Abstract

Chronopotentiometric measurements with wire anodes have shown that the transition time is diffusion controlled up to 0.7% $\text{Al}_2\text{O}_3$ on gold and up to 1.6% $\text{Al}_2\text{O}_3$ on platinum. The diffusion coefficient is $(2.51 \pm 0.12) \times 10^{-5}$ cm$^2$ s$^{-1}$ (Std. Error) at 1020°C. At higher concentrations, formation of oxide films becomes the limiting factor; effectively, the electrodes are being anodized. On an anodized gold electrode, fluorine can be discharged. If the current density is high enough ($\sim 250$ A cm$^{-2}$), the discharge is diffusion controlled, and seems to correspond to 'free' (i.e. uncomplexed) fluoride. In pure cryolite, this is estimated to be about 5% of the total fluorine present (corresponding to $\sim 16\%$ dissociation of $\text{AlF}_6^{3-}$ to $\text{AlF}_4^{-}$); it is reduced by addition of $\text{Al}_2\text{O}_3$, and also by addition of $\text{AlF}_3$; it is increased by adding NaF.

Introduction

To the aluminum industry an instrumental method of determining the alumina content of molten cryolite in situ in the electrolytic cells would obviously be of immense interest, and this has led to work on chronopotentiometry. Both Richards and Russell(1) and Thonstad(2,3) have employed graphite anodes, and seem to have got good results. Nonetheless, graphite as an anode material has its problems. The surface is liable to be rough and/or porous, it is subject to air oxidation during introduction into and removal from the cell, and, above all, it is difficult to get a small, reproducible, surface area. Since alumina concentrations to be measured are high by most electroanalytical standards (2 - 8 wt%), with a corresponding need for high current densities, this is important.
An obvious way out of the problem is to try metal wire electrodes, which means, in effect, the noble metals since oxygen is going to be liberated. The temperature involved is above the melting point of silver. The work reported here was carried out with platinum and gold.

Initial work in the range 2 – 8 wt% Al₂O₃ gave most confusing results. At high current densities, transitions leading to anode effects were readily observed (i.e. the voltage rose to ~50V when the transition occurred, leading to destruction of the wire unless the current was promptly interrupted), but for Pt the transition time was independent of alumina content and with Au it decreased as the Al₂O₃ content went up. Reproducibility with Au was not good enough for the phenomenon to form the basis of an analytical method. In order to sort out the problem the work was extended to alumina concentrations below the range of industrial interest.

**Experimental**

Several circuits were used in this work, but their principle was the same. Capacitors were charged with a dc power supply and then discharged through a resistor by triggering a General Electric C30D SCR electronic switch. If the capacitor has capacity C and the total resistance in the circuit is R, then the time constant for the discharge is RC. Provided that RC \(\gg \tau\), the transition time, then the circuit is effectively constant current for the period of time required. The current itself is given by \(V/R\), where V is the voltage on the capacitor.

Depending on the capacity and voltage rating of the capacitors available, and the voltage of the power supply, different circuits can be constructed to suit the current density and transition time ranges desired. Two in particular were used: 6,000 µF charged to 40 V and 2,400 µF charged to 160 V. Current densities as high as 360 A cm\(^{-2}\) were obtained.

It is desirable (and indeed essential when dealing with anode effects where the voltage rises to 50 V or more) to have some means of cutting the flow of current when the transition is over. For the high-voltage circuit, this was done with a second SCR across the cell. The gate was connected through a Zener diode: as soon as the voltage rose to the level where the diode conducted the second SCR was triggered and the cell was shorted out. For the low-voltage circuit, the current was interrupted by an electro-mechanical relay which opened some 4 – 10 ms after the current was started.

In some of the very high current density work, the electrode was depolarized between pulses with a 4 mA cm\(^{-2}\) cathodic current. This did not seem to make any significant difference.
Transition times were read directly from an oscilloscope by eye. Although somewhat subjective, this was not a factor limiting the accuracy of the results. The current was measured by determining the voltage drop across a standardized resistor (either 1 ohm or 0.1 ohm), again with the oscilloscope, the voltage scale of which was calibrated.

Melts were made up by weight from Greenland cryolite and Bayer alumina, and were held in graphite crucibles which served as cathode. The anode wires were immersed 1 cm; their diameters (nominally 0.5 mm) were measured with a travelling microscope.

Results

To give an overview of the problem, Figure 1 shows values of \( iT^2 \) (where \( i \) is current density and \( T \) is transition time), interpolated for \( T = 1 \) ms, as a function of current density. A diffusion controlled region does exist at low alumina contents, terminating at about 0.8% \( \text{Al}_2\text{O}_3 \) for gold and 1.7% \( \text{Al}_2\text{O}_3 \) for platinum. Beyond that, it is apparent that some other process has intervened.

