

STUDIES OF PERFLUOROCARBON FORMATION ON ANODES IN CRYOLITE MELTS

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Keywords: CF₄, COF₂, anode effect, PFC

Abstract

The aluminium industry is today the primary source of perfluorocarbon (PFC) to the atmosphere. These gases have a lifespan of several thousand years, and a greenhouse warming potential (GWP) 6500-10000 times that of CO₂. It is therefore of essential to understand, and reduce, the PFC emissions.

Controlled potential electrolysis with gas analysis was utilized to study the PFC production in a laboratory cell during regular electrolysis conditions, and during anode effects. A 3-electrode setup with an Al reference electrode was utilized to monitor the anodic voltage. The combination of Mass Spectrometry (MS) and Fourier Transformed Infrared Spectroscopy (FTIR) was used to characterize the off gas. Traces of CF₄ were found in the anode gases at anodic voltages as low as 2.9 V VS the Al reference electrode, confirming that the PFC production can occur unrelated to the anode effect. However C₂F₆ was only detected during anode effects.

Introduction and Theory

Introduction

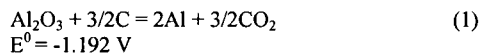
A significant amount of today's PFC emissions originates from the aluminium industry. The industry managed to reduce the PFC emissions by 80% from 1990 to 2007 [1]. This has mainly been achieved by reducing the total anode effect (AE) time of each cell by improving on cell control and feeding.

Further reductions in PFC emissions are harder to achieve as the AE frequency and duration now is considerably shortened. Other mechanisms for PFC emissions should therefore be evaluated

By studying the behavior of cells before and during AE, and the composition of the off-gases more knowledge of the mechanisms involved are collected. This can possibly be used to identify signs that can be used as early warnings for AEs.

Background

The principal reaction of a Hall-Heroult cell is:

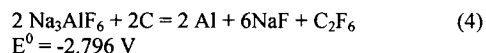
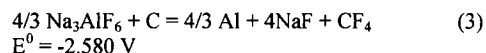
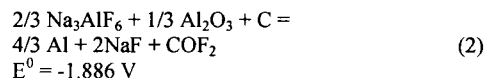


Calculated by FactSage [2] using pure solid α -Al₂O₃, graphite, Al and pure CO₂ gas as standard states.

In a typical industrial cell the current densities will be about 1 A/cm², and the anodic overvoltage around 0.5 V. These cells are operated in a constant current manner. [3]

When the supply of oxide to the anode surface gets lower than the consumption, other reactions will have to occur in order to sustain the line current in an industrial cell. These reactions will consume

the electrolyte, and lead to fluoride emissions from the cell. The reactions might be:

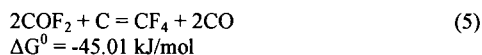


All potentials are calculated for 960°C, using FactSage [2], with pure gases, pure liquid NaF, Al and Na₃AlF₆, and solid C(graphite) and α -Al₂O₃ as standard states.

A good summary of different AE studies is given by Thonstad *et al.* [3]. The most thermodynamically favored of these reactions is reaction (2), the formation of COF₂, which starts at a potential of only 1.88 V. However, COF₂ is rarely reported, and not reported to be a large fraction of the typical AE gas composition. [3] The main fluorine containing gas species during AE are CF₄ and C₂F₆, and are believed to be formed according to reactions number (3) and (4).

In an industrial cell, the full AE will lead to a rapid increase in cell voltage, as the current is forced through the cell at a constant rate. The exact mechanisms are still not completely agreed upon [3], but it is likely that formation of an insulating surface layer, a de wetting of the electrolyte, gives a passivation of the anode surface. Most aluminium companies use a definition of AE based on a critical cell voltage.

In laboratory studies by Dorreen *et al.* [4] COF₂ was identified by MS studies of cell gases in the final minutes before the onset of an AE. They also suggested several possible decomposition reactions for COF₂ with both their BN linings and C, reaction (5).



Calculated by FactSage [2] using pure gases and graphite as standard states.

Zhu *et al.* [5] also studied anode effects in cryolite melts, they utilised a gas chromatograph (GC), and was not able to see any signs of COF₂. A GC is, however, not the most suited apparatus to detect small amounts of COF₂.

Fluoride emissions from an aluminium smelter can also occur in a continuous manner, and with the successful reduction of AE in most modern cells, compared to older ones, the amount of PFC produced in the cell in a continuous manner will constitute a

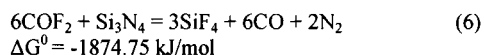
larger share of the total PFC emissions from the cell. The understanding of continuous emissions has therefore attracted the attention of researchers the latest years.

