage. In this work we define overvoltage as a deviation from the reversible potential occuring by passage of current

$$\eta_i = E_i - E_{i=0}$$

regardless of the cause of the deviation, except for ohmic resistance. When this definition is used, all previous investigators (1-3) have found appreciable cathodic overvoltage on aluminium in cryolite-alumina melts.

Overvoltage can be caused by slow charge transfer, slow mass transfer or slow chemical reaction. Charge transfer reactions for deposition of metals in molten salts are usually fast, while mass transfer and chemical reactions can be retarded and give rise to overvoltage.

The ions present in $NaF\text{-}AlF_3$ melts appear to be Na^+, AlF_6^{3-}, AlF_4^-, F^-. In presence of Al_2O_3 the O^{2-} and F^- ions can substitute each other, forming eg. $A10F_3^{2-}$. One notice thaf sodium is present as free cations, while aluminium is bound in anionic complexes. This fact is reflected in the transport properties, as the transport number of sodium is close to one [4].

According to recent publications the discharge potential of sodium gas at 1 atm. pressure is 270 mV negative to that of aluminium in cryolite [5] [6]. This difference approaches zero as the cryolite ratio (CR = mol NaF/mol AlF_3) is increased.

By electrolysis a concentration gradient is set up at the cathode surface because the sodium ions is the carrier of current and aluminium is deposited at the cathode. The resulting enrichment of sodium fluoride at the cathode surface will facilitate sodium discharge. Furthermore, $NaF\text{-}AlF_3$ melts in contact with aluminium contain dissolved metal, which appearently consists of sodium as well as aluminium [7] [8]. The metal solubility increases strongly with increasing CR. Cathodic formation of dissolved sodium might then be possible at potentials below that of sodium gas evolution.

On the background of this information and of previous works by Antipin [9], Piontelli et al. [1], Lozhkin and Popov [2] and others, the present investigation was started in order to determine the magnitude and the origin of the cathodic overvoltage.

2. EXPERIMENTAL

The cells used in the laboratory investigation normally consisted of an aluminium cathode, an aluminium reference electrode and a graphite or aluminium counter electrode. The sizes and the positioning of the electrodes were varied. The type of cell used for steady state current-voltage measurements is shown in Figure 1. The overvoltage was determined as the potential difference between the cathode and the reference electrode, corrected for the ohmic voltage drop.

In industrial cells an aluminium reference electrode of the type shown in Figure 2 was dipped into the bath. The potential difference between the cathode metal and the reference was recorded after the series current was interrupted.

3. RESULTS AND DISCUSSION

Recordings of the cathode potential of 140 kA industrial cells after switch-off are presented in Figure 3. A steady but slow decrease in the polarization potential was observed. As an average, the overvoltage appeared to be about 100 mV. A similar result was obtained by moving the reference up and down through the metal/bath interface during current passage.

Overvoltages of the same magnitude were found also in the laboratory experiments. The cathode potential became increasingly negative with respect to the reference electrode as the current was increased, and at a normal cd of 0.5 A/cm² it amounted to 90-130 mV.

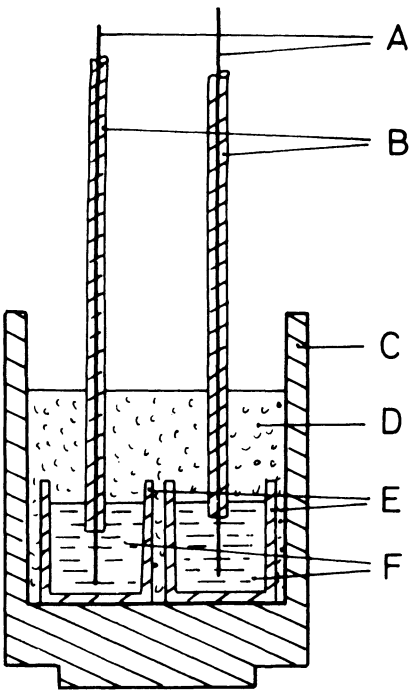

Fig. 1. — Laboratory cell for steady state current-voltage measurements. A - Mo wire, B - Alumina sheaths, C - Graphite-crucible, D - $NaF-AlF_3-Al_2O_3$-melt, E - Alumina crucible, ID 16 mm, F - Aluminium.

