The reaction occurring between gaseous CF_4 and oxides dissolved in different molten fluorides. Some practical aspects

C. E. CASTELLANO, A. J. CALANDRA

ALUAR Aluminio Argentino SAIC, Research and Development, Department of Electrochemical Processes, Puerto Madryn, Chubut, Argentina

When CF_4 is bubbled through molten fluorides containing dissolved oxides within the range 900–1020° C, a chemical reaction takes place which decreases the oxide concentration and yields CO_2 and F^- ions. The possibility of the reaction between the CF_4 evolved at the anode and dissolved alumina, occurring during the anode effect in aluminium reduction cells, is discussed. This reaction provides a simple and convenient method for removing oxides and hydroxides from molten fluorides.

1. Introduction

During normal electrolysis the anode reaction in industrial aluminium cells involves the discharge of oxide ions at the carbon electrode with formation of CO_2 as the primary anode product [1] (the term primary anode product defines the gas leaving the anode–electrolyte interface without undergoing any reaction with species present in or outside the electrolyte). However, the outgoing gas consists of a mixture of CO_2 and CO because CO_2 can undergo secondary reactions with aluminium. The anode effect is preceded by a depletion of oxide ions at the anode surface. As a result, the potential of the electrode increases and the fluoride ion discharge becomes feasible with the formation of gaseous CF_4. In a recent publication [2] it was proposed that the establishment of the anode effect may be caused by an increasing coverage of the electrode surface by intermediate fluorocarbon compounds of the type $(CF_x)_n$ which undergo thermal decomposition yielding gaseous CF_4 formation.

Typically, in industrial cells, the gas composition may change from 70% CO_2 + 30% CO during normal electrolysis to 20% CO_2 + 60% CO + 20% CF_4 as a result of the anode effect. If CF_4 constitutes the main primary anode product, the question is why the exit gas contains CF_4 as well as such large quantities of CO_2 and CO. Recently, laboratory cell experiments [3], made at a constant potential within the anode effect potential region have shown that the CF_4 content in the anode gas increases as the alumina concentration dissolved in the cryolite decreases. In pure cryolite 90% CF_4 has been reported in the anode gas. From this it could be concluded that CF_4 reacts with the alumina dissolved in the cryolite to form CO_2. If this reaction proceeds at a sufficiently high rate it may explain the formation of CO_2 as a result of the anode effect. The presence of CO in the anodic gas may be attributed to the reaction of CO_2 with aluminium.

On the other hand, any possible reaction between CF_4 and the oxides present as impurities in different molten fluorides may provide the basis for a new method of purifying these melts.

It is of great interest, therefore, to try to identify any possible chemical reaction between CF_4 and the dissolved oxides, and to answer the above question.

2. Experimental details

The gas-tight reaction vessel was made of refractory steel, nickel or alumina in the shape of a vertical jacket enclosing a graphite crucible which played the dual role of molten mixture container and cathode.

This arrangement was made in order to follow the variation of the oxide concentration in the melt during the experiment by applying the single potential sweep technique [4]. A graphite anode, a graphite reference electrode, a thermocouple, a tube 2 mm i.d. for flushing the CF_4 located 20 mm above the bottom of the crucible, and a tube for gas sampling were inserted through the top cover of the reaction vessel. A jacket-insulated, Teflon sealed, co-axial bar screwed to the bottom of the crucible served as the cathode contact. The whole assembly was placed in a vertical furnace, controlled by a proportional regulator.

Chemicals of Analar quality were used. The following salts or mixtures were used: cryolite synthesized from AR grade NaF and sublimed AlF_3, LiF–NaF–KF eutectic (46.5–11.5–42.0 mole %, mp 454° C) (commonly known as Flinak), NaF–LiF (40–60 mole %) and pure NaF. The height of the melt in the crucible was of the order of 60 mm. This corresponds to approximately 0.3 kg of salt. The reactant gas was CF_4 (Matheson 99.7%).