The possibility of such CF_4 emissions from Hall-Heroult cells have been studied by Li *et al.* [6]. They discovered that some of the cells had measurable amounts of CF_4 in the off gases, and investigated several factors, such as non-uniform current distribution, but could not make any conclusions. There were variations within one cell line operating at same current and under the same conditions. The PFC might originate from a non-uniform alumina distribution, giving a localized anode effect at only one of the anodes in a cell. This type of localized AE would typically be present in high gradient cells.

Theory

In our studies, we wanted to look into the gas composition in the timeframe leading up to the full anode effect, and through the anode effect. The purpose was to gather a better understanding of what happens on the anode in this timeframe, and perhaps be able to see if there are any signs that can be used to predict an AE.

A decomposition of our Si_3N_4 refractory, similar to that described by Dorreen *et al.* [4] for BN is possible,



Another reaction that COF_2 can undergo is decomposition into CF_4 and CO_2



Both reactions are calculated with FactSage [2] for 960°C using pure gases as standard state and solid Si_3N_4 as standard states.

Reaction (7) is not thermodynamically favorable at 960°C , but with decreasing temperature, the reaction becomes more favorable, as can be seen from the plot of $\log(K)$ VS temperature in Figure 1.

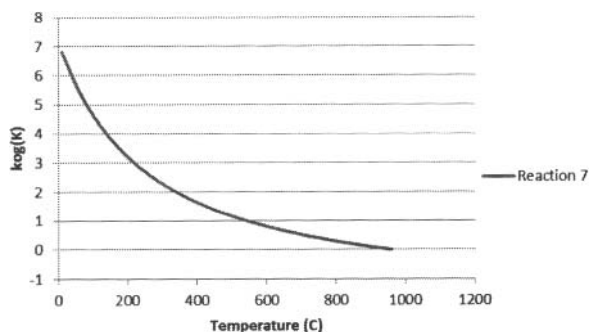


Figure 1: $\log(K)$ for reaction (7), calculated with FactSage [2], using pure gases as standard state.

In mass spectroscopy (MS) gas analysis it is possible that several different gas molecules have the same weight, or can split into fractions that have the same weight. Hence great care must be taken to consider all possibilities when analyzing the results. In Table 1 a short summary of the most relevant masses, and their

possible source. Usually the different gas molecules will have some masses where they are the only contributor, or they can be separated by analyzing the ratio between heights of the peaks.

Table 1: Different MS masses and their probable sources

Mass	Possible molecules
47, 66	$\text{SiF}_4 / \text{COF}_2$
69	$\text{CF}_4 / \text{C}_2\text{F}_6$
85	SiF_4
119	C_2F_6

Experimental

A laboratory cell was constructed with focus on rapid extraction and recovery of the anode gases. Therefore, a hollow anode rod was used as the gas escape vent, and the anode was sloped inwards with a hollow center, directing most of the produced gases into the anode rod. In addition, a Si_3N_4 shielding around the anode extending 0.5 cm below the anode helped direct the gases through the center hole. On the lower part of the anode rod, just above the anode, a hole was drilled to allow the inert flushing gas to escape. This helped to increase the gas velocity through the rod. The furnace was flushed with 400 mL/min of Ar.

The anodes were made from graphite, and the active anode area was approximately 25cm^2 .

The cell was contained in a cylindrical furnace with inner diameter 10 cm, and assembled as shown in Figure 2. The crucible was made of graphite and lined with Si_3N_4 .

A reference electrode was utilized to be able to study the anodic overvoltages separately. The reference electrode was a boron nitride (BN) tube with closed bottom, where a small pool of pure Al (0.5 g) was the active electrode. A hole in the BN tube 1 cm from the bottom allowed electrolyte to flow into the reference electrode. The bulk concentration of Al in the electrolyte was assumed to be constant.

However, the measured potential between the anode and the reference electrode still includes the ohmic losses in the anode current connection, in addition to the anodic voltage. The resistance in the anode current connection was estimated to be between 0.05Ω and 0.09Ω , however none of the reported voltages are corrected for these ohmic losses.

The cell potential or current (depending on experiment conditions) was supplied with a Hewlett Packard 6032A power supply controlled by a computer. All potentials were recorded with a Keithley 2000 multichannel logger.

The gas composition was analyzed with mass spectroscopy (MS) and fourier transform infra red spectroscopy (FTIR). The combination of the fast response of the MS and the high resolution of the FTIR gave a powerful tool to determine the gas composition.

The electrolyte used in the laboratory cell was an 80% Na_3AlF_6 , 12% AlF_3 , 5% CaF_2 and 3% Al_2O_3 .

The FTIR unit used was a Protea Protir 204m.

