

PFC evolution characteristics during aluminium and rare earth electrolysis

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Abstract

In addition to aluminium electrolysis, the electrolysis of rare earth (RE) metals from fluoride melts is a significant source of perfluorocarbon (PFC) emissions to the atmosphere. These processes have many similarities, they are both based on molten fluoride salt electrolysis at temperatures around 1000 °C, and are utilizing carbon materials as the anode. Although PFC emissions from aluminium industry and rare earth electrolysis have similar overall reactions, they are often reported to have different characteristics. In order to get a better understanding of these differences and similarities, different laboratory experiments focusing on anode reactions and gas compositions in Al_2O_3 saturated cryolite and $\text{REF}_3\text{-LiF}$ melts during aluminium and rare earth metal electrolysis were studied. The results obtained, combined with thermodynamic data analysis allowed to better understand onset, evolution and termination behaviour of PFC evolution in molten fluoride systems of different chemistries.

1. Introduction

Both aluminium and rare earth (RE) electrolysis are conducted in molten fluoride salts, PFC emissions from aluminium production have received substantial focus over the last 10 years, whereas the focus on PFC emissions from rare earth emissions have been less. This can be explained by an insignificant yearly production of rare earth compared to aluminium, but nevertheless high PFC emissions from the process does matter in an environmental setting; in addition the fluoride loss can give process control challenges.

Although there are several similarities between the processes, there are also some differences. In rare earth electrolysis, the electrodes are usually vertically positioned, compared to the horizontal electrode arrangement in a Hall-Heroult aluminium cell. This will result in different convection patterns, and different holding time for gas bubbles at the anode surface that in theory could affect how easily an anode gets blocked.

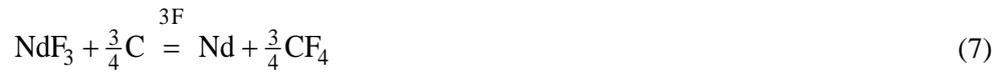
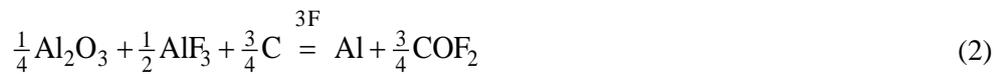
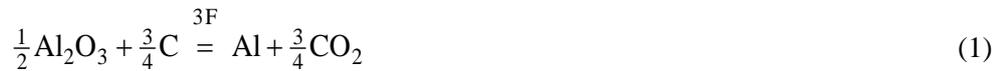
Laboratory experiments have several advantages compared to industrial cells, the gases can be produced in a closed atmosphere, and hence be recovered at higher concentrations. However, there are several challenges that arises regarding how representative a laboratory setup is compared to the industrial equivalent. Although it is well known that great care has to be taken in order to recover produced anode gases and to ensure that as little secondary reactions as possible occur, experimental design is difficult. Often several other considerations include anode and cathode geometry, and desire to recover cathode product. Scaling down a cell linearly will affect surface areas by the power of 2 and volumes by the power of 3, and hence alter surface:volume ratios etc. Also, the simple fact that the small dimensions in a laboratory cell requires the use of insulating refractory materials to regulate current distribution on the electrodes will also be a priority. This necessitates a greater care when evaluating experimental results.

One example here is the recovery of COF₂ from laboratory cells, although COF₂ is expected to be formed before CF₄ it is rarely reported. Doreen et. al. [1] designed a special setup to ensure rapid gas recovery, where they found COF₂ in the gas. COF₂ have also been observed as a product during OP-FTIR studies of an electrolysis cell at anode effect. [2]

In this work, the off gas composition, and PFC evolution in particular, was studied during various rare earth alloy and Al electrolysis by on line gas analysis. The experiments were conducted in various REF₃-LiF (50:50 molar ratio) -REO (1-2 wt%) systems and Cryolite respectively.