When a known quantity of alumina was added to the molten cryolite, the latter was subjected, prior to fusion, to rigorous vacuum drying for several hours, with an increasing temperature programme. Experiments with Flinak, pure NaF and also some cryolite were carried out without any treatment of the salts prior to melting.

After fusion the initial oxide content in the melt and its variation while CF_4 was being bubbled through the melt was determined by using the single potential sweep technique [4]. Simultaneously the concentration of CO, CO_2 and CF_4 were followed in the effluent gas with an on-line gas chromatograph using Porapak Q and Molecular Sieve 5 Å columns. In the case of cryolite, the decrease of the cryolite ratio was also determined for molten salt samples which were withdrawn periodically before and during the experiment using an X-ray diffraction technique [5]. As described below, the reaction between CF_4 and Al_2O_3 produces AlF_3 which changes the cryolite ratio. The Al_2O_3 content in cryolite was also analysed by means of an X-ray method [6].

3. Results and discussion

The nature of the chemical reaction seems to be independent of the different molten fluorides used as oxide solvent, but for the sake of clarity, it is convenient to consider the results obtained with cryolite and those with NaF, NaF–LiF and Flinak independently, especially because of the different technical applications given to the different molten fluoride systems [7, 8].

3.1. Alumina–cryolite

The free energy data available in the literature [9] show that the following reaction is thermodynamically favourable:

$$3CF_4 + 2Al_2O_3 = 3CO_2 + 4AlF_3. \tag{1}$$
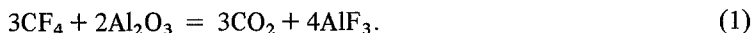
The change in standard Gibbs free energy ΔG^0 for this reaction, at 1000° C, is $-344.9 \, kJ \, mol^{-1}$. The alumina can either be dissolved or be in a solid form.

When gaseous CF_4 and alumina dissolved in cryolite were brought into contact at 1010° C, Equation 1 was found to occur from left to right. The gas chromatography technique allows an instant determination of CO_2, excess CF_4 and CO in the exiting gas. Blank experiments were conducted by passing CF_4 through the reaction vessel at 1000° C, excluding the molten salt. The gas analysis showed the appearance of minor quantities of CO_2 and CO. The presence of the former may be explained by considering that CF_4 may have reacted with the surface oxide present in the materials of the reaction vessel. The appearance of the latter may be explained by the occurrence of a Boudouard reaction on the surface of the carbon crucible and when stainless steel or nickel jackets were used, by the oxidation of the metals by CO_2 forming CO. CF_4 was found to react also with solid alumina at 1000° C. Experiments carried out using a sintered alumina tube of 2 cm i.d. through which a flow of CF_4 was passed, show the

formation of AlF$_3$ crystals on the internal surface of the colder part of the tube and the presence of CO$_2$ in the exiting gas. These lateral reactions slightly distort the information obtained from the gas analysis.

Experimental runs were made with an initial alumina concentration in cryolite of approximately 2 wt %, a total amount of melt of 0.3 kg at 1005° C, and a CF$_4$ flow rate of approximately 10 cm s^{-1} showed that, initially, the oxide concentration diminished at a rate of approximately 0.5 g per min. At the same time the percentage conversion of CF$_4$ was of the order of 26%. The AlF$_3$.concentration increased according to Equation 1.

