Influence of Heat Transfer on Anode Reactions When Electrowinning Metal from Its Oxides Dissolved in Molten Fluorides

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Abstract

A wide range of oxides dissolve in melts containing their molten fluorides or other halides and some of these melts present a path for electrowinning the metal when using carbon anodes. While aluminum smelting is the most notable commercial example, an analogous process has also been developed for electrowinning rare earths, while it has also been demonstrated that alkali earth metals can also be similarly produced. Interest in the anode reaction mechanisms has been revived during the last decades following the development of more sensitive gas analysis instrumentation that can detect low levels of co-evolved perfluorocarbons (PFC’s) which have exceptionally high global warming potential. These have been found to occur at substantially lower anode potentials than expected from the conventionally assumed PFC formation reaction

\[ \text{Al}_2\text{O}_3 + 2\text{Na}_3\text{AlF}_6(l) + 9/2\text{C} = 4\text{Al} + 3\text{CO}_2(g) + 3/2\text{CF}_4(g) + 6\text{NaF}(l) \]

This is supported by experimental verification of the intermediate. The entropic energy deficit is linked to the buildup of the resistive or passivating intermediate fluoride film on the carbon anode surface which is capable of generating Joule heat enabling the various parallel reactions to occur with or without an anode effect.

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Heat Transfer During Electrowinning

Vogt drew an appropriate analogy between heat transfer gas evolution at an electrode and boiling, which provides the entropic energy (T ΔS) for the phase transformation the final gaseous state. Generally the energy gaps highlighted in Table I are also consistent in magnitude with those typically associated with that required for a phase transformation such as boiling (T ΔS).

For an electrochemical cell operating at an electrode potential of $E_{\text{anode}}$ and in the absence of a resistive film on the electrode surface, the energy requirement for the gas release as given by the difference between the value listed as $E_{\text{isothermal}}$ in Table I and the operating potential needs to be provided by absorption of heat from either the electrode or the electrolyte. (This is based on arbitrarily setting the reversible potential of the metal deposition reaction at 0 V.)

Hence we can express the thermal energy requirement (Q) for the specific reaction by the relationship:

$$Q_{\text{reaction complete}} \text{(Js}^{-1}\text{m}^{-2}) = i_{\text{reaction}} \times (E_{\text{isothermal}} - E_{\text{anode}}) \quad [3]$$

where $i_{\text{reaction}}$ is the current density (A/m²) being sustained by that reaction.

In commercial electrowinning cells most of the heat required to sustain the operating temperature is generated by the ohmic resistance of the electrolyte within the cell making the electrolyte hotter than the electrodes, thus providing a driving force for both heat transfer and the dissolution of the replenishing additional oxide.

Thus we have the following relationship applicable for provision of the thermal energy

$$Q_{\text{reaction}} \text{(Js}^{-1}\text{m}^{-2}) = h_x \times (T_{\text{electrolyte}} - T_{\text{electrode surface}}) \quad [4]$$

where $h_x$ is the heat transfer coefficient. While no measurements exist for the value of the driving force ($T_{\text{electrolyte}} - T_{\text{electrode surface}}$) it would be less than the operating “superheat” of the electrowinning cell electrolyte which is ($T_{\text{electrolyte}} - T_{\text{liquidus}}$) since cell operation, requires the frozen electrolyte layer be maintained on the sidewall of the cells to prevent leakage through the physical joints involving different materials of construction of the cell lining. The “superheat” seldom exceeds 10°C. Any difference in the temperature gradient at the anode interface is expected to be toward a reduction due to the combination of interfacial depletion of the Al₂O₃ solute and also the competing heat conduction through the anode carbon. While no measurements exist for the heat transfer coefficient at a gas evolving electrode either, the average value of $h_x$ determined in aluminum smelting cells for electrolyte flowing against the sidewall is about 670 Js⁻¹m⁻² with the maximum value for turbulent zones being less than twice that. Hence a value in this band is to be expected at the anode interface. In self-heating smelting cells, the anodes also are a source of heat loss and this requirement must be satisfied by the same electrolyte/electrode heat flux. Based on measurements and cell modelling the typical electrolyte–electrode heat flux required for anode heat loss is about 5 kW/m², ignoring the reaction requirements.

Most of the fundamental data generated for mechanistic interpretation has been obtained in the laboratory cells that have substantially different heat and mass transfer conditions through being externally heated with very large electrolyte volume at high superheats using cell designs that have a high heat capacity reservoir. Furthermore the duration of laboratory experiments is short and often transient. With these differences the relevance of heat transfer can be significantly different in lab based studies and this needs to be taken into account in mechanistic interpretations for operating systems.