1. The Diffusion Controlled Region

Values of \( iT^2 \) are effectively independent of current density in the range 1-35 A cm\(^{-2}\). The potential - time curve can be analyzed by plotting potential against \( \ln (T^2 - t^2) \). The slope (= \( RT/nF \)) corresponds to \( n = 2.2 \). This treatment is based on the premise that the oxidation product is left on the electrode at constant activity, so that only the concentration of oxide enters the Nernst equation. If, on the other hand, one assumes that soluble \( \text{O}^\cdot \) is being formed then the proper function to plot is \( \ln (T^2/t^2 - 1) \). \( n \), however, is then found to be 3.4, which is completely inconsistent with the hypothesis. It is therefore apparent that a 2-electron oxidation of \( \text{O}^2^- \) is occurring.

Figure 2 shows a more detailed plot of the diffusion controlled region. The line is straight but does not quite pass through the origin, implying that the Greenland cryolite used has a small alumina content itself. The intercept of the line shows this to be 0.027% for this particular batch of cryolite. This may be compared with wet chemical analysis which gave 0.15% \( \text{Al}_2\text{O}_3 \). After displacing the origin to allow for the blank, the line may be represented by

\[
\text{wt}\% \text{Al}_2\text{O}_3 = (1.914 \pm 0.046) (iT^2)
\]

with a standard deviation of \( \pm 0.04\% \text{Al}_2\text{O}_3 \). The uncertainty of the slope is a standard error.
There is no significant effect of temperature over the $8^\circ$ range encountered, and there is no significant difference between the results with gold and platinum wires. It is therefore permissible to apply the Sand equation to determine the diffusion coefficient of oxide in the melt:

$$\frac{i t^2}{n FC} = \frac{(nD)^{1/2}}{2}$$

where $i$ is the current density ($A \text{ cm}^{-2}$), $t$ is the transition time (s), $n$ is the number of electrons involved (= 6 for $\text{Al}_2\text{O}_3$), $F$ is the Faraday (96,487 coulombs/g. equiv), $C$ is the concentration (g. mole/ml), and $D$ is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$). It should be noted that the product $nC$ is totally independent of any assumptions which may be made about the form in which alumina exists in the melt (e.g. as $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{OF}_2$, etc). For a solution containing 1 wt% $\text{Al}_2\text{O}_3$ at 1020°C, $C = 2.03 \times 10^{-4}$ mole/ml. Hence, with the constant in equation (1), $D = (2.51 \pm 0.13) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The uncertainty is a standard error. This value may be compared with $2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ given by Desclaux and Rolin (4) from rotating disk experiments on the rate of solution of alumina, and $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ found by Thonstad (2) from chronopotentiometric experiments with graphite anodes. His low value shows that his transition times were short in comparison with the present ones, and suggests that on a graphite electrode not all the surface is working. (A maximum of 75%.) This is readily understandable if graphite crystallites can only be attacked on the edges and not on the basal plane.

2. *Initial Oxide Film Formation on Platinum*

With platinum wires at low alumina contents, two separate transitions were observed. One is the diffusion controlled transition discussed above; the other comes in general at much shorter times. Figure 3 shows these other transitions plotted on the basis of $\log t$ vs $\log i$; the line drawn has a slope of -1, implying that $i^1/2$ is constant, rather than $i^1$ being constant as in the case of diffusion control. It is a quantity of charge, and is

$$i t = 735 \mu \text{coulombs/cm}^2 \pm 182 \text{ (Std. devn.)}$$
$$\pm 35 \text{ (Std. error)}$$

This represents formation of a surface film (presumably of platinum oxide) of constant thickness. Similar phenomena have been observed by Mayell and Langer (5) in aqueous solution. They detect several different types of film, but say that 760$\mu$C cm$^{-2}$ corresponds to a monolayer of PtO$_2$. Although their reasoning regarding the composition is open to question, there seems little doubt that the transitions observed correspond to the completion of the first layer of oxide; the number of oxygen atoms discharged per sq. cm is, however, more

355
than would be expected if the surface is covered with a single close-packed layer of oxygen ions. The radius of an oxygen ion is 0.132 nm, so that, in a hexagonal array, each ion covers 0.0603 mm², and one expects $1.66 \times 10^{13}$ atoms/cm². 735 μC cm⁻² corresponds to $2.30 \times 10^{15}$ atoms/cm². Either the oxygen ions are forming more than a monolayer, or the surface is rough with a roughness factor of 1.4.

