Natural Gas Anodes for Aluminium Electrolysis in Molten Fluorides

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Industrial primary production of aluminium has been developed and improved over more than 100 years. The molten salt electrolysis process is still suffering from low energy efficiency and considerable emissions of greenhouse gases (CO_2 and PFC). A new concept has been suggested where methane is supplied through the anode so that the CO_2 emissions may be reduced significantly, the PFC emissions may be eleiminated and the energy consumption may decrease significantly. Porous carbon anodes made from different graphite grades were studied in controlled laboratory experiments. The anode potential, the anode carbon consumption and the level of HF gas above the electrolyte were measured during electrolysis. In some cases it was found that the methane oxidation was effectively participating in the anode process.

Introduction

Aluminium is produced by the Hall-Heroult process, which was patented independently by Hall and Heroult in 1886. The overall primary cell reaction is:

$$Al_2O_3\,(diss) + 3/2\,C\,(s) = 2Al\,(l) + 3/2\,CO_2\,(g) \qquad (1)$$

Alumina is dissolved in a molten fluoride electrolyte based on cryolite (Na_3AlF_6) containing AlF_3 and CaF_2[1]. Modern cells are equipped with so called prebaked carbon anodes and operating at ~ 955 ^oC in a horizontal electrode design. The theoretical anode carbon consumption is 333 g per kg Al, and consumed anodes must be replaced. Research to find inert anodes for oxygen evolution has not been successful. An alternative is to supply natural gas (methane) through the anode, which will give the following cell reaction:

$$Al_2O_3\,(diss) + 3/4\,CH_4(g) = 2Al\,(l) + 3/4\,CO_2\,(g) + 3/2\,H_2O\,(g) \qquad (2)$$

The reversible cell potentials of reactions (1) and (2) are very similar; the standard potentials being ~1.2 V. The use of methane will reduce the amount of CO_2 evolved by up to 50 %, and the anode process will occur at a lower anode potential due to the very low overvoltage. In principle methane oxidation will eliminate replacement of anodes and the socalled anode effect which leads to the formation of PFC gases (CF_4 and C_2F_6) that are strong greenhouse gases.The main challenge related to the use of methane in this process is the formation of water vapour which may lead to the presence of HF gas. Consumption of carbon anodes according to reaction (1), the yield of methane consumption in reaction (2) and possible cracking of methane are other important issues.

The anodic overvoltage during industrial aluminium electrolysis is quite high, about 0.4 V at ~0.7 A/cm^2 for socalled prebaked anodes[1]. At lower current densities there is a linear relationship between anodic overvoltage and log current density.

Considerable research has been carried out to develop an inert oxygen evolving anode to replace the consumable carbon anode[2]. So far no inert anode material has been developed for industrial operation. The most promising inert anode candidates have been based on tin oxide and nickel ferrite. In the case of using an inert anode the cell reaction will be the following:

$$Al_2O_3\,(diss) = 2Al\,(l) + 3/2\,O_2\,(g) \qquad (3)$$

The reversible potential of reaction (3) is ~2.2 V.

Studies of socalled gas anodes for electrowinning in molten salts have been reported to some extent. Porous carbon was mainly used as the anode and a small depolarisation effect was observed in molten cryolite for aluminium electrolysis[3-5]. Magnetite has also been studied as the anode, but it was found to be unstable in molten cryolite during electrolysis. The use of hydrogen as an anodic reactant in porous or non-porous non-carbon electrodes, including metallic, metal oxide and refractory materials, was reported in a US patent in 1972[6.]. In 2000 another US patent on designing a non-consumable anode of the type used for solid oxide fuel cells (SOFC) with solid oxide membrane supplied with reformed natural gas was suggetsed for aluminium electrolysis[7]. More recently recently papers[8-10] are related to applying the solid oxide membrane technology to produce metals from their oxides in molten salts, with the introduction of hydrogen. A similar approach was applied in magnesium production in molten chlorides resulting in the depolarisation effect and the formation of HCl gas[11.] In addition a thermodynamic analysis considering carbon and nickel-based hydrogen diffusion anodes in the electrolyte (Na_3AlF_6-AlF_3-Al_2O_3) was carried out to identify optimum operating parameters in aluminium production in 2007[12] and a nickel-based hydrogen diffusion anode was used in an experimental study of aluminium electrowinning, showing measurable depolarization of the anode potential in 2011[13].