### Studies of CO₃ Evolution from Al₂O₃ –AlF₃ – Alkaline Fluoride Systems

There have been numerous measurements of the over potential in electrolytes used for aluminum electrowinning and using different carbon electrode structures. Significantly all of the interpretations have been based on the assumption that carbon dioxide is the only anodically formed product prior to the anode effect, and the general conclusion drawn has been that the anode overpotential obeys Tafel’s law prior to the onset of concentration polarization at higher current densities. Haupin used current interruption technique and oscillographic response recording, and found at higher current densities where deviation from Tafel behavior occurred there was evidence of formation of a resistive film on the anode surface in that zone. This film formation was subsequently supported by Zuca et al. and also the studies of Frazer and Welch. Dewing and van der Kouvée’s data gave strong evidence of two electrode processes in the CO and CO₂ potential zone while the data approached conformity with Tafel behavior. Re-plotted the data of both Zuca et al. and Haupin on a semi-logarithmic current basis also gives a distinct inflection Tafel curve at low current densities.

Key features of our anode overpotential measurements presented in this paper have been described earlier. The strategic positioning of the Luggin capillary ensured all contributions other than those arising from overpotential and any electrode surface film were excluded. Simultaneous variations in both current and voltage were achieved from overpotential and any electrode surface film were excluded.
by altering the power available to the cell by the use of a rheostat. Handpicked Greenland cryolite was used as the base solvent to avoid introduction of any impurities, while the highest purity grades of LiF, AlF₃, CaF₂, and Al₂O₃ were used after drying to ensure absence of any moisture. As an added crosscheck, the electrolyte was also subject to pre-electrolysis using an auxiliary electrode.

Typical overpotential curves resulting from increasing the applied power, and then subsequently reducing it are presented in Figure 1 for a solvent electrolyte of Na₃AlF₆ + 8.5% CaF₂ containing 9.2 wt% of dissolved Al₂O₃ at 982°C. This data exhibits “hysteresis” a feature commonly observed for either new electrodes having their first electrolysis cycle, or for an electrode after a significant pause at the rest or reversible potential. While the decreasing current/power curve tends toward more classical Tafel behavior all curves invariably showed a small deviation/inflexion in the current density range 0.05–0.1 A/cm². The current density for the inflection was found to increase with temperature, and hence heat transfer conditions, as illustrated in Figure 2.

In studying the overpotential linked with the transition to PFC emissions, a series of measurements were performed at different alumina concentrations at 1012°C under conditions that enabled determination of the steady-state current and voltage conditions as the applied power to the cell was incrementally increased. In each of the curves measured and illustrated in Figure 3 the anodes ultimately went on a classical anode effect, these occurring at the point indicated by the break in the curve to a dashed line. It is seen in each of these curves that the electrode potential at high current densities showed deviation from the apparent Tafel behavior at all alumina concentrations, but the deviation was at a rate that is inconsistent with it being solely due to oxide depletion at the interface. However the data also shows alumina concentration in the electrolyte also plays a part in the increase in anode potential, even though none of the curves display a shape consistent with progressing to a classical limiting current.

It is also evident that the magnitude of the “apparent overpotential” at which the anode effect occurred was substantially in excess of that necessary to directly evolve CF₄(g) according to the equation given in the abstract. Based on the experimental conditions these recorded “overpotential” curves can include an ohmic contribution for any resistive intermediate layer formed at the electrode interface as found by Haupin. Such a layer would also provide additional heat that would enable release of the gaseous product–thus delaying the onset of an anode effect.

Complimentary Gas Analysis Studies

The inflection in the anode polarization curves below 0.2 A cm⁻² in Figs. 1 and 2 suggests that there is a change in anode product such as a transition from CO to CO₂. We have performed three separate sets of experiments whereby the anode gas product as a function of temperature, current density, carbon quality and alumina concentration can be cross-linked to changes in anode potential. Two of the experiments conducted include the cell transition to a sustained anode effect.

Figure 4 presents results for the gas analysis when using anode samples with three different qualities when characterized by the standard ISO-N804 method for the carbon dioxide reactivity. The cell design and operating conditions enhanced heat transfer to the electrode surface. Electrolysis was conducted at different current densities...
using an electrolyte containing 10% excess AlF₃, 5% CaF₂ and 5% dissolved Al₂O₃ at 975°C. As evident from the results, the reaction product is influenced by the material used.

Irrespective of anode quality CO(g) was always the dominant product at current densities below 0.2 A/cm². This low current density dominance can only be explained by substantial direct electrochemical formation of CO even though heat-treatment and consequential reactivity also have a major impact on gas composition.

A second sequence of gas analyses were performed in a 75A laboratory cell designed to simulate a smelting cell and simultaneously minimize contact of the evolved gases with any reactive material so that an oxygen balance could be performed. During electrolysis the oxide concentration was depleted to a point where an anode effect occurred in each experiment. Figure 5 presents the trends in the gas analysis during one such electrochemical depletion where the electrolyte initially contained 6 wt% Al₂O₃ using a traditional solvent electrolyte that gave a liquidus temperature of 959°C.

Because of the cell’s ohmic resistance and the high current applied, the temperature increased to above 990°C during electrolysis, thus substantially increasing the superheat and the driving force for heat transfer. The continuous oxygen balance being monitored showed the faradaic efficiency was constant at 84.5±1.0%, and therefore the increased proportion of CO(g) as evident in the 15 minute period prior to the Anode effect and shown in Figure 5 can only be explained by electrochemical co-evolution. During the depletion of the alumina the cell voltage increased more than 0.25 V which can only be attributed to changing interfacial potential at the anode.