The above experiment could be used to estimate roughly whether the extent of Equation 1 is sufficient to modify the CF$_4$ content in the anode gas during the anode effect in industrial cells. In these cells the anode effect normally arises at alumina contents between 1 and 2 wt%. If one admits that during the anode effect, CF$_4$ is the primary anode product, then the rate at which it is evolved is of the order of 2×10^{-1} cm s^{-1} at 1000° C. When this rate is compared with that used in the experiments described above, a higher percentage conversion of CF$_4$ into CO$_2$ in industrial cells during an anode effect might be expected. Under these circumstances according to typical gas analyses given in the literature, the percentage conversion of CF$_4$ is around 80%. Following the same reasoning the presence of CO can be explained by considering the reoxidation of Al with CO$_2$ which is produced according to Equation 1. Thus, the relationship between gas composition and current efficiency (CE) during an anode effect can be obtained on the basis of the following assumptions:
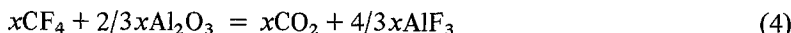
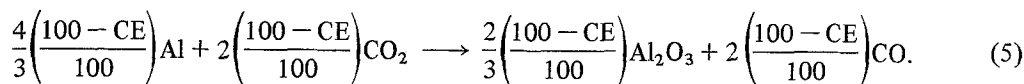(a) The primary cell reaction under an anode effect is either

$$C + 4/3AlF_3 = 4/3Al + CF_4 \tag{2}$$

or

$$C + 4/3Na_3AlF_6 = 4/3Al + 4NaF + CF_4 \tag{3}$$
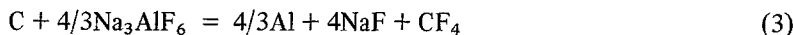
(b) The extent of Equation 1 is related to the percentage conversion of CF$_4$ (PC) according to

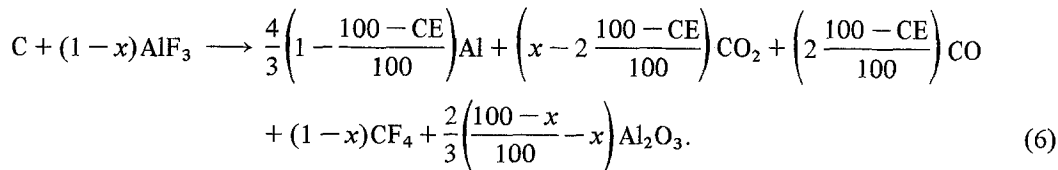$$xCF_4 + 2/3xAl_2O_3 = xCO_2 + 4/3xAlF_3 \tag{4}$$

where $x = (\text{PC})/100$.

(c) The loss in CE is due only to aluminium reoxidation with CO$_2$. Its extent can be related to the CE in the following way [1]:

$$\frac{4}{3}\left(\frac{100-CE}{100}\right)Al + 2\left(\frac{100-CE}{100}\right)CO_2 \longrightarrow \frac{2}{3}\left(\frac{100-CE}{100}\right)Al_2O_3 + 2\left(\frac{100-CE}{100}\right)CO. \tag{5}$$

The overall reaction is obtained by adding, for example, Equations 2, 4 and 5:

$$C + (1-x)AlF_3 \longrightarrow \frac{4}{3}\left(1 - \frac{100-CE}{100}\right)Al + \left(x - 2\frac{100-CE}{100}\right)CO_2 + \left(2\frac{100-CE}{100}\right)CO$$

$$+ (1-x)CF_4 + \frac{2}{3}\left(\frac{100-x}{100} - x\right)Al_2O_3. \tag{6}$$

From Equation 6 it can be seen that:

$$CE = 50(2-x) + \tfrac{1}{2}\% \, CO_2 \tag{7}$$

$$CE = 100 - \tfrac{1}{2}\% \, CO. \tag{8}$$

Equation 7 is a corrected version of the Pearson–Waddington equation [1] which accounts for the different origin of CO$_2$. In Equation 7 it is supposed that CO$_2$ is produced by Equation 1 whereas in the Pearson–Waddington equation CO$_2$ is produced by the primary anode reaction. Equation 8 corresponds to the Pearson–Waddington equation since in both cases it is supposed that CO is produced by Equation 4.

After applying Equation 7, using typical values of the gas analysis related to the anode effect, the CE turns out to be of the order of 70%, which is a reasonable figure if one considers the particular conditions prevailing in a cell during the anode effect.