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The concept of applying gas anodes has not been fully implemented in industrial electrolysis processes. The research has mainly been focused on the use of porous carbon anodes and the type of SOFC with a zirconia-based solid membrane. For carbon anodes, there are competing reactions between carbon and reducing gases on the anode, resulting in partly consumption of the anode. The unacceptable dissolution of zirconia-based materials in molten cryolite is an obstacle for using SOFC-type inert anodes for aluminium electrolysis[14]. Therefore, a type of stable inert anode material is needed.

In a more recent activity the depolarisation effect of hydrogen and methane was demonstrated in laboratory experiments[15-17]. The authors have demonstrated the depolarisation effects of Pt and SnO_2-based gas anodes (H_2) in molten chlorides as a model system for further studies in more corrosive molten cryolite[15-17]. Figures 1 and 2 show results obtained during electrolysis in molten cryolite-alumina based electrolytes at 850 ^{o}C[18]. The depolarising effect of methane was demonstrated both for galvanostatic and potentiostatic electrolysis. It was found to be challenging to maintain the depolarising effect over long time, more than ~30 - 60 minutes.

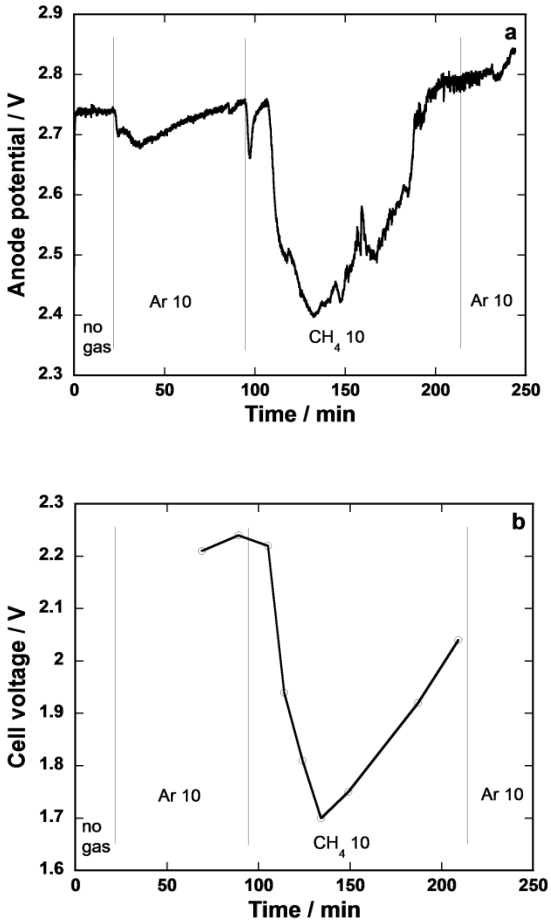

Figure 1 Anode potential (a) and cell voltage (b) versus time during constant current electrolysis (0.2 A; 0.2 A cm^{-2}) using a porous SnO_2-based anode in molten Na_3AlF_6-AlF_3-Al_2O_3 (4.5 wt%) at 850 °C[18].

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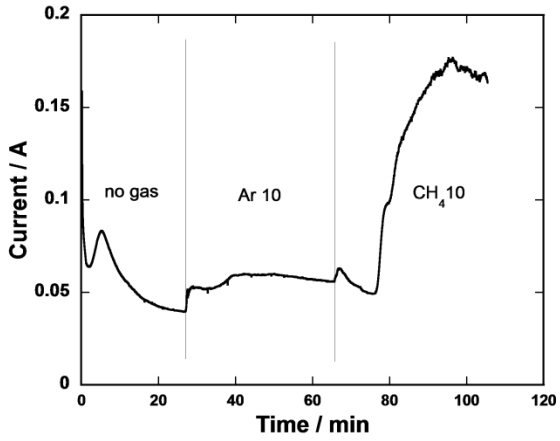

Figure 2. Current versus time during electrolysis at constant anode potential (2.2 V; apparent anode area, 1 cm^2) using a porous SnO_2-based anode in molten Na_3AlF_6-AlF_3-Al_2O_3 (4.4 wt%) at 850 °C[18].