The third gas analysis test sequence was performed on two operating smelting cells where the alumina additions were stopped. Anode gas samples were taken for analysis at 30 min intervals until an anode occurred and thereafter the frequency of sampling increased. Some results are presented in Figure 6 and the analysis shows that during normal electrolysis the anode gas fluctuated around 84% CO₂ and 16% CO. However in the 30 min period before the anode effect a measureable decrease in CO₂ content was observed. In the period after the anode effect onset the gas composition stabilized near 68% CO, 18% CO₂, and 14% CF₄. These values are similar to those reported by Holliday and Henry after adjusting for contaminants.

The trends in anode gas composition prior to anode effect indicate there is a change in electrochemical process that could involve co-evolution of CF₄ and extra CO as illustrated by the equation in the abstract.

Experimental Determination of PFC Transition Potentials

Using very fast linear sweeps Calandra et al. identified peaks consistent with the COF₂ formation potential in both the system Na₂O–NaF and Al₂O₃–NaF–AlF₃. They also proposed surface passivation with a fluorocarbon intermediate was the primary cause of an anode effect. More recently a C–F intermediate has also been identified on the anode surface. These findings are consistent with the finding that a resistive film formed on the electrode surface. The thermodynamic predictions of Table I indicate that only a limited increase in anode potential from that traditionally used would be needed for this to occur.

Figure 7 presents the graphical output plotting data recorded at 2 kHz when using the voltammetric technique we developed for electroanalytical purposes. In that research the total surface of the small (ca. 0.75 cm²) graphite electrode was vertically oriented in order to prevent blockage by any gas bubbles formed electrochemically, and the graphite crucible counter electrode had a large surface area, so that
it did not polarize. The cell had a circuit resistance of $0.3 \pm 0.02 \Omega$. This arrangement enabled us investigate changes in anode potential for different alumina concentrations by applying the relationship

$$V = E_{\text{Nernst}} + \eta_{\text{anode}} + iR_{\text{circuit}} + iR_{\text{anode surface film}}$$  \[5\]

to the cell voltage sweeps over a $5 \text{ V}$ range, at a sweep rate of $20 \text{ V/s}$, and then reverse to the starting potential at $200 \text{ V/s}$. The solvent electrolyte used was of similar composition to that commonly used in smelting in electrowinning. The study encompassed the dissolved oxide range normally experienced in smelting cell, ranging from 0.75 to 4.55 wt% $\text{Al}_2\text{O}_3$.

The data clearly shows a change in electrode process occurring at $1.82 \pm 0.25 \text{ V}$ that is initiated by depletion of alumina when using the low oxide concentration solutions. The only other oxidisable anion in the electrolyte is the fluoride anion, which appears to have a fast charge transfer reaction as displayed by the fast rate of change in current when the alumina concentration is low. However, consistent with Calandra et al.\textsuperscript{15,16} and the resistive film theory, passivation of the electrode surface subsequently occurs. Based on reported surface areas of the type of carbon used, the amount of charge passed between the time of initiation of a second anod discharge and completion of the passivation to its residual current of approximately $30 \text{ mA}$ would account for less than five atomic layers. For the higher oxide concentrations the higher rate of co-discharge of the oxy anion retards the passivation as is evident from the current decreasing curve in the forward sweep. There is also significantly higher thermal energy input through the higher current density and resistive voltage drop which is concentrated at the electrode interface for the higher alumina concentrations. This gives further strong support for the important role heat transfer plays in the reaction kinetics. Once the electrode tends to a high degree of passivation, the drop in current results in very limited heat generation to aid the evolution of gas and the resulting low current density at high voltages is similar for all alumina concentrations. During the reverse sweep, anion oxidation increases again at a voltage below ca. $2.4 \text{ V}$ at a similar rate for all alumina concentrations. This voltage is significantly below the potential required for $\text{CF}_2$ but within the band co-evolution is enabled and therefore necessitating co-oxidation of oxy-anions.

Given the limited accuracy of the thermodynamically predicted reaction potentials the data gives strong support for the formation of $\text{COF}_2$ as the initiating species for PFC emissions, but a chemical reaction is likely to follow while forming the final product. The data also supports heat transfer being a controlling step in the release of oxidized anions from the carbon surface as illustrated by the ability to pass higher current during co-evolution of fluoride anions when the alumina concentration is high.

Figure 8. Schematic representation of the equivalent circuit for current flow through a multi-electrode aluminum smelting cell.