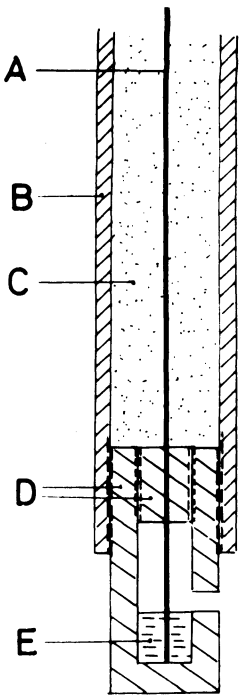

Fig. 2. — Aluminium reference electrode for use in industrial aluminium cells. A - Mo wire, B - Steel tube, OD 25mm, C - Alumina powder, D - Boron nitride container, E - Aluminium.

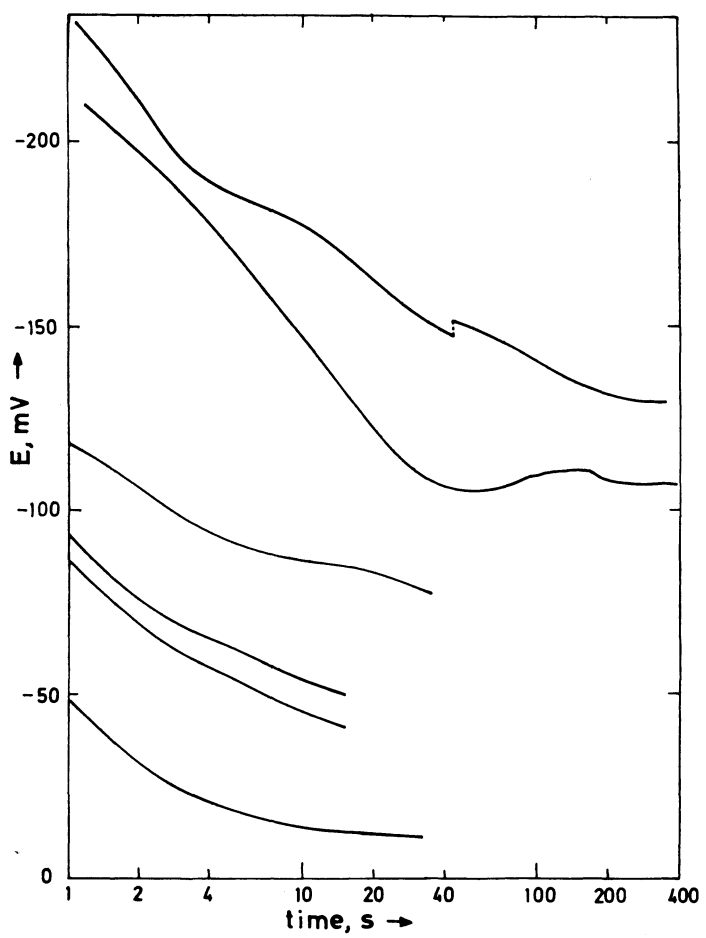

Fig. 3. — Decay of cathode potential by current interruption in industrial cells.

Several electrochemical methods were applied in order to clarify the nature of the overvoltage. Socalled double pulse measurements revealed that the charge transfer overvoltage was negligible, being only a few mV at normal cds. Similar results were obtained with the ac impedance method, but no clue was found as to the origin of the overvoltage.

However, other observations pointed in the direction of slow mass transfer. The sluggishness with which a constant potential was reached by current connection and interruption could be explained in this way. In agreement with theory, rectilinear plots of E versus the square root of time were obtained for the initial period after the current was connected. A solid piece of evidence of the establishment of a concentration gradient was found in AlF_3-rich melts at temperatures below the melting point of cryolite. Due to the enrichment of sodium fluoride, the cathode became covered by a solid crust of cryolite at above a certain cd. The same phenomenon was previously observed by Gadeau [10] and by Antipin and Vazhenin [11].

Further support to the mass transfer hypothesis was found in the fact that the overvoltage decreased by stirring, as shown in Figure 4 for steady state measurements. Somewhat surprisingly, the steady state data could be satisfactorily represented by Tafel lines, i.e. η versus log in plots. The content of alumina was found no to have any significant influence on the overvoltage within the limits of error. The overvoltage decreased markedly with increasing CR. In Figure 5 average Tafel lines for various CR's are depicted.