2. Theory

The anode reactions for aluminium and rare earth electrolysis will in principle be identical, evolution of CO, CO₂ or C-F_x gases from a molten fluoride salt containing dissolved oxide. There are, however, some differences, among them the temperature, and the anion to cation ratio. The following reactions is based on thermodynamic calculations [3] for NdF₃-Nd₂O₃ reactions (5-8), and AlF₃-Al₂O₃ reactions (1-4), but calculations for other RE-elements will be similar, the standard voltages are plotted in Figure 1.



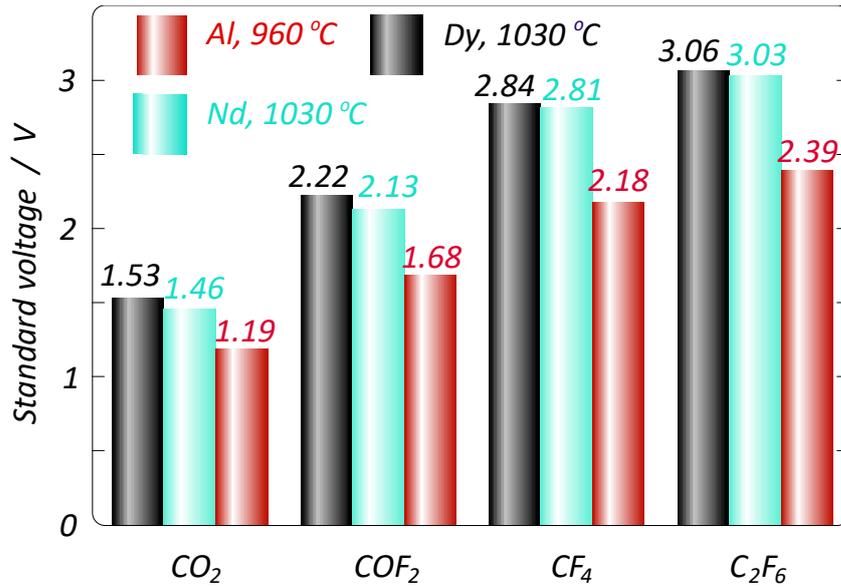


Figure 1: Illustration of how similar the different potentials for CO₂, COF₂, CF₄ and C₂F₆ are in Al, Nd and Dy electrolysis based on thermodynamic calculations of reactions (1-8), and similar equations for Dy. Only minor differences between Dy and Nd is observed.

In the case that COF₂ is formed several additional reactions should be considered, depending on which materials are available to take part in the reaction. Some reactions relevant for this paper are listed in Table 1, reactions (12-16), COF₂ is strongly reactive towards many common oxides and nitrides often used as lining materials, and will also self-decompose to CO₂ and CF₄ according to reaction (12), the reaction balances just at equilibrium around 1000 °C, but becomes more thermodynamically favorable at lower temperatures as can be seen in Figure 2. From Figure 1 we can see that the separation voltage between CO₂ and COF₂ is similar in both systems, the difference in E⁰ increases slightly when going from CO₂ to COF₂, and further to CF₄. This should in theory make it easier to avoid C-F gas evolution in Nd electrolysis.

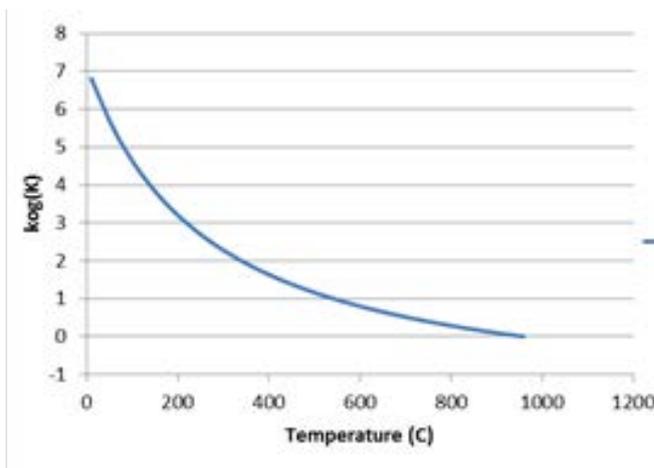


Figure 2: The Equilibrium constant for the COF₂ decomposition as a function of temperatures.