In a recent paper[19] the production of HF was studied by gas analysis during electrolysis in molten cryolite-alumina electrolytes using porous SnO_2 inert anode with methane supply. High levels of HF were detected (up to 0.2 wt%) during depolarising of the anode. It was suggested that the HF problem could be resolved by capturing the produced HF and let it react with alumina to form AlF_3 which could be fed back to the cells to make up for the loss of electrolyte in the hydrolysis reaction[19]. It was also shown that hydrogen gas supply gave a similar depolarising effect.

Methane is an attractive oxidiseable gas due to its relative abundance, high purity and low price. In this paper porous carbon anode materials with the introduction of methane were used and studied as the gas anodes during aluminium electrolysis in laboratory experiments. However, methane may undergo cracking especially at higher temperatures. This will cause the formation of carbon which may precipitate at fill up the pores of the carbon anodes. Cracking of methane will take place according to the following reaction scheme:

$2\ CH_4\ (g) \rightarrow C_2H_6\ (g) + H_2\ (g)$ (4)
$C_2H_6\ (g) \rightarrow C_2H_4\ (g) + H_2\ (g)$ (5)
$C_2H_4\ (g) \rightarrow C_2H_2\ (g) + H_2\ (g)$ (6)
$C_2H_2\ (g) \rightarrow 2\ C\ (s) + H_2\ (g)$ (7)

Decarburation may occur as follows:

$2\ CH_4\ (g) \rightarrow 2\ C\ (s) + 4\ H_2\ (g)$ (8)

Reaction (5) is not complete at temperatures lower than 1350 °C without the use of a catalyst such as nickel.

The presence of CO_2 may change the methane reaction according to:

$CH_4\ (g) + CO_2\ (g) = 2\ CO\ (g) + 2\ H_2\ (g)$ (9)

Small amounts of moisture are introduced to the electrolyte by surrounding air and alumina. This will cause the formation of gaseous HF according to the following reaction:

$AlF_3\ (diss) + 3/2\ H_2O\ (g) = 3\ HF\ (g) + 1/2\ Al_2O_3\ (diss)$ (10)

Using a methane oxidising anode will cause the formation of a significant amount of moisture according to reaction (2). This may represent a major challenge for the gas anode concept if high amounts of HF are produced. Another concern is the consumption of electrolyte in the form of AlF_3.

Experimental

The electrolyte composition was Na_3AlF_6 (natural cryolite, Greenland) with an excess of 6 wt. % AlF_3 (Noralf, Boliden Odda AS) and 5 wt. % CaF_2 (Merck, > 97 %) in addition to ~4.5 wt. % anhydrous γ-Al_2O_3 (Merck, > 98 %). The amount of alumina was close to saturation. The electrolyte composition is close to the electrolyte commonly

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used in industrial aluminium electrolysis. Figure 3 shows the schematic of the experimental set-up. The electrolyte was contained in a graphite crucible with a lining of sintered alumina, while the bottom of the crucible was the cathode. A hollow steel tube attached to the porous carbon anode was used as the current collector. The anode and cathode were positioned horizontally with respect to each other. A molybdenum wire (Norsk Spesialmetall, 99.9 pct, 1 mmØ) was used as the current lead. The wire was passed through an alumina tube which was placed inside another alumina tube with a closed bottom. The closed tube contained aluminium at the bottom, and was fitted with a hole above the metal so that electrolyte could enter. The whole system served as an Al^{3+}/Al reference electrode. All potentials were measured against this aluminium reference electrode. The crucible containing the bath was dried in air at 120°C over night. The furnace and the cell with electrolyte were also dried at 200°C in N_2 for a few hours before heating up the furnace to the working temperature at 970°C. The furnace was continuously flushed with N_2. The inlet gas composition for the anode was controlled using mass flow controllers (Bronkhorst) and the inlet gas pressure was measured. The whole electrochemical cell was placed in a vertical tube furnace heated by resistance wires, and connected to a temperature controller. The gases were purged into the porous anode with a gas flow equal to 20 ml min^{-1}.