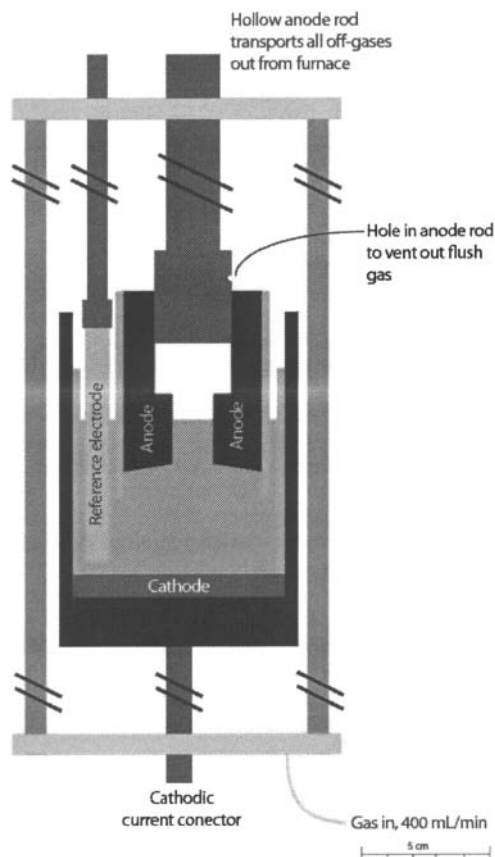


Figure 2: Cell setup

Results and Discussion

The results of a given experiment are shown in Figure (3), (4) and (5). In this experiment the cell voltage was adjusted, while the off-gases were monitored in the first part of the experiment. Then the cell was set at a constant current to run until an anode effect occurred.

In the first part of the experiment the signal at mass 69 in Figure (3) increases without any increase in signal at mass 119 indicating small amounts of CF_4 in the off-gas. This happens at what would be considered to be quite low anodic voltages, 2.95 V according to Figure 4. When compensated for an ohmic loss of 0.05Ω , the most conservative value of our interval, the actual anode voltage is 2.10 V, which is less than the E^0 required for reaction (3). This CF_4 formation also appears while the cell is working normally in all other ways. Further increase in the cell voltage gave increased, sustainable current, as can be seen in Figure 4. Except for the detected CF_4 the cell seems to operate normally without any signs of anode effect. The amount of CF_4 detected is also very low, at 10^{-12} A measured current on the MS the concentration in the off gas is about 5 ppm, this means only a very small fraction of the current would be carried by reaction (3), and the majority of the current would be due to the regular CO_2 evolution, reaction (1).

In other words, the CF_4 appears without the cell being in a typical AE.

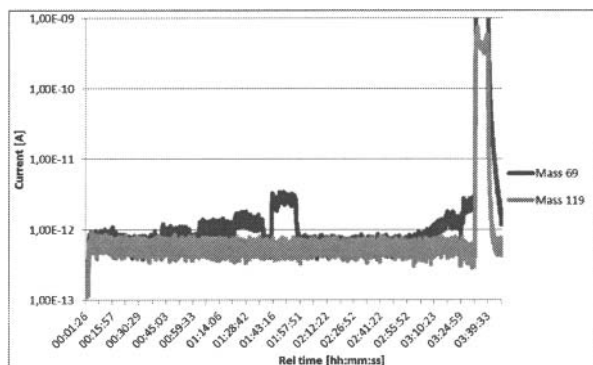


Figure 3: MS data for mass 69 ($\text{CF}_4 / \text{C}_2\text{F}_6$) and 119 (C_2F_6)

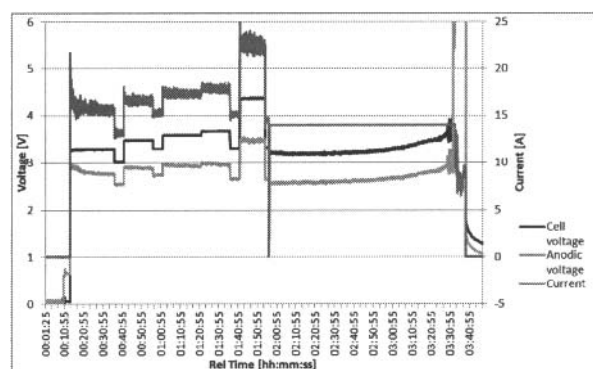


Figure 4: Voltage and current data for the same experiment as the MS date in figure 1

The cell also ran for more than an hour afterwards without any PFC components being detected, before a full typical AE started at the end of the experiment, due to oxide starvation, as there was no feeding of Al_2O_3 to the cell during the experiment.