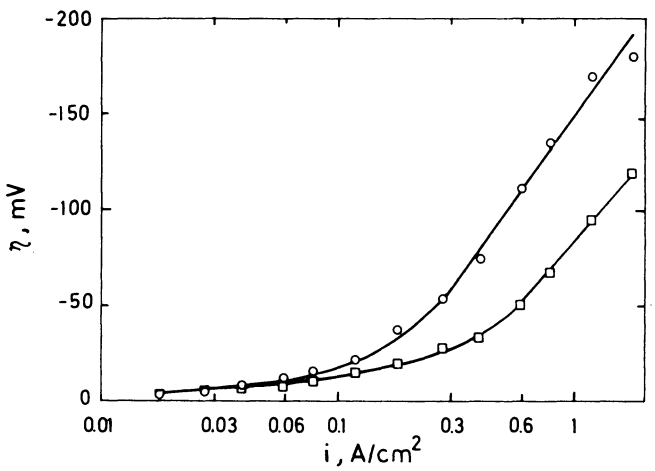

Fig. 4. — Cathodic overvoltage, steady state measurements.
o - Without stirring, □ - With mechanical stirring of the melt.

An explanation of this behaviour can be found in the dependance of the emf of an aluminium electrode on the CR of the melt. This relationship was investigated with the galvanic cell

$$\mathrm{Al} \left| \begin{matrix} \mathrm{NaF,\ AlF_3} \\ \mathrm{Al_2O_3\ sat} \end{matrix} \right| \begin{matrix} \mathrm{Al_2O_3} \\ \text{diafragm} \end{matrix} \left| \begin{matrix} \mathrm{Na_3AlF_6} \\ \mathrm{Al_2O_3\ sat} \end{matrix} \right| \mathrm{Al}$$

where the CR is varied in the left hand compartment. The emf of this cell can be expressed by

$$E = \frac{RT}{3F} \mathrm{Log_e} \frac{(a_{AlF_3})_1}{(a_{AlF_3})_2} \frac{(a^3_{NaF})_2}{(a^3_{NaF})_1}$$

Yoshida and Dewing [12] reported results for CR's from 0.5 to 4, and we have extended the measurements to higher CR's. The results are given in Figure 6.

Returning to electrolysis, a concentration gradient is set up near the cathode when current is passed, as indicated in Figure 7. Due to the increase in CR at the surface, the emf of the cathode becomes negative with respect to the potential at zero current. By

means of Fick's 1. law of diffusion, the concentration gradient and thereby the shift in emf can be estimated and compared with the experimental data.

$$\frac{i}{nF} = D\,\frac{c_{surf.} - c_{bulk}}{\delta} = D\,\frac{\Delta c}{\delta}$$

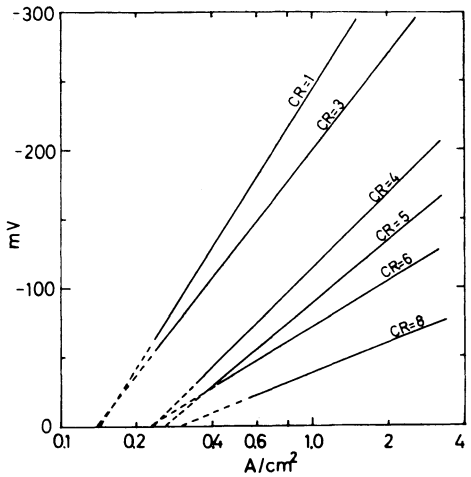

Fig. 5. — Average experimental Tafel curves at various CR's (mol NaF/mol AlF_3).

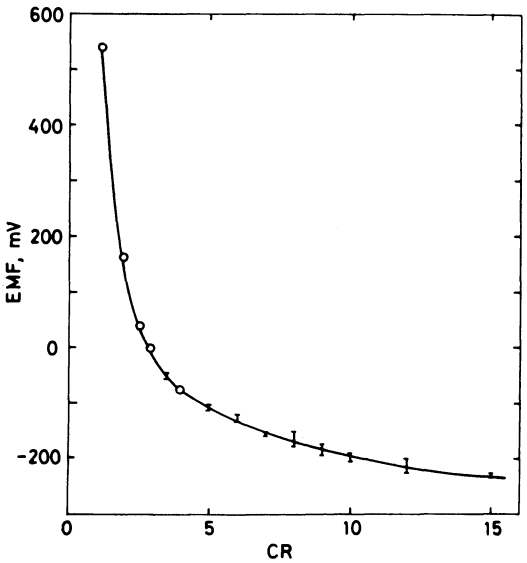

Fig. 6. — Emf of the galvanic cell Al|NaF, AlF_3, Al_2O_3 || Na_3AlF_6, Al_2O_3 | Al at varying CR (mol NaF/mol AlF_3) in the left hand compartment. o - Yoshida and Dewing [12], I - present work.