Table 1: Different reactions possible for CF₄ and COF₂ along with dG for 960 °C and 1030 °C [4].

	dG ^{960 °C} [J/mol]	dG ^{1030 °C} [J/mol]	Reaction
$3\text{CF}_4 + 2\text{Al}_2\text{O}_3 = 4\text{AlF}_3 + 3\text{CO}_2$	-1,141,379	-1,147,471	(9)
$3\text{CF}_4 + \text{Si}_3\text{N}_4 = 3\text{SiF}_4 + 2\text{N}_2 + 3\text{C}$	-1,739,662	-1,764,282	(10)
$\text{CF}_4 + \text{SiO}_2 = \text{SiF}_4 + \text{CO}_2$	-398,307	-410,870	(11)
$2\text{COF}_2 = \text{CF}_4 + \text{CO}_2$	-3	2,540	(12)
$3\text{COF}_2 + \text{Al}_2\text{O}_3 = 2\text{AlF}_3 + 3\text{CO}_2$	-570,693	-569,924	(13)
$6\text{COF}_2 + \text{Si}_3\text{N}_4 = 3\text{SiF}_4 + 2\text{N}_2 + 6\text{CO}$	-1,874,634	-1,927,876	(14)
$2\text{COF}_2 + \text{SiO}_2 = \text{SiF}_4 + 2\text{CO}_2$	-398,309	-408,330	(15)
$2\text{COF}_2 + \text{C} = \text{CF}_4 + 2\text{CO}$	-44,990	-54,531	(16)
$4\text{HF} + \text{SiO}_2 = 2\text{H}_2\text{O} + \text{SiF}_4$	-16,644	-9,961	(17)

3. Experimental

In this work, the off gas composition, and PFC evolution in particular, was studied during various rare earth alloy and Al electrolysis by on line gas analysis. The experiments were conducted in various RE₃-LiF (50:50 molar ratio) -REO (1-2 wt%) systems and Cryolite respectively. The systems studied are shown in Table 2. If observations are linked to only one of these systems the system will be referred to, if observations are present in both Re-systems, then it will be referred to as Re.

Table 2: List of the different molten salt studies used

System	Cathode product	Temperature °C	Cathode
DyF ₃ -LiF (50 mol% LiF)	DyFe alloy (l)	1050	Fe alloying cathode
DyF ₃ -NdF ₃ -LiF (50 mol % LiF)	NdDyFe alloy (l)	1050-1100	Fe alloying cathode
Na ₃ AlF ₆	Al (l)	960	Al (l)

Two different setups were utilized. For the experiments in Na₃AlF₆-Al₂O₃ with aluminium as cathode product, a setup using a Si₃N₄ lined graphite crucible were used as shown in Figure 3. This setup has earlier been described in [5], and is shown in Figure 3-right.

For the RE-experiments, a different setup was used. This setup consisted of a graphite crucible with an inner cylindrical graphite anode submerged. The anode can be seen in of Figure 3-left. Inside the anode the consumable Fe or inert Mo cathode rods, feeding tube and gas outlet tubes are positioned. In both cases, a gas tight furnace lined with a mullite tube was used and all experiments were run under Ar 5.0 atmosphere.

In the RE experiments, the glassy carbon crucible was used as a "quasi reference electrode" so that the anode and cathode voltages could be monitored. Ca. 700 grams of equimolar RE₃-LiF had been mixed with 2 wt% REO, pre-melted and cooled in a graphite crucible. The obtained chunk of salt was then placed in the glassy carbon crucible, and the furnace was sealed off with the electrode set up in place and heated to the working temperature the day before the experiment and left molten overnight. To verify that all the oxide had dissolved, a melt sample

was taken next morning and analyzed with respect to oxide content by carbothermal method, using LECO TC-436 DR (Leco Corp., USA). Subsequent amounts of oxide were fed batch-wise during the course of the electrolysis. The oxide additions could be carried out without opening the cell to the atmosphere, so the gas analysis could take place during the entire experiment without disturbance. A melt sample was taken at the end of the experiments and analysed with respect to oxide content.