**Co-Evolution of PFCs During an Al Smelter Cell Operation**

The situation is more complex in modern multi-electrode aluminum smelting cells which operate under different energy input constraints. Cells in a potline are interfaced in series and operated at constant current, thus the total current for each cell is constant. However while the voltage between the connection of each anode to the anode beam and common metal pad is the same for each current pathway, the current distribution for each anode to metal pad pathway is dependent on the magnitude of the individual resistances and potential gradients of each anode path illustrated by the equivalent circuit presented in Figure 8. Resistances of individual anodes change independently with time in cell because of their electrochemical consumption which is staggered for practical reasons. Also work practices and spatial conditions can result in varying alumina concentrations, localized temperature and differing inter-electrode distances all contributing to differing electrolyte resistances. Any of these can bring about changes in both the electrode overpotential and the current distribution between individual anodes and the metal pad. Equation 5 is therefore modified as follows for each anode to metal pad pair

$$V_{\text{anode to metal pad}} = E_{\text{Nernst}} + \eta_{\text{anode}} + i_{\text{anode}}(R_{\text{anode i}} + R_{\text{electrolyte-bubble layer i}} + R_{\text{anode surface film i}})$$  \[6\]

with the constraints that

$$i_{\text{cell}} = i_{\text{line}} = \sum I_i$$  \[7\]

The cell voltage ($V_{\text{cell}}$) used for alumina feeding and cell heat balance control (directly or indirectly) is given by the relationship

$$V_{\text{cell}} = V_{\text{anode to metal pad}} + i_{\text{cell}}(R_{\text{cathode}} + R_{\text{external circuit}})$$  \[8\]

Consequently it becomes extremely difficult, if not impossible, to know the potential gradient existing at any individual anode. Cell voltage changes are a consequence of changes in individual condition for each anode to metal pad pathway. Normally the combination of average alumina concentration, and a cell’s ohmic resistances are set so that the resulting voltage maintains the target heat balance as well as the average current carried by each anode being the same during their life cycle. For modern designs and operating conditions this results in the combination of Nernst potential and average anode overpotential being in the band of 1.7–1.8 V. These constraints are expected to result in a fairly even current distribution except for the 30 to 48 h period following individual anode replacement. Since the alumina concentration affects the anode potential and electrolyte resistance, in order to maintain close to the optimum value and simultaneously generate a signal for control the feed rate of the alumina to the cell is usually modulated by increasing the feed rate beyond the predicted consumption rate to give an estimated concentration increase (and hence lower the overpotential), and then lowered a similar amount by lowering the consumption rate whilst monitoring the cell voltage change.

Based on this strategy we have monitored the composition of the gases emitted from an operating smelter cell during normal operation, and then following a stepwise reduction in the alumina concentration as well as for other process changes.\textsuperscript{13} A sensitive FTIR analyzer that could detect PFC’s in the parts per billion was used. Following the alumina concentration reduction the cell gas composition changed...
from having no PFC co-evolution, to a situation where PFC's appeared as shown in Figure 9. The PFC emission rate is seen to cycle with variations in dissolved alumina concentration induced by the modulation of the alumina feeding as is evident from aligning with the operating feeding cycle. The increase in cell voltage is primarily attributed to a change in average anode potential, which was less than 50 mV. The PFC co-evolution ceased after raising the alumina concentration through increasing the duration of the over-feed to revert to the same average alumina operating concentration. This supports the transition voltage for co-evolution being close to that predicted by the thermodynamic analysis in Table I and the analysis of voltage sweep data presented in Figure 9.

PFC Co-Evolution in Other Molten Salt Systems

As part of wide-ranging studies of electrowinning and electrodeposition from oxide halide melts studies were made of the composition of the anode gases evolved for varying current densities and anode potentials changes in a MgF2:2LiF melt saturated with MgO and for a 2NaF:3LiF + 10 mole% NiF2 melt saturated with NiO when using a graphite anode. The alkali fluorides were added to both stabilize the metal fluoride melts and enable lower operating temperatures even though this was at the expense of significantly lowering the oxide concentration to an unknown value. The study was conducted in the temperature band 627 to 925 °C and electrochemical measurements were conducted under both potentiostatic and galvanostatic control with the anode potential changes being measured against the respective metal/metal oxide reference electrode. A Fischer dual column gas chromatograph fitted with an integrator enabled semi-quantitative analysis of the gases evolved although it had low sensitivity to PFCs.

Figures 10 and 11 present two of the many measured current changes as the anode potential increased from rest at a scan rate of 240 mV/min. During each measurement the recorded current range scale was changed by an order of magnitude to ensure maximum sensitivity to the decreasing current level.
sensitivity. Simultaneously gas analyses were recorded, and supplementary experiment also conducted with more prolonged electrolysis to establish characteristic trends and these are also annotated on Figure 10.

Consistent with the thermodynamic analysis presented in Table I the electrolysis in the MgO-MgF2-LiF system starts at approximately 1.4 V, and in the data zone between this voltage and approximately 1.9 V the anode process tends to obey Tafel law. In Figure 10 there is clear evidence of moving into a concentration polarization zone at approximately 1.94 V but this is absent in Figure 11 where there is a significantly higher dissolved MgO concentration, and better heat transfer conditions. The anode gas formed when electrolysing in this zone was dominantly carbon dioxide and, like aluminum smelting electrolytes, always at a concentration in excess of that predicted from the thermodynamic equilibrium. It is evident the discharge of a second anion initiates near or just above 2 V. This change was always accompanied by an increasing proportion of carbon monoxide and greater fluctuations in the current signal. The gas composition tends to reach approximately equally molar whenever there is a change in electrode condition that reduces the available electrode surface area. A passivating peak occurs near 2.7 V (Figure 10). In this instance the process could correspond to the onset of parallel co-evolution of CF4. During galvanostatic electrolysis at higher current densities the cell voltage tended to increase and also fluctuate but significant amounts of CF4 were detected.