Provided the diffusion coefficient D and the diffusion layer thickness δ are constant, we see that the current i is proportional to the concentration gradient Δ c, given in mol/cm³. Plots of E versus log Δ c should then have the same shape as the experimental plots of E versus log i.

In order to test this hypothesis the emf data were replotted as a function of wt % NaF (wt % is approximately proportional to mol/cm³), and E versus log Δ c NaF curves were constructed for several starting compositions. This calculation could equally well be carried out with the concentration of AlF_3 as the variable. The result can be represented by practically straight lines, are shown in Figure 8. A comparison between the slopes of these curves and the slopes of the experimental Tafel lines is made in Table I.

TABLE I

Comparison between the slopes of experimental E vs. log i and calculated E vs. log Δc curves.

mol NaF/mol AlF_3	*Experimental mV/decade*	*Calculated mV/decade*
1	290	500
2	—	300
3	230	200
4	180	160
5	150	—
6	110	100
8	75	60

Except for the acidic melts the agreement is satisfactory. We can then conclude that the principal reason for the cathodic overvoltage is the accumulation of NaF near the

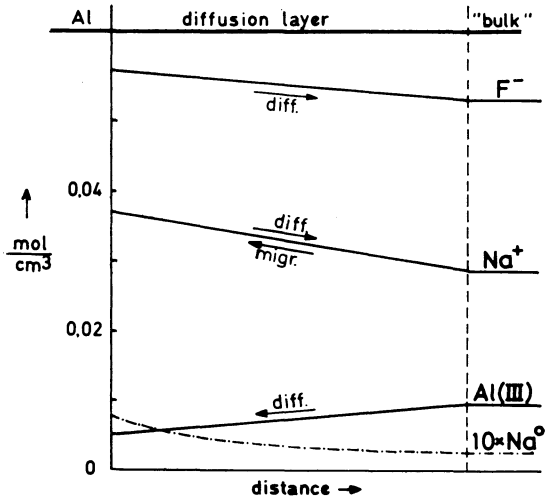

Fig. 7. — Schematic diagram of the concentration gradients near an aluminium cathode in a cryolite melt.

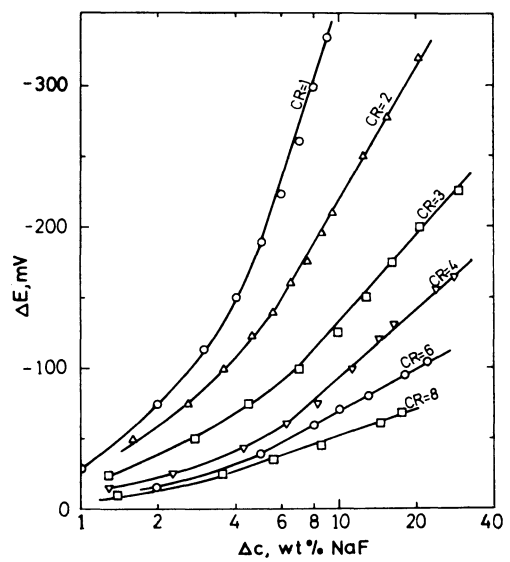

Fig. 8. — Semilogaritmic plots of emf versus changes in surface concentration of NaF calculated from the emf curve (see text).

surface, which changes the potential of the aluminium cathode in a negative direction. The emf shift is particularly great in acidic and neutral melts, which then exhibit higher overvoltage than basic melts.

However, this effect does not explain all observations that were made. By connecting one aluminium electrode to another which previously had been polarized cathodically, an appreciable current flowed. The amount of current was larger than what could merely be due to equalization of a concentration gradient with respect to CR.

Since we known that metal is soluble in the melt, it is reasonable to assume that also dissolved metal, including dissolved sodium, accumulate near the cathode surface. The sodium ion probably populate the electric double layer at the metal/melt interface, and it will have easier access to the cathode surface than the bulky AlF_6^{3-} or AlF_4^- anionic complexes. Discharge of sodium ions to form an intermediate dissolved species or a dispersion

should then be feasible, and it should become increasingly probable with increasing cd and overvoltage. At high cds sodium gas evolution can be observed at an iron cathode. Consequently, the following overall reaction sequences may take place concurrently

1. $$AlF_4^- \rightarrow Al^{3+} + 4\ F^-$$
$$Al^{3+} + 3\ e \rightarrow Al$$

and

2. $$3\ Na^+ + 3\ e \rightarrow 3\ Na_{diss.}$$
$$3\ Na_{diss} + AlF_4^- \rightarrow Al + 3\ Na^+ + 4\ F^-.$$

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