After typically 5-6 hours of electrolysis, the furnace was cooled down under argon atmosphere to room temperature. The next day the cell was opened, the salt crushed, and any metal produced recovered.

A Fourier Transform Infrared Spectrometer (FTIR) apparatus (Protea ProtIR 204m with a 1cm^{-1} resolution) was used for online analysis of the off-gases (CO , CO_2 , C_2F_6 , CF_4) from the cell. Existing models were used in order to transform the FTIR readings to actual gas concentrations, upon calibration of the apparatus. The argon flow through the furnace was kept constant during the whole experiment to 700 mL/minute, and the out gas was led through the FTIR via an 8-mm alumina or nickel out gas tube. For safety reasons, a pressure gauge was placed on the gas inlet side of the cell to monitor the pressure build up that often occurs during gas analysis due to high resistance on the outlet side caused by filters, high gas flows, condensation of bath etc.

In the RE electrolysis experiments oxide was added regularly when CF_4 was detected in the off gas, or a small increase in the voltage indicated that the anode potential started to increase in order to counteract the low solubility in the system. For the aluminium electrolysis experiment additions were not made as the cryolite system have a higher oxide solubility, and a higher total electrolyte volume. The RE electrolysis experiment, as well as the last half of the aluminium electrolysis experiment were run under constant current conditions. The first part of the aluminium electrolysis were run with constant voltage.

The cell voltage and current as well as the temperature were logged during the course of the experiment by means of a multichannel Keithley 2000 Multimeter. The temperature was monitored continuously using a thermocouple type S (Pt-Pt 10%Rh) situated above the melt.

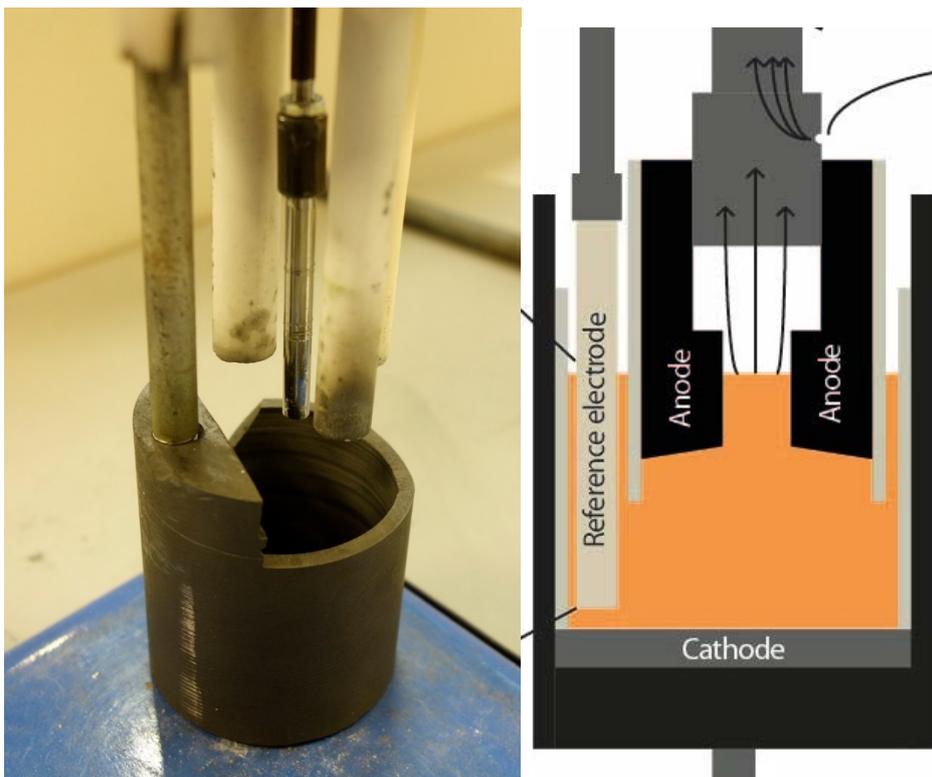


Figure 3: Experimental setups used: Figure 3-left the setup used for RE electrolysis studies. Setup is shown without crucible, the anode is the carbon cylinder, and the cathode is the iron rod. The alumina tubes are feeding tube and gas outlet tube., and Figure 3-right the setup used in cryolite systems.