Studies in the nickel oxides nickel fluoride alkali fluorides system were more challenging because thermodynamically the metal extraction reaction did not require an electrochemical potential to be applied. The experimental design minimized contact of the electrode with the electrolyte excepting when experiments were being performed. Trial measurements of the gas analysis indicated that little if any reaction was occurring without electrolysis, but as a precaution surplus nickel oxide was present in the electrolyte. The curves show numerous similarities to those for other molten oxide fluoride systems (Figure 12).

While an electrode process change might be expected at about 0.5 V, there was no sign of concentration polarization, although the signal became increasingly noisier. The transition to fluoride co-discharge in this zone would be consistent with an increasing passivation, and the peak formation. The characteristic current spiking occurring above 1 V can be explained by vacant sites being created by removal of the passivation fluoride layer through gas release. This is consistent with the changes in gas analysis that was observed during these and both potentiostatic and galvanostatic electrolysis whilst analyzing the gas. Like the other systems, at low overpotential and lower current the proportion of carbon dioxide exceeded that expected from thermodynamic equilibria. Again based on heat transfer this is expected since CO2 required less thermal energy for gaseous product release than if CO were being formed. Beyond the potential whereby COF2 (and hence CO + CF4) can be coevolved there is always an increase in

Figure 11. Recorded sweep current voltage curves for anode potential changes in a MgO saturated MgF2-LiF melt at 912°C for a graphite electrode with 3 different surface areas (B = 4 cm², C = 1 cm² and 0.4 cm²).

Figure 12. Current voltage scans at 125 mV/min for a graphite electrode in a 2NaF:NiF2 + 10% NiF2 melt saturated with NiO. (Lower curve increasing volts at 747°C, Upper curve decreasing voltage at 928°C).
the CO(g) concentration with it becoming the dominant gas at higher electrode potentials.

Figure 13 presents general pattern of gas analysis when linked to the polarization curve and/or the galvanostatic operation when generating the gas stream for analysis. The dashed polarization curve represents a typical curve similar to those illustrated in Figure 11. The amplitude of the second peak varies with process conditions. Under potentiostatic control the solid double arrow lines represent typical variations that can occur in the anode potential. Operating at constant current induces significant swings in the potential after a time as the conditions of the electrode surface coverage varies and can move rapidly to the other side of the peak and then oscillate to the rising curve that initiates after approximately 1.5 V.

This trend is illustrated by the horizontal dashed lines with the double arrows. When electrolyzing at current densities near the initial peak the cells invariably went to an anode effect within a few minutes. Under galvanostatic conditions the electrode would invariably have an AE once the potential exceeded 1.5 V. During an anode effect the CO2 content would typically drop below 50\% while the CF4 content would range from 15 to 20\%.

**General Discussion**

The results arising from the various studies that have been conducted highlight several important points.

The first is that while CO can be evolved as the dominant product at low current densities, whenever the interfacial electrode potential exceeds the reversible value that enables both CO and CO2 to be formed, the rate of formation of CO2 exceeds the thermodynamic equilibrium proportion. However as the experimental design or conditions favor enhanced interfacial heat transfer, the CO content of the gas moves closer to that expected for equilibrium conditions.

Once the electrode potential has risen above that required for formation of COF2(g) co-oxidation of both oxides and fluorides ions occurs and reaching this state does not solely require concentration polarization through oxide depletion. Current density, structure of the carbon, partial surface coverage, and temperature can also be contributors to the interfacial potential gradient.

Once enabled, the kinetics of the charge transfer for the fluoride anion co-oxidation is fast, but the subsequent steps to achieve gas release mechanism are slow except under conditions that give rise to high interfacial energy generation. This leads to passivation of the anode surface resulting in a rapid decrease in current when under voltage control. During the formation of the passivation layer when at constant current the ohmic resistance increases with surface coverage so the increased interfacial voltage drop contributes Joule heat that becomes available thermal energy required for the gas release. This is particularly evident in the curves presented in Figures 12 and 13 where at a given current density there are three different voltage states possible. Transitions between them can occur because of the successive buildup of resistance layers and removal as a consequence of the fluctuating joule heat.

Normally under galvanostatic conditions the increase in concentration polarization through depletion of the oxide initially increases the potential, but when combined the effect of the buildup of the passivating fluoride layer causes an increase in the interfacial voltage to the extent that arcing will occur causing a breakdown of the layer. While this phenomena was not visually observed in the studies, rapid and substantial increases in voltage did occur, and the arcing is readily observed in smelting cells.

**Importance of Energy Transfer and Reaction Mechanisms**

Exemplification of this focuses on aluminium smelting electrolytes, since more data exists, but because of the similarity trends observed it would be applicable to all cases.