At 7.5% Al₂O₃, the number of coulombs required to form the first layer of oxide seems to have gone up, and at the same time it is not quite constant, ranging from 1040 μC cm⁻² at 5 A cm⁻² to 1760 μC cm⁻² at 0.3 A cm⁻². The reason for this effect is not known.

3. Thicker Oxide Film Formation on Platinum

Figure 4 shows the results obtained with platinum at high alumina contents. Statistically, temperature and alumina content are not significant, and the slope of the log - log plot is −1.38 with a standard error of ±0.07. A value of −1.5 is thus within the 95% confidence interval (2 standard errors), and, since this is a value which can be interpreted, it has been adopted. The line drawn in Figure 4 has a slope of −1.5.

The situation thus is that three separate transitions have been identified. The first, on a log - log plot, has a slope of −1 (i.e. $\tau = \text{constant}$) and corresponds to the completion of the first layer of oxide. The second has a slope of −2 (i.e. $\tau^2 = \text{constant}$) and corresponds to diffusion control. The third has a slope of −1.5 (i.e. $\tau^{2/3} = \text{constant}$); to what is it to be attributed? The situation is shown in Figure 5 from which all points have been omitted for clarity.

The hypothesis is going to be advanced that the third transition is due to the discharge process being limited by the rate of growth of a relatively thick oxide film (i.e. many atomic layers thick). For such films (which are normally regarded as thin) the growth law when they are forming in the presence of an unrestricted supply of oxidant is often cubic, i.e.

$$kt = x^3$$  \hspace{1cm} (3)

or

$$x \propto t^{1/3}$$  \hspace{1cm} (4)
where \( x \) is the thickness of the film and \( t \) is time, and \( k \) is a constant. At large thickness (above \( >100 \) nm), the exponent changes from \( 1/3 \) to \( 1/2 \), leading to the normal parabolic law. (For discussion of the implications of these laws, see Hauffe\(^6\).) From equation (3), which it must be realized represents the maximum rate of film growth,

\[
\frac{dt}{dx} \propto x^2
\]

and

\[
\frac{dx}{dt} \propto kx^{-2}.
\]

This gives an infinite rate at \( x = 0 \), and the rate decreases as the thickness increases.

In the case of electrolytic oxidation with a constant current density, \( i \), the thickness of the film is proportional to the number of coulombs passed, so that

\[
\frac{dx}{dt} \propto i
\]

It is assumed that the transition at time \( \tau \) occurs because the rate of electrolytic oxidation has become equal to the maximum rate, so that

\[
\frac{dx}{dt} \propto i \propto kx^{-2} \propto (i\tau)^{-2},
\]

Hence

\[
i^3\tau^2 = \text{constant}
\]

or

\[
it^{2/3} = \text{constant},
\]

which is what is observed.

If this explanation is correct, it implies that the oxygen discharged at the anode is not liberated as gas but goes to form an oxide film. Diffusion control of the transition ceases when the alumina concentration becomes high enough that more oxygen is generated than the oxide film is capable of holding; after that, the transition time (for a given current density) becomes independent of the oxide content of the melt.

4. Initial Oxide Film Formation on Gold

With gold electrodes, no reproducible transitions, analogous to those for the initial oxidation of platinum, occur. Transitions (usually two separate ones) in the appropriate region are sometimes seen, but not always.
5. **Thicker Oxide Film Formation on Gold**

The results are shown in Figure 6. Again, a slope of -1.5 is obtained, but this time the values vary somewhat with alumina content. This variation is shown in Figure 1, where the values interpolated to 1 ms are plotted. The implication is that the inherent rate of oxide film growth is faster in high-alumina melts, and this can only be accounted for if the composition of the film is changing. The only change which can be envisaged is that some fluoride ions are being incorporated in the film, the proportion of them varying with alumina content.

At 8 – 9% Al₂O₃ the line can be extended up to very high current densities – over 300 A cm⁻². The least-squares slope is -1.39 with a standard error of ±0.04. Above about 100 A cm⁻² the transitions were anode effects.

**Discussion of Oxide Film Formation**

To postulate that oxide films are forming on platinum and gold at over 1000°C is unorthodox, since they are thermodynamically unstable, but it must be born in mind that the times are less than 5 ms and the current densities are correspondingly high. In 5 ms with \( i = 7 \) A cm⁻² a total of 35 mC cm⁻² are passed, and they will give an oxide film about 14 nm thick. With 200 A cm⁻² for 44 μs, a total of 8.8 mC are passed and the calculated thickness is 3.6 nm. These thicknesses are well within the limit of 100 nm below which the cubic growth law can be expected to hold.