4. Results and Discussion

Plots from a representative Al and RE electrolysis experiment are shown in Figure 4. For RE electrolysis the main off gas product seems to be CO rather than CO₂. The most likely explanation is the low anodic current density caused by the large anode surface area. In addition, the large area of exposed carbon over the electrolyte will give an additional surface where the Boudouard reaction can occur.

Voltages

Direct voltage comparison across the different experiments is difficult, since in the RE electrolysis experiments there was no proper reference electrode used. Only the glassy carbon crucible was used as a quasi-reference to ensure that no refractory materials could back-react with the formed RE metal.

However, looking at the voltage trends there is a similar transition trend, with the lack of a well-defined transition or voltage step, in both the RE and the Al electrolysis when the system changes from producing only CO/CO₂ and into CF₄ co-evolution regime. The voltage is increasing gradually, and only by a few 100mV while CF₄ concentration in the off gas increases.

In the RE electrolysis oxide feedings were done based on an increase of the voltage signal that had been established to correlate with an onset of CF₄. However it can be seen that even if it successfully terminates the CF₄ evolution, the total amount of CF₄ emitted is high, when

comparing $\text{CF}_4:\text{CO}_2$ or $\text{CF}_4:\text{CO}$ ratios with the aluminium electrolysis experiment. Despite the feeding strategy not all of these anode effects were stopped before they developed to a full blockage.