For the second half of the experiment the cell was operated in a constant current mode, and was left to run until a full anode effect developed. This happened in the final part of the experiment, and here the voltages went to the equipment maximum, without being able to sustain the 14 A current that was set. In this part a rise in the signal at mass 119 indicates that C_2F_6 is formed along with CF_4 .

SiF_4 was observed throughout the experiment by a response at masses 85 and 47 in the MS data, as shown in Figure 5. This indicates the attack of the cell lining, possibly according to reaction (6).

The CF_4 detected in combination with the relatively low voltages in the first part of the experiment is interesting. It occurred at an actual anodic voltage of approximately 2.10 V, which is too low to directly form CF_4 according to reaction (3). However COF_2 would thermodynamically be expected to form at this potential according to reaction (2).

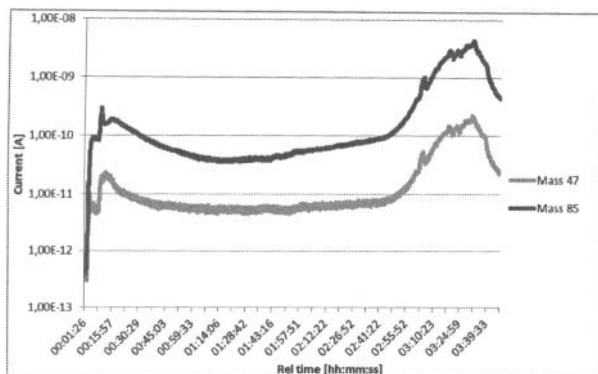


Figure 5: MS data for mass 47 ($\text{CO}_2 / \text{SiF}_4$) and mass 85 (SiF_4)

One possibility is the indirect formation of CF_4 , by decomposition of the highly reactive COF_2 . Several decomposition reactions are possible in our setup, i.e. reaction (5), (6) and (7), and two of these reactions give CF_4 . Reaction (5) will require the presence of carbon in contact with the gas for sufficient time to convert all COF_2 , in our setup the gas is rapidly extracted away from C sources and a total conversion of all COF_2 in this timeframe would be surprising. In reaction (6) it would be even more difficult to achieve complete conversion since the anode slopes away from the lining. On the other hand, reaction (7) only requires the presence of COF_2 , and hence the conversion to CF_4 can continue in the gas phase as long as there is COF_2 present, and the temperature is sufficient to achieve sufficient kinetics.

Reaction (7) has a slightly positive ΔG^0 at 960°C , but as can be seen from Figure 1, the reaction becomes more favorable with decreasing temperature. The gases are cooled down in the anode rod, and analyzed at about 200°C , which means that it is possible for the gas to react during this time.

The COF_2 is difficult to observe with MS in our lab setup due to the material choices in our laboratory cell. On the other hand analysis of the collected FTIR data does not indicate any COF_2 present in the off-gas. Hence if the CF_4 originates from COF_2 reactions (5), (6) and (7) have to completely convert all COF_2 before it reaches the gas detection equipment.

Another possibility is that should be considered is that changes in activities can give reaction (3) a reversible potential less than the E^0 . This could give a direct formation of CF_4 , however, there would have to be a significant change in activities and these changes would affect reaction (2) in similar ways, keeping reaction (2) more thermodynamically favorable.

Studies of industrial cells have also confirmed that COF_2 actually can form at graphite anodes in cryolite melt. [7] This supports the theory that COF_2 is produced at the anode in our laboratory cell, but that our setup gives it sufficient time to decompose into other gas species before we could positively detect it.

It is therefore possible, and probable, that there is a significant production of COF_2 in the cell, but that a combination of reactions (5) and (7), and possibly reaction (6) converts it to CF_4 , and possible SiF_4 . This would explain why CF_4 is detected in the gas when the anode is polarized at a less anodic potential than what would be required to directly produce CF_4 .

Some of the COF_2 might react according to reaction (6), but due to the high SiF_4 background it is impossible to see any changes in the SiF_4 concentration.

The possibilities for COF_2 formation should also be considered as a potential CF_4 source along with the localized anode effects, as the reversible potential for COF_2 production is close to the anode potential of an industrial cell.

Conclusions

In these laboratory experiments COF_2 was not detected, even if the anode was at potentials where COF_2 thermodynamically should form. However, CF_4 is detected, when the anode is polarized at potentials significantly below the E^0 of CF_4 formation. This CF_4 might originate from COF_2 that have decomposed into CF_4 and CO/CO_2 . This decomposition would explain both the lack of COF_2 traces and the positive identification of CF_4 in the off-gas.

Acknowledgement

We would like to acknowledge "Norsk Hydro's Fond for SINTEF" for the financial support.

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