It is likely that Equation 1 may be under mass transfer control of the reactants. Therefore, its rate

will depend largely upon the contribution of convection in the reaction vessel employed to run the experiments. Consequently, the present results are not unrestrictedly applicable to industrial cells.

The assumption that CF_4 is the only primary anode product is an extreme situation. The pulsating gas evolution during an anode effect [10] could cause increased convection which might bring alumina-rich melt up to the anode; then, the electrolytic production of CO_2 becomes feasible. Local overheating in the anode region, during an anode effect, could also enhance convection. An answer to these questions will be possible once additional quantitative information about anode gas composition and carbon consumption during an anode effect is obtained, especially taking into account the existence of Equation 1. This, however, will be a difficult task since the result might be obscured by a side reaction of the type mentioned above.

3.2. NaF, NaF–LiF and Flinak

The main contaminant present in fluorides salts is water. When these salts are melted, hydrolysis occurs and a significant concentration of oxide (and to a lesser extent of hydroxide) appears in solution [8].

When molten NaF and Flinak, containing the above mentioned impurities, were treated with CF_4 in the same way as cryolite, the formation of CO_2 and a decrease in the oxide content in the melt were also observed in the exiting gas. In the case of NaF, the process can be visualized as occurring in accordance with the following equation:

$$CF_4 + 2Na_2O = CO_2 + 4NaF \qquad \Delta G^0 = -826.8 \, kJ \, mol^{-1}$$

and

$$CF_4 + 2NaOH = CO_2 + 2NaF + 2HF \qquad \Delta G^0 = -297.3 \, kJ \, mol^{-1}.$$

When Flinak was used the experiments were conducted within the interval 750–960° C with an initial oxide concentration of approximately 0.7 wt%. At 750° C no reaction was observed during a period of 15 h. The reaction rate was observed to increase gradually with increasing temperature. At 960° C the reaction is fast and in approximately 1 h, the oxide concentration was reduced to approximately 0.08 wt%, with a flow rate of 50 cm^3 min^{-1} of CF_4.

Anodic voltammograms obtained before and after CF_4 was bubbled through a molten mixture of NaF–LiF at 1000° C for 1 h at 50 cm^3 min^{-1} are shown in Fig. 1. The faradaic process occurring at 1.25 V corresponds to the discharge of residual oxide ions, which remain in the mixture after melting, with electrochemical formation of CO_2 [4], whereas that occurring at 1.93 V might be related to the formation of COF_2 by simultaneous discharge of oxides and fluoride ions [4]. The process at 2.60 V leads to the onset of the anode effect, and it corresponds to the electrochemical formation of CF_4. It can be seen in the figure that there is a marked decrease of the current after the bubbling of CF_4 in the potential region where oxide ion discharge occurs.

The decrease in the oxide concentration was estimated from the ratio between the anodic current before bubbling and the anodic current after bubbling. This implies a linear relationship between the current and the oxide ion content, which could be considered correct for sweep rates greater than 20 Vs^{-1} [4]. The experiments shown in Fig. 1 give a ratio of about 15 with an initial oxide content of approximately 0.70 wt%.

The voltammograms corresponding to the pure solvent melt are not known. Therefore, it is difficult to obtain the true anodic current at low oxide contents where the contribution of the residual current is important.