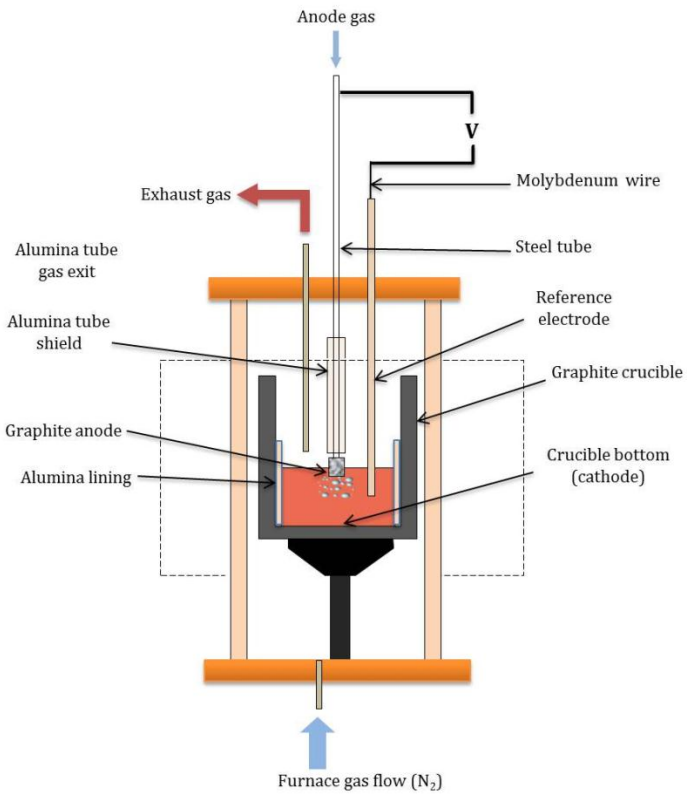

Figure 3: Sketch of the experimental electrolysis cell.

Galvanostatic electrolysis experiments were performed using porous anodes made of three different graphite grades (Tokai Carbon Group). Some of the properties of the graphite grades used for preparing anodes are given in Table I. Each experiment was started by applying a constant current of 2.3 A to the cell, corresponding to an apparent current density of 0.4 Acm^{-2}, while N_2 was passed through the porous anode for the first 45 min of the electrolysis time and afterwards changing the gas to CH_4 and continuing the electrolysis for an additional time of 4 h. This procedure made it possible to detect if there was any depolarisation due to the oxidation of methane at the anode. Also another series of electrolysis experiments was carried out without using methane in order to have a better insight of the process and for comparison. In this series, only nitrogen was purged through the anode; while the rest of the experimental conditions were unchanged. The weight of the anodes was measured before and after each experiment to check the consumption of the anodes and it was compared with the theoretical values.
The used anodes were examined by Scanning Electron Microscope (SEM, Hitachi S-3400 N).

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Table I: Typical properties of different graphite grades [20]

Grade name	Specific gravity (g/cm^3)	Porosity (%)	Grain size (μm)	Grade
G347	1.85	12	11	Isotropic
G348	1.92	8	8	Isotropic
G140	1.7	20	1000	Moulded
KWPSY	1.6	20	2000*	Extruded

*Maximum grain size

A new anode concept was designed in order to try to improve the methane oxidation reaction in more recent experiments. A denser graphite (G348, Table I) with low permeability was used to shield the main graphite anode (G347, Table I). The new anode is shown in Figure 4.

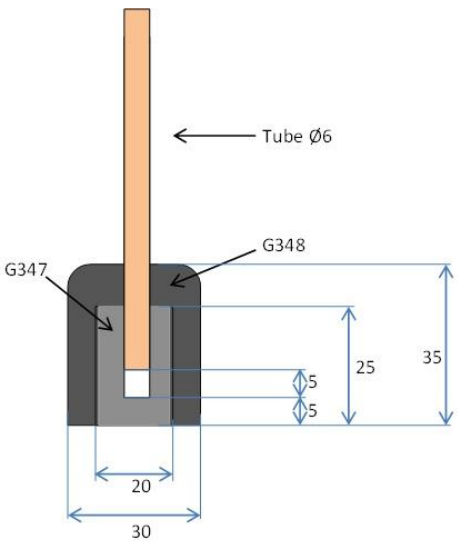

Figure 4: Sketch of a new anode design with two different graphite grades.