A diverse range of structural mechanisms has been proposed for NaF-AlF3-Al2O3 melts based on a range of measurements and assumption. There is strong support that the solvent electrolyte is dominantly an ionic mixture of Na+\(^+\), AlF6\(^3−\), AlF4\(^−\), and F− but the dissolution of Al2O3 proceeds via an endothermic reaction such as either:

\[
\text{AlF}_6^{3−} + \text{Al}_2\text{O}_3(s) ⇌ 3 \text{AlOF}_2^{−} \quad [9]
\]

or

\[
2\text{AlF}_6^{3−} + 2\text{Al}_2\text{O}_3(s) ⇌ 3\text{Al}_2\text{O}_2\text{F}_4^{2−} \quad [10]
\]

While the oxide anion existing in the molten electrolyte is predicted to be as complex as AlOF2\(^−\) or Al2O2F4\(^−\), irrespective of the structural species they will have some dissociative equilibrium for releasing oxide anions. For convenience of discussion we work on the basis of the anion being AlOF2\(^−\). Based on accepted dissociation constants\(^2\)\(7\) for typical industrial electrolytes used, Na+ is the dominant cation at a concentration of approximately 6 g mol/l while the concentration of free F− anions would be 1.2 g mol/l and the oxyanion concentration being approximately half of that.

The carbon being oxidized has a basic graphitic structure although it is often disordered giving a higher surface area and reducing the energy required for oxidation.

CO(g) formation involves oxidation and bonding to the carbon of an oxyanion, structural rearrangement to form an independent molecule, energy transfer to form the gaseous species and its release.

\[
\begin{align*}
\text{Step 1} & \quad \text{AlOF}_2^{−} + x \text{C} ⇌ \text{C}_x\text{O} + 2e + \text{AlF}_2^{+} \\
\text{Step 2} & \quad \text{C}_x\text{O} \rightarrow \text{CO}_{(ad)} + (x − 1)\text{C} \\
\text{Step 3} & \quad \text{CO}_{(ad)} + Q_{CO} \rightarrow \text{CO}(g)
\end{align*}
\]

where Q\(_{CO}\) is the magnitude of heat to be transferred beyond that provided through the polarization and any Joule heat from the resistive surface layer.

If the first step is rate limiting Tafel behavior would be expected, and the slope of the semi-logarithmic overpotential curve (\(\delta\eta/\delta\ln i\)) correspond to RT/2\(\beta\)F where R is the universal gas constant, T the absolute temperature, F Faraday’s constant and activation energy \(\beta\) the symmetry factor which is expected to be approximately 0.5. However either no or a limited linear portion is evident – if anything it shows signs of polarization through surface coverage. The rate of any structural rearrangement (step 2) would be proportional to surface coverage and it would proceed to an equilibrium influenced by the heat transfer rate across the electrode interface, and hence the driving temperature gradient.

For CO2\(_2\) formation the first step would be the same as the first step for carbon monoxide formation, but subsequently there is a need to either directly or indirectly discharge a second oxyanion onto the same carbon atom as depicted by step 2a. Thereafter, like CO formation, structural rearrangement to surface CO2 and uptake
of energy to enable release as a gaseous phase is required. Hence we would have the following four steps

\[
\text{Step 1a: } \text{AlOF}_2^- + xC \leftrightarrow C_xO + 2e + \text{AlF}_2^+ \\
\text{Step 2a: } \text{AlOF}_2^- + C_xO \leftrightarrow \text{OC}_xO + 2e + \text{AlF}_2^+ \\
\text{Step 3a: } \text{OC}_xO \rightarrow \text{CO}_x\text{(surface)} + (x - 1) \text{C} \\
\text{Step 4a: } \text{CO}_x\text{(surface)} + Q_{\text{CO}} \rightarrow \text{CO}_2(\text{g})
\]

where \(Q_{\text{CO}}\) is the magnitude of heat to be transferred beyond that provided through the polarization.

Although the effect of non-standard state conditions of the reactants impacting the Gibbs energy is uncertain, the experimental results give good agreement with the thermodynamic predictions that once the interfacial electrode potential exceeds approximately 1.8 V, co-oxidation of fluoride anions becomes enabled. The rapid rate of increase in current with electrode potential, as displayed by the sweep voltammograms, demonstrate that the kinetics of fluoride anion oxidation is fast.

Mechanistically we would still have the oxidation of the oxide anion occurring at the rate given by its kinetics at the time and is given by equation

\[
\text{Step 1c: } \text{AlOF}_2^- + xC \leftrightarrow C_xO + 2e + \text{AlF}_2^+ \\
\]

but with the fluoride anion oxidation there would be a parallel reaction step:

\[
\text{Step 2c: } \text{F}^- + C_xO \leftrightarrow \text{FC}_xO + e
\]

where the \(\text{F}^-\) may be bonded to the same or a neighboring carbon atoms. As demonstrated in Table I, while structural rearrangement can lead to \(\text{COF}_2\) less energy is required to release it as a gaseous mixture of \(\text{CO}\) and \(\text{CF}_4\). Additional steps in the mechanism could be

\[
\text{Step 3c: } \text{F}^- + \text{FC}_xO \leftrightarrow \text{F}_x\text{C}_xO + e \\
\text{Step 4c: } \text{F}_x\text{C}_xO \rightarrow \text{CO}_x\text{(surface)} + (x - 1) \text{C}
\]

Irrespective of the reaction intermediates heat transfer again must occur and can play a role. If the magnitude of heat required is high, this can result in surface coverage or passivation reducing available surface area if operated at constant potential. Clearly the intermediate fluorinated surface is a poor electrical conductor, and there is a thermal or kinetic barrier retarding release of the new product in the gaseous phase.