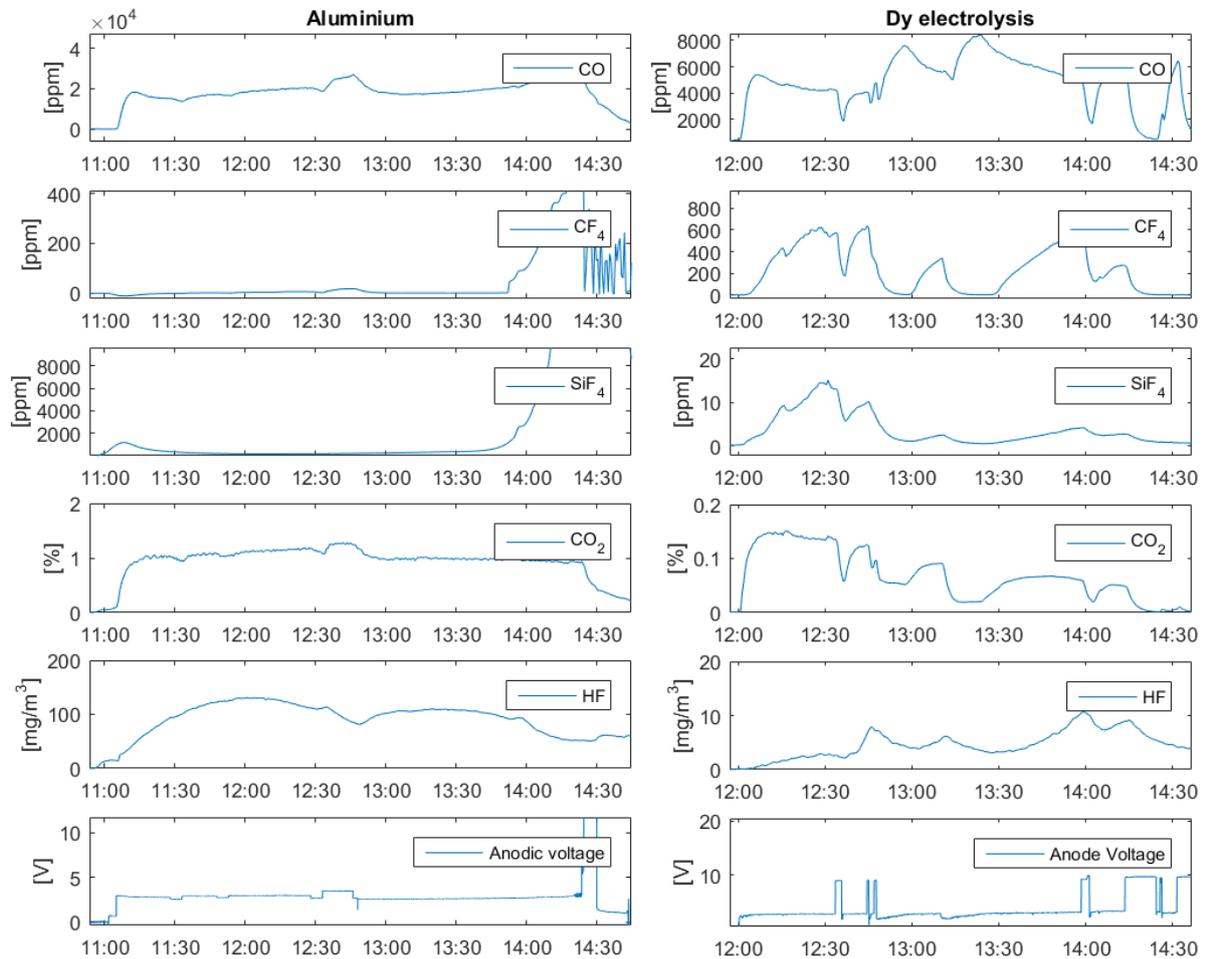


Figure 4: Different trends for gas species in Al [Left] and Dy [Right] electrolysis experiments. The Al experiment (left) were first run in a constant voltage mode before it was put in constant current from 12:45. The Dy electrolysis (right) was run with constant current all through the experiment

SiF₄

There is SiF₄ present in all the experiments. In the RE electrolysis experiments only minor amounts (<20 ppm) are present, while in the Al experiments concentrations higher than 1000 ppm were observed in virtually all experiments. Initially it was believed that SiF₄ could be a result of HF reacting with lining materials, or worse, exposed parts of SiO₂ on the back side of the FTIR internal mirror. However, after estimating the trends and concentrations of SiF₄ the trends for SiF₄, and HF do not correlate well, and the SiF₄ concentrations is usually significantly higher than what could be explained from HF formation.

As can be seen from Figure 4 SiF₄ have a peak at the start of the experiments, this behavior was common in many of the experiment, and could probably be attributed to evaporation of dissolved Si that could exist as impurities in the electrolyte by increased convection from the

gas bubbles formed at the anode. During the experiments, however, the SiF₄ trends seems to differ a bit more.

When CF₄ formation starts in the Al-electrolysis experiments, SiF₄ concentrations in the off gas increases before any other gases in the timespan leading into the full anode effect in Al systems, however it does not seem to change when small amounts of CF₄ are co-evolved such as in the timeframe between 12:30 and 12:45. A bit later in the experiment leading into the anode effect at 13:45, we can see that SiF₄ is the first species to increase in concentration, almost 10 minutes before any change in CF₄ can be observed, and no significant change in anode voltage can be seen. Hence the anode and electrolyte temperature should not change much in this timeframe, ruling out heating and evaporation of dissolved SiF₄ from the molten salt. The most probable remaining explanation is that SiF₄ is formed electrochemically, or chemically by an electrochemically formed anode product that is different from the ones produced between 12:30 and 12:45. This could be CF₄, or COF₂, being formed due to the lower oxide content in the electrolyte. Both of these gas species will, theoretically, react with the lining and refractory materials, Si₃N₄ and SiO₂ to form SiF₄ according to reactions (10) and (11). One could further speculate that either CF₄ or COF₂ have a significantly better kinetics to form SiF₄. So that one of them does not form SiF₄, but appears as CF₄ in the emerging gas from the furnace, and hence explains the peaks of CF₄ without any SiF₄.