The logic for accepting the oxide film hypothesis is as follows:

1. There are only three anodic processes possible - discharge of \( O^{2-} \), discharge of \( F^- \), and dissolution of Au (or Pt).

2. In the diffusion-controlled region, there is no doubt that \( O^{2-} \) is being discharged.

3. If it were being discharged as gaseous oxygen, substantial amounts of gas would be formed. For example, with platinum and 1.64% \( Al_2O_3 \), a transition time of 1720 μs was recorded at 21.1 A cm⁻². This corresponds to 36 mC cm⁻² and would generate a gas layer 10 cm thick. At the same time, the thickness of the diffusion layer \( = \sqrt{2Dt} \) is \( 3 \times 10^{-4} \) cm. Generation of this volume of gas would thus inevitably disrupt the diffusion layer and lead to a breakdown of the Sand equation, and yet no such deviation from the Sand equation is observed.

4. If the oxygen is not appearing as gas, it must be present either as an oxide film or in solution in the melt. The latter is inherently unlikely; oxygen is not appreciably soluble in cryolite.
and such a mechanism would not account for the difference in results between gold and platinum or for the behaviour of the transition outside the diffusion region.

5. There can be no question that, when sufficient alumina is present to be beyond the diffusion region, the discharge prior to the transition is of oxygen.

6. The law $i = \text{constant}$ is, as already shown, consistent with oxide film formation.

7. In melts with no added alumina, chronopotentiometry at high current densities does not lead to anode effects, and the wire dissolves. Similar experiments in melts with 2% or more alumina give anode effects and the wire dissolves very little. This implies that the surface of the electrode is physically changed when operating in the presence of alumina. Some barrier has been formed which prevents gold dissolving.

8. Since gold oxide ($\text{Au}_2\text{O}_3$) and platinum oxide ($\text{PtO}_2$) are different substances, the difference in behaviour of gold and platinum is readily accounted for. Tyurikov et al. have also found differences in the discharge of oxygen from molten carbonate on Au and Pt, although they talk in terms of adsorbed oxygen rather than relatively thick layers of oxide.

Fluorine Discharge

Under some circumstances, electrolysis on gold continues after the transition due to film growth limitation. It is not possible that oxygen is still the only ion being discharged; if it were, the diffusion controlled transition would be observed subsequently. Presumably, oxygen is still discharged as fast as the growing film can absorb it, but the rest of the current must either dissolve gold or discharge fluorine, and little gold dissolution is observed. (If the film formation hypothesis is correct, gold solution would be impossible, as Au ions are presumably already diffusing through the film at the maximum possible rate in order to permit the film to grow.) One therefore concludes that $\text{F}^-$ discharge is occurring.

At current densities less than about 100 A cm$^{-2}$ no further transitions were observed, but at very high current densities anode effects occur. This implies that no subsequent electrochemical process was available to carry the current.

For a melt containing 2% $\text{Al}_2\text{O}_3$, the situation is shown in Figure 7, which gives the observed line for film formation control, where the oxide diffusion control line would be if it were observed, and the
experimental results. At very high current densities ($i > 150 \text{ A cm}^{-2}$ or $\tau < 200 \mu\text{s}$) the line has a slope of -2, showing diffusion control. At lower currents, the product $i t^2$ increases rapidly, and below about 100 A cm$^{-2}$ the anode effects are no longer observed at all. Figure 8 shows how the product $i t^2$ varies with alumina content and NaF/AlF$_3$ ratio; values have been averaged over the range 200-300 A cm$^{-2}$. It is apparent that transition times become shorter as Al$_2$O$_3$ is added and longer as NaF is added.

The most plausible explanation of the results is that fluorine is indeed being discharged, but that not all the fluorine in the melt is available for discharge in times of the order of 100 $\mu$s. For many years models of cryolite melts in terms of partially dissociated AlF$_6^{3-}$ ions (and other complex species) have been invoked to explain the shapes of liquidus curves; the most common equilibrium proposed is

$$\text{AlF}_6^{3-} \rightleftharpoons \text{AlF}_4^- + 2F^-.$$ (11)

Without wishing to tie ourselves to this stoichiometry, we propose that the observed transitions are due to discharge of the 'free' fluoride only. On this basis, we can account for the following features:

1. At high current densities the transition is diffusion controlled; at lower currents and longer times the 'free' fluoride is replenished by dissociation of complexes (or, possibly, the diffusion is disrupted by gas-bubble formation). According to Paunovic(8) "a decrease in the product $i t^2$ with current density is a diagnostic criterion for the occurrence of a prior chemical reaction, e.g. dissociation of a complex".