It should be noted that there is also the possibility that a totally different C-F intermediate product could be being formed on the electrode surface at the enabling potential found and is simply being disregarded in mechanistic analysis because there is no thermochemical database listing. For example the highly insulating compound referred to as Teflon (-C2F4-), has thermal stability over a range of temperatures and the electrode potential can enhance its stability under the conditions.

### Table II. Estimating the change in proportions of electrochemically produced CO an CF4 following onset of AE’s in operating cells.

| Gas                        | Tabereaux, Richards and Satchel\(^{12}\) | Holliday and Henry\(^{22}\) |
|----------------------------|------------------------------------------|-----------------------------|
|                            | CO\(_2\) | CO | CF\(_4\) | CO\(_2\) | CO | CF\(_4\) |
| Air free Gas % before AE   | 69 to 72 | 15 to 30 | 0 | 62 to 70 | 28 to 35 | 0 |
| Air free Gas % after AE    | 15 to 18 | 65 to 70 | 14 to 16 | ~13 | ~74 | ~13 |
| % Current by gas before AE | ~93 | ~5 | 0 | ~90 | ~7 | 0 |
| % Current by gas after AE  | ~31 | ~37 | 30 | ~31 | ~34 | ~31 |
| Ratio Electrochem CO to CF\(_4\) | ~2 | | |

### The Role of CO\(_2\) in Anode Effects

While passivation of the electrode surface has been proposed as the primary cause of an anode effect in aluminum electrowinning,\(^{23}\) the most common explanation in publications is that the anode effect caused by depletion of the oxide anion arising from the alumina in the interfacial electrolyte causing a change in interfacial tension leading to current blockade through a gas film/ non-wetting. However the fast sweep voltammetry results presented (Fig. 7) demonstrate a change in electrode process involving a second anion - presumably F\(^-\) occurs once the anode potential exceeds approximately 1.82 V. The curves show this change in electrode process leads to passivation unless the co-oxidation of oxygen anions can continue at a similar rate and there is adequate heat transfer.

A noticeable superimposed wave becomes evident on the I-V sweep curves (Fig. 7) in the zone of co-oxidation, which is consistent with the following sequence:

- Oxide and fluoride ions oxidation results in intermediate build up and localized passivation
- There is an increase in voltage through the added resistance
- A Consequential increase in joule heat results
- The extra heat aids more reaction completion
- Release of product enabling further oxidation and current increase

The potential band at which reaction resumes during the reverse sweep indicates that the overall reaction remains consistent with either COF\(_2\) evolution, or as indicated by gas analysis its decomposition product from simultaneous reaction according to Eq. 2 CO:CF\(_4\) in the ratio 2:1.

Using independent studies of anode gas during an AE\(^{12,22}\) there is also strong evidence to support the final step in the AE reaction being consistent with the PFC’s originating from a final chemical step consistent with Eq. 2.

In both instances the cells of those studies had sustained anode effects while monitoring the composition of the evolved cell gases. The resulting gas compositions, after adjusting for impurities and sampling impurities, is given in the first row of Table II. In both instances approximately 2% of the current was also carried by electrochemical reactions associated with the impurities introduced with the raw material while in the cells used by Holliday and Henry the current efficiency was lower and the anode reactivity higher thus generating more non-electrochemical carbon monoxide. After allowing for these factors and applying faradays law we have estimated the percentage of the current carried for the formation of each of the three products both before and after onset of anode effect. After allowing for the non-electrochemical carbon monoxide the ratio of extra \(\text{CO}\) to the newly generated \(\text{CF}_4\) comes within 5% of 2:1 in both instances. During these anode effects the cell voltages exceeded 8 V with all the increase being at or near the anode interface. Consequently there was more than adequate joule heat generation to enable completion of the reaction. This analysis suggests that all PFC’s originate according to the equation in the abstract irrespective of whether formed at voltages similar to normal operation or under circumstances consistent with the definition of an anode effect.
Further Analysis of Heat Transfer in the System
Al₂O₃-AlF₃-NaF

In the aluminum smelting cells the equilibrium gas composition, once reaction initiates, should be ~97.5% CO(g), but as the anode potential increases the proportion of CO₂(g) co-evolved increases through a kinetic controlling phenomenon, with the only notable feature being CO₂(g) requires less energy for gas release than for the equivalent amount of electrochemical reaction if CO is formed. Thus if the rate of heat transfer is limiting this would explain the co-evolution of CO₂ in the proportion greater than the equilibrium amount as has been found to be the case in every system studied. The increase in CO(g) formation at high anode potentials, and especially in conjunction with PFC co-evolution, adds strong support to the importance of interfacial heat transfer and generation.