In RE electrolysis SiF₄ generally always follows the CF₄ trends, but the amount of SiF₄ is significantly lower than in the Al electrolysis. This can be explained by the fact that SiO₂ is only available as impurities in the Al₂O₃ ceramic gas outlet tube.

CO₂ and CF₄ correlation

For the REF₃-LiF system it was observed an interesting correlation between CO₂ and CF₄. CO₂ seems to correlate very well with CF₄ evolution at CF₄ concentrations up to a few 100 ppm. Since CF₄ also correlates with anode voltage the CO₂ correlation could in theory be caused by the need for a higher overvoltage present at the anode giving more CO₂. However, there is nothing in the thermodynamic data that supports this, as the separation between CO₂ and COF₂ or CF₄ (Figure 1) evolution is virtually unchanged between the systems.

CO₂ correlation with CF₄ can have at least two other possible explanations. CF₄ will react with Al₂O₃ to form AlF₃ and CO₂ according to reaction (9). COF₂ can also have the same reaction with Al₂O₃, given in reaction (11), but there is also the possibility that COF₂ will self-decompose according to reaction (12). This reaction will have increased thermodynamic strength as the gas cools on the way out of the furnace.

On the cryolite based experiments we have not been able to see if this relationship exist due to the generally higher CO₂ concentration throughout the experiment, making it impossible to detect CO₂ level changes below 100 ppm.

Hard and soft anode effect

Hard and soft anode effects is not very clearly defined, but a hard anode effect is the typical sudden rise in voltage, and complete blockage of the anode surface, giving a sudden shift between seemingly normal operation and anode effect. A soft anode effect is a more gradual, but still clearly apparent voltage increase combined with the appearance of PFC gases in the off gas. It has traditionally been claimed that rare earth electrolysis does have a softer anode effect

than aluminium electrolysis [6]. One explanation could be due to the fact that increased bath conductivity always carries some current and act as a buffer.

In our experiments, we do not see anything that supports this statement. In several of the RE experiments we can show that with constant current CF_4 increases while CO / CO_2 decreases at a faster rate. No other possible product gases were observed either, indicating that the anode produces less gas than it should when taking the current into account.

However, we do also see in laboratory cells that CF_4 can be produced at extremely high levels, way beyond the quantification capability of our equipment, while the cell is operating only at slightly elevated voltages, and do not have any signs of running in a "hard" anode effect with high and erratic voltage. On the other hand, the classic anode effect can also be provoked to occur both in RE systems.

In aluminium experiments the condition of high CF_4 (above 1000ppm) with only 1V or less increase in the cell voltage have also been observed, although not so often. This difference can be explained by the generally lower anodic current densities in RE electrolysis (often 0.1-0.2A/cm²), while aluminium experiments rarely is run at current densities below 0.6 A/cm². The reduced current density might give the slower CF_4 formation kinetics enough time to take all the current at moderate overvoltage in the RE systems while the overall reaction kinetics might be very similar to that of the aluminium electrolysis

The reduced occurrence of hard anode effect in both electrolyte systems could possibly be attributed to the shape and geometry of the anode rather than the actual chemical composition of the electrolyte. In RE electrolysis the anode surface is vertical rather than horizontal, and this might help create additional circulation, and allow for CF_4 bubbles to escape easier despite good wetting of the anode.

Due to the reduced geometry of a laboratory cell, there will be a much higher ratio of vertical side wall to horizontal anode surface in most laboratory setups.