2. Addition of NaF increases the supply of free fluoride, addition of Al$_2$O$_3$ reduces it, presumably by forming complexes of the type AlO$_n$(F$^{n-1}$). It looks as if the 'free' fluoride is being titrated with Al$_2$O$_3$, with an end point around 7% Al$_2$O$_3$ for an NaF/AlF$_3$ molar ratio of 3.0, and around 8.5% Al$_2$O$_3$ for a ratio of 3.9.

3. Numerical interpretation is reasonable. For a ratio of 3.0, extrapolation to zero alumina (where the transition cannot be observed because of the absence of the protective oxide film) gives $i t^2 = 2.8 \text{ A cm}^{-2} \text{ s}^2$. From this must be subtracted a correction for the formation of the oxide film, which is taking all the current initially and some of it subsequently. If the first process of two successive reactions is diffusion controlled the proper procedure(9) is to subtract $i t^2$ for the first transition; in this case this will not be accurate, but the error will not be serious for the present purpose. We therefore subtract 0.9 A cm$^{-2}$ s$^2$ to give $i t^2 = 1.9 \text{ A cm}^{-2} \text{ s}^2$. Using the Sand equation (2), and with an estimated value of $D = 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, C is found to be 0.0031 moles F$^-$/ml. The density of cryolite at 1020°C is 2.077 g/ml, so that 1 mole (210 g) occupies 101 ml, and the same volume contains 0.32 moles 'free' F$^-$. In terms of equilibrium (11) this represents

360
16% dissociation of $\text{AlF}_6^{3-}$. A decrease of a factor of 2 in the estimate of D would increase the calculated dissociation to 23%, but it is unlikely that D for 'free' F is as low as $2.5 \times 10^{-5}$ cm$^2$ s$^{-1}$ since that is the value found for $\text{Al}_2\text{O}_3$ which is present as bulky $\text{AlOF}_n$ complexes.

Gilbert, Mamantov, and Begun have published work on the Raman spectrum of molten cryolite from which they deduce that the $\text{AlF}_6^{3-}$ ions are about 25% dissociated. In view of the totally different type of experiment and the different assumptions made in working out the results, the agreement is good enough to lend strong support to the view that we are observing transitions due to the discharge of 'free' F, and that the latter does have a real physical existence.

Although we have not been able to give any quantitative treatment, to explain the departure from the diffusion controlled line in Figure 7 requires a lifetime for $\text{AlF}_6^{3-}$ ions of the order of a millisecond.

The lines in Figure 8 could form the basis of an analytical method for determining alumina in molten cryolite, but the sensitivity of the calibration to the NaF/AlF$_3$ ratio (and probably also to CaF$_2$ content) limits its attraction.

References

(1) Richards, N.E., and Russell, E.R. Paper presented at ECS meeting, New York, May 1969.

(2) Thonstad, J. Electrochim, Acta, 14, 127-34 (1969).

(3) Thonstad, J. Light Metals 1974, vol 1, pp 137-149. Met. Soc. AIME, ed. by H. Forberg.

(4) Desclaux, P., and Rolin, M. Rev. Int. Hautes Tempér. et Réfract., 8, 227-236 (1971).

(5) Mayell, J.S., and Langer, S.H. J. Electrochem. Soc., 111, 438-46 (1964).

(6) Hauffe, K. Oxidation of Metals, New York, Plenum Press, 1965.

(7) Tyurikov, G.S., Vasilistov, N.P., Silakov, A.V., and Pashkov, Yu.M. Elektrokhimia, 3, 309-12 (1969).

(8) Paunovic, M. J. Electroanal, Chem., 14, 447-74 (1967).

(9) Berzins, T., and Delahay, P. J. Amer. Chem. Soc., 75, 4205-13 (1953).
1. Plot of $i \tau^{3/2}$ (interpolated for $\tau = 1$ ms) against wt % Al$_2$O$_3$. Temperature 1018-1026°C.

2. Diffusion controlled transition times ($\tau$) as a function of alumina content.

3. Initial oxide film formation on platinum. The transition time ($\tau$) is proportional to $1/i$. 

(10) Gilbert, B., Mamantov, G., and Begun, G.M. J. Chem. Phys., 62, 950–55 (1975).
4. Transition time as a function of current density for alumina contents above 1.96% (Pt wires). Line drawn has a slope of -1.5.

5. Transition times as functions of current density (Pt wires - schematic).

6. Transition times as functions of current density for alumina contents above 0.99% (Au wires).

7. Transition times as a function of current density for melts containing 2% \( \text{Al}_2\text{O}_3 \) (Au wires).
8. Transitions at Au anodes at current densities 200–300 A cm$^{-2}$. 

---

364