Results and discussion

The desired situation is when methane oxidation, reaction (2), is the only anode process. In this case the anode potential will be considerably lower than the anode potential during normal electrolysis due to the high overvoltage during normal electrolysis without supplying methane. In reality these two oxidation reactions will take place at the same time, and the carbon anode will be depolarised based on the partial current densities of these two reactions.

Table II gives the consumption of the porous graphite anodes in electrolysis experiments. The theoretical carbon consumption based solely on reaction (1) is 1.2 g.
The isotropic graphite (G347) was found to behave quite differently compared to the other grades. There is a significant change in weight loss of the anode during electrolysis when CH_4 was supplied through G347 compared to when N_2 was supplied through the anode. The moulded (G140) and extruded (KWPSY) grades were also consumed slightly less, when CH_4 was flushed into the anode but the difference is less significant compared to G347. It seems when isotropic grade was used, CH_4 participated in the anodic reaction remarkably, while for the two other grades the anode consumption was almost equal to the theoretical value. The weight loss difference of the extruded grade anode (KWPSY) with and without CH_4 is not very small. But this is due to the fact that this anode showed a higher consumption when N_2 was used, compared with the two others. The reason for this is not clear at the moment.

Generally the anode carbon consumption is expected to be higher than the theoretical value. This is due to other anode carbon consumption reactions such as CO_2 burn (Boudouard reaction) especially when the gas penetrates into the pores of the anode, air-burn, and dusting[1]. Dusting, which means that unreacted carbon particles detach from the anode, is not believed to be an important issue in controlled laboratory experiments.

However, it is seen here that for all the graphite grades when CH_4 was applied, the weight loss was less than the theoretical consumption. Hence, it is likely that CH_4 was involved in the anodic reaction - at least to some extent -

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for all the graphite grades. This conjecture sounds more probable when we consider the likely thermal cracking of CH_4 resulting in precipitation of carbon in the porous structure of the anode. Methane becomes unstable in terms of its elements from 530°C. However, the kinetics are slow. The equilibrium constant for cracking of methane is 87 at T = 970°C[21]. Therefore, this reaction is most likely to happen in our experiments, at least to some extent. Precipitated carbon can add to the final weight of the anodes. One experiment was performed to check this, where all the conditions were unchanged, except that no current was passed. So, the sole factor influencing the anode weight was the amount of carbon precipitation. It was found that around 0.2 g carbon was precipitated in 4 h (the same time CH_4 was flushed into anodes during electrolysis experiments). This suggests that the real carbon consumption was less than reported in Table II. A more recent experiment using the new anode design (see Fig. 2) gave a carbon concumption of 87 % of theoretical during electrolysis with a mixture of nitrogen and methane supply to the anode.

Table II: The consumption of graphite anodes when supplied with only N_2 and when supplied with N_2 + CH_4 during electrolysis in cryolite-based electrolyte at 970 °C for 285 min. The theoretical carbon consumption is 1.2 g.

Graphite type	Anode gas	Weight loss (g)	Consumption (%)
Isotropic (G347)	$N_2 + CH_4$	0.67	56
	N_2	1.28	107
Moulded (G140)	$N_2 + CH_4$	1.15	96
	N_2	1.24	103
Extruded (KWPSY)	$N_2 + CH_4$	1.16	97
	N_2	1.4	117

Apart from the electrochemical reaction and cracking reaction, there exists another factor which might have caused weight loss changes. This is due to possible penetration of electrolyte into the porous structure of the graphite during electrolysis and can add to the final weight of the anode. However, this should be negligible since the anode was pulled out of the bath and flushed with N_2 for 1 hour after electrolysis. SEM studies of the graphite anodes also confirmed that the graphite structure was essentially free from electrolyte after the experiments.

The gas pressure before the anode was measured while the anode was placed above the molten electrolyte. The isotropic grade showed the largest pressure increase, around 0.5 bars, the moulded grade showed less increase, around 0.25 bars; while the extruded grade did not show any pressure increase. This difference can be attributed to the large difference in grain/pore size of these graphite grades.

Figures 5 - 7 show the cell potential and pressure changes during electrolysis using isotropic grade (G347) anode for two different experiments; Figure 3 shows anode potential only N_2 supplied through the anode and Figure 4 shows when N_2 was supplied through the anode 45 min prior to introducing CH_4 and the electrolysis was continued for 4 more hours.