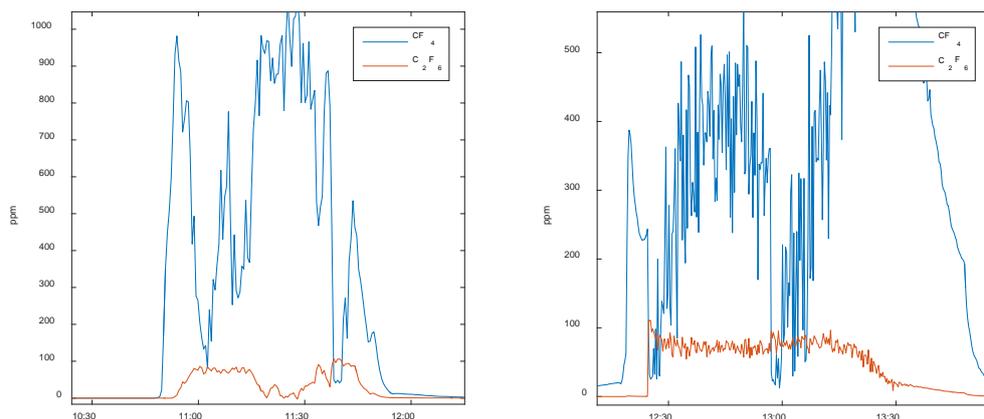


Figure 5: Comparison of C_2F_6 and CF_4 evolution in RE electrolysis (left), and Aluminium electrolysis (right)

CF_4 and C_2F_6

CF_4 is often formed without any traces of C_2F_6 in both Al electrolysis and RE electrolysis, even with CF_4 levels beyond 500 ppm there is no signs of C_2F_6 with a detection limit around 1

ppm. However, when C_2F_6 appears it is usually present in a ratio of 1:10 on a molar basis compared to CF_4 in Al electrolysis. None of our experiments in the binary REF_3 -LiF system showed any sign of C_2F_6 , while one (of total 4) experiments in a $NdF_3:DyF_3$ -LiF electrolyte showed C_2F_6 as well in an anode effect, as can be seen in Figure 5. The ratio in the REF_3 -LiF system is approximately 1:10 given the uncertainties of the measurement equipment. However, one interesting thing can be observed. While C_2F_6 seems to appear very suddenly in Al electrolysis, the rise in C_2F_6 concentration for the RE electrolysis was more gradual as can be seen from Figure 5. Given that this is only one experiment it is not enough to make a conclusion, but in light of how sudden C_2F_6 evolution usually are both in laboratory measurement and industrial cells it is interesting to note.

5. Conclusions

Both CF_4 and COF_2 have the potential to react with many common high-temperature materials such as Al_2O_3 and Si_3N_4 , and in our lab-cell SiF_4 seemed to be the first indication of an upcoming anode effect.

The anode reaction in cryolite system for aluminium electrolysis seems to behave similar to the anode behavior in REF_3 -LiF based electrolytic systems for RE electrolysis when it comes to transition between pure CO/CO_2 evolution and CO/CO_2 with CF_4 co-evolution. Due to the lower current densities of the anode the RE systems can produce a higher amount of PFC before rapid anode voltage increase is observed.

For RE systems there seems to be an increase in CO_2 together with low levels of CF_4 .

Acknowledgements

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References

1. M. M. R Doreen, D. L. Chin, J. K. C. Lee, M. M. Hyland, B. J. Welch, Sulfur and fluorine containing anode gases produced during normal electrolysis and approaching an anode effect, *Light Metals 1998*, 311-316 (1998)
2. T. A. Aarhaug, *Mapping of primary Aluminium Raw Gas Composition by Online Fourier Transform Infrared Spectroscopy*, 10th Australasian Aluminium Smelting Technology Conference, Launceston, Tasmania (2011)
3. O. Knacke, O. Kubaschewski, and K. Hesselmann (Eds.), *Thermochemical Properties of Inorganic Substances*, 2nd Edition, Springer-Verlag (1991)
4. Factsage 6.4, thermodynamical software, Thermfact and GTT-technologies (2013)
5. O. S. Kjos, T. A. Aarhaug, E. Skybakmoen, A. Solheim, *Studies of Perfluorocarbon Formation on Anodes in Cryolite Melts*, *Light Metals 2012*, 623-626, (2012)
6. Rudolf Keller, Kirk Larmier, *Electrolysis of Neodymium oxide*, US Department of Energy report, DOE ID 13104, (1997)