The reaction described in this work provides a simple and extremely convenient method for removing oxides and hydroxides from molten fluorides [11]. The procedure does not introduce new impurities into the system since the excess reactant (CF_4) and the reaction products (CO_2 and HF) can be removed by flushing an inert dried gas through the melt.
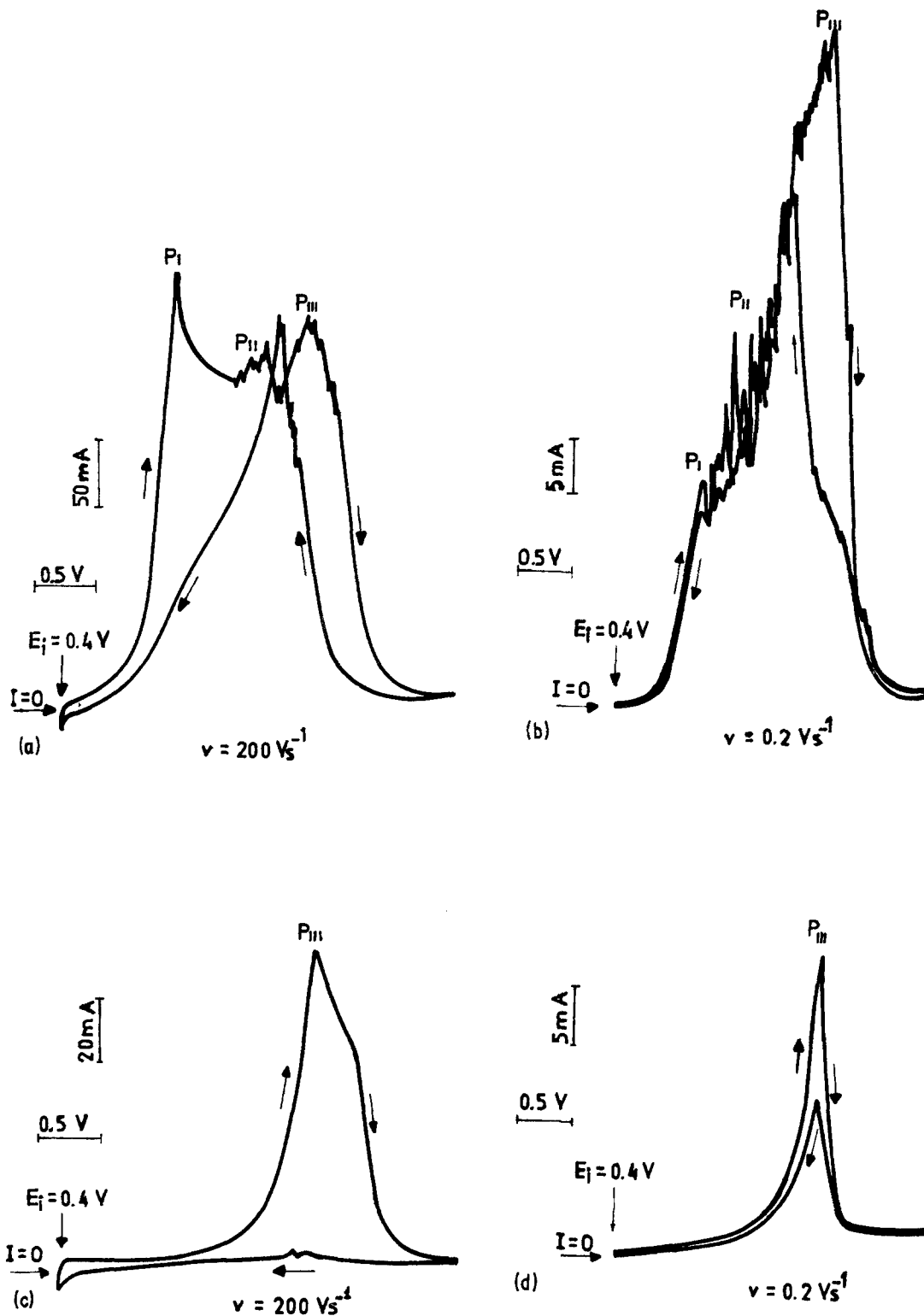
Fig. 1. Voltammograms obtained on a graphite electrode in NaF–LiF (40–60 mole %) melt at 1000° C. (a) and (b) before, and (c) and (d) after, bubbling with CF$_4$. The apparent electrode area was 0.26 cm^2.

Acknowledgements

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