The typical operating conditions for cells of the type studied by Tabereaux et al.¹² were an alumina concentration of 2.5 wt% and an anode potential of ~1.65 V. The calculated current density after allowing for current on the sides of the anodes is ~7000 A/m² while the average electrolyte to sidewall temperature gradient driving heat loss is ~8°C. Based on both thermal modelling and the experimental measurement it has been established that each anode contributes approximately 29,500 kJ toward the cell’s heat loss under the operating conditions, but because of the average anode resistance, 10,500 kJ are generated by the joule heating, leaving 19,000 kJ as the required heat to be transferred from the electrolyte to the electrode under these conditions. However if the heat transfer conditions are similar to those existing at the electrolyte- sidewall interface this would leave between 6000 and 7000 to kJ/m² anode available to satisfy the enthalpy of reaction beyond that provided by the total electrode potential. Using these values, we have performed a mass and energy balance correlating interfacial potential gradients and gas compositions, and superheat. Two examples of the outcome are presented in Figure 14. The upper curve (Figure 14A) gives the expected trend as the electrode polarizes through surface coverage or oxide depletion. It indicates that the cell gas composition will become enriched in carbon monoxide which is what has been found in our studies as the cell approaches an AE. The lower curve (Figure 14 B) gives an alternative trend for when the electrode polarizes and temperature is able to simultaneously change to maintain the gas composition. This is consistent with observed trends for low cell energy operation. However in both instances because of limitations in the accuracy of such predictions they must be regarded as presenting trends rather than absolute values.

Similar analyses for when fluoride co-evolution occurs would give consistent trends, highlighting the importance of heat transfer in balancing chemical reactions when they are occurring in parallel.

Concluding Remarks

By the combined studies linking electrode potential, thermodynamic energy requirements, cell design, and operating conditions and the changes in the composition of gas released, it is evident that heat transfer conditions plays an important role in determining the proportion of the gaseous components released.

When both CO and CO₂ are the only products electrochemically enabled, there is still a significant energy gap required for the gases to be evolved and this can only be satisfied by interfacial heat transfer. Since CO₂ requires less thermal energy, it is released at a rate greater than expected from thermodynamic equilibria. This discrepancy is reduced by increasing the thermal gradient for the energy transfer. However at all current densities and electrode potentials some CO is always electrochemically formed, the proportion depending on superheat and other heat transfer conditions.

The initiation of fluoride anion co-discharged always initiates once the anode potential exceeds approximately 1.82 V irrespective of the bulk alumina concentration of the electrolyte. While this is close to the value expected for initiation of the formation of COF₂, the gaseous product released as a consequence of this change is consistent with the overall chemical reaction

\[ 2\text{COF}_2(\text{surface intermediate}) + \text{C} = 2\text{CO}(g) + \text{CF}_4(g) \]

which requires additional thermal energy unless the electrode potential gradient exceeds approximately 2.65 V.

The resulting build-up of a resistive layer on the electrode surface originally proposed by Haupin is confirmed by the results presented here (Fig. 3). The extent of its buildup at any current density/anode potential depends on local heat transfer rates and cell conditions. Whether the ultimate rate controlling step is heat transfer or chemical kinetic cannot be conclusively distinguished. This combination explains the following three different operational deviations observed in smelting practices.

1. The difficulties of terminating AE’s that occur in cells when the temperature exceeds about 1010°C – especially those in start-up cells when accompanied by reduced alumina feeding rate.

Under these conditions the normal thermal energy requirements can be satisfied easier resulting in the dissolved oxide concentration dropping to an extremely low value, but introducing alumina dissolution and mixing kinetic constraints when remedial action is initiated to terminate the AE.

2. Why practically full passivation initiates an AE in operating cells prior to the voltage rise exceeding the amount required for the anode potential to achieve a value that either enables direct CF₄ formation or the entropic thermal energy requirements to be satisfied.

Confirmation of this is based on examining the recorded cell voltage readings recorded at 1.25 second intervals for six cells that proceeded to an anode effect. In every instance the voltage increased to in excess of 8 V between successive readings when the prior value corresponded to an anode potential gradient (including the ohmic resistance of any film) being less than 2.5 V. However once an anode effect is initiated considerable heat generation at the interface occurs.

3. Why a surge of CF₄ is evolved after an AE has initiated and the cell voltage has risen?

It has been well established,¹² that CF₄ is only released in a short period and after the initial surge CF₄ becomes the sole fluorocarbon product while the cell remains on and anode effect.

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Figure 14. Trends expected in process variables when conditions that impact the interfacial heat transfer change. (A) predicted anode gas composition change as the electrode polarizes, (B) The predicted reduction in interfacial temperature gradient that would result if the anode gas does not change.
Surface coverage by a highly resistive or passivating intermediate product layer on the anode once co-deposition of fluoride anions occur, which was first detected in 1956, provides a more logical explanation of the cause of the anode effect when compared against those explanations promoted in the literature today.

The studies also demonstrate the same link between electrode potential and gas composition occurs in all other oxide fluoride systems with heat transfer playing an important role in the distribution of products.

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