As can be seen, when only nitrogen was supplied to the anode, the potential increased gradually during the electrolysis, but the pressure remained constant. This is due to the consumption of graphite resulting in decrease of surface area and consequently increased current density. This is in agreement with previous studies demonstrating an increase in the anodic overvoltage when current density is increased[22].

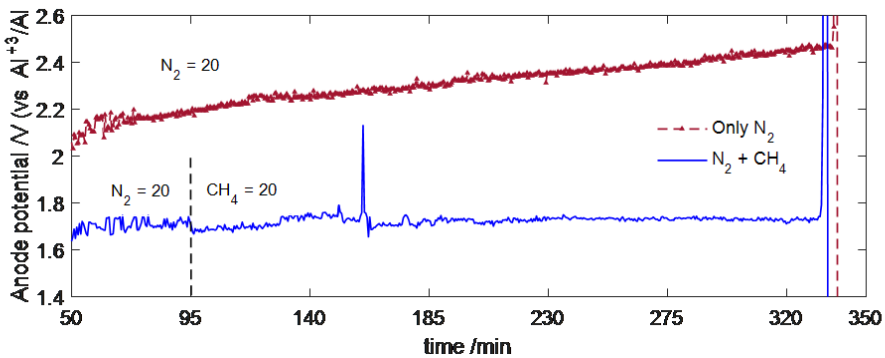

Figure 5: Anode potential vs time during aluminium electrolysis for two experiments where in (a), only N_2 and in (b) N_2 + CH_4 were flushed into the porous anodes. The anode was made of isotropic graphite (G347). i = 0.4 $A.cm^{-2}$, T = 970°C. The values in the figure are flow of the gas in $ml.min^{-1}$.

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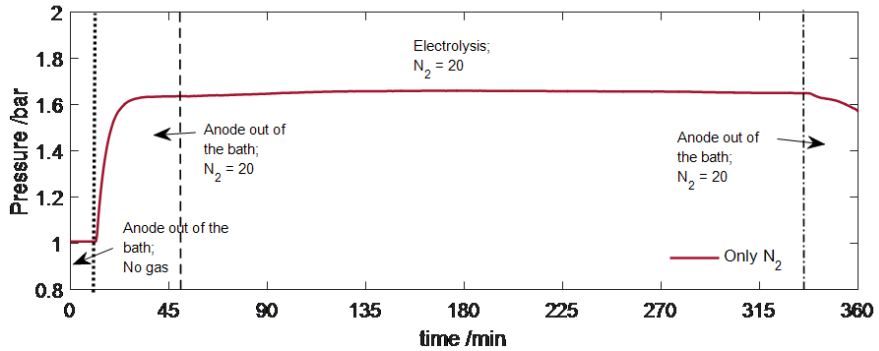

Figure 6: Pressure changes during aluminium electrolysis where only N_2 was flushed into the porous anodes. The anode was made of isotropic graphite (G347). i = 0.4 A.cm^{-2}, T = 970 °C. The values in the figure are flow of the gas in ml.min^{-1}.

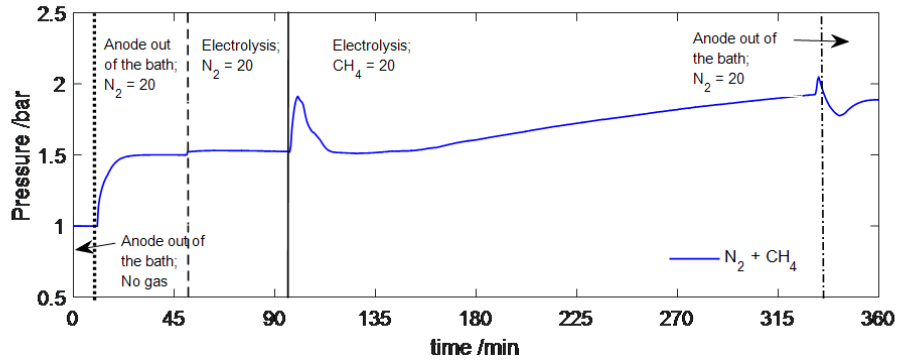

Figure 7: Pressure changes during aluminium electrolysis for where in N_2 + CH_4 were flushed into the porous anodes. Anode was made of isotropic graphite (G347). i = 0.4 A.cm^{-2}, T = 970 °C. The values in the figure are flow of the gas in ml.min^{-1}.

A rough calculation demonstrates that the change in the surface area was noticeable. The surface area prior to electrolysis was 6.28 cm^2 and the approximate value for the final surface area was ~5 cm^2. The final surface area was calculated based on the geometrical surface of the anode after electrolysis. Assuming the change in surface area and a constant current the apparent current density increased from 0.37 A.cm^{-2} to 0.46 A.cm^{-2} during electrolysis.

However, when CH_4 was introduced to the anode the potential became stable and it remained almost constant throughout the electrolysis period. The vertical lines in **Error! Reference source not found.** (b) represent the time where the gas anode was shifted from nitrogen (dashed line) to methane (solid line). There was an abrupt increase and decrease in pressure which is because of supply of both gases during the shifting time. After that as can be seen, introduction of methane to the anode caused a gradual pressure increase which lasted as long as methane was flushed; *i.e.* until the end of electrolysis. This is due to carbon precipitation from the cracking reaction of methane. If the electrolysis continued for a longer time, this might have led to clogging as observed earlier[4].

The change in cell voltage agrees with the weight loss data (**Error! Reference source not found.**). It is clear that methane was significantly involved in the anodic reaction, so the potential was stable and did not increase. However, the problem of clogging might prevent long term electrolysis. A suitable anode design could possibly prevent the probable and undesirable clogging.

There is a small difference in the cell potential in the beginning between these two experiments, although the anodes were similar and both experiments were started by supplying N_2 to the anode. The reason is not clear. However, it is expected that during supply of methane the anode potential should be lower due to lower overpotential.

Similar electrolysis experiments using moulded (G140) and extruded (KWPSY) graphite grades did not give significant anode potential differences when supplying nitrogen and methane. In both cases the anode potential was found to increase during the course of electrolysis due to the consumption of carbon which will change the

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active anode area. These results suggest that the contribution of the methane in the anodic reaction was not significant for these graphite grades, which is in agreement with results from the weight change results as given in Table II. Also the pressure build up was much less for these anodes.

Figures 8 - 10 show results from a recent electrolysis experiment using the new anode design consisting of two graphite grades as shown in Figure 4. Based on the carbon weight loss the carbon consumption was ~87 %, indicating that methane participated in the anode process to some extent. This is also supported by the results from measuring the HF level above the electrolyte and the anode potential variation. The anode potential (Figure 10) was not found to increase significantly during the course of electrolysis, although short time variations were observed. High levels of HF was measured during methane supply. These observations indicate that methane oxidation was more important than the carbon weight loss indicated, which suggests that cracking of methane must have contributed to carbon formation. Also the pressure build up increased significantly upon introduction of methane, as shown in Figure 8.

Shielding of the carbon anode by using carbon is not ideal. Using an insulating shielding material is challenging due to the agressiveness of molten cryolite. Sintered alumina may be used in alumina saturated electrolytes, but it is difficult to obtain a good seal between graphite and alumina.

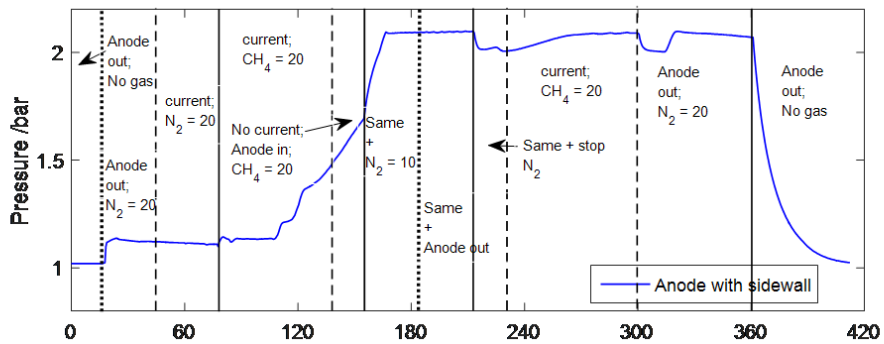

Figure 8: Pressure changes during aluminium electrolysis when supplying N_2 + CH_4 to the porous anode. i = 0.5 A.cm^{-2}, T = 970 °C. The values in the figure are flow of the gas in ml.min^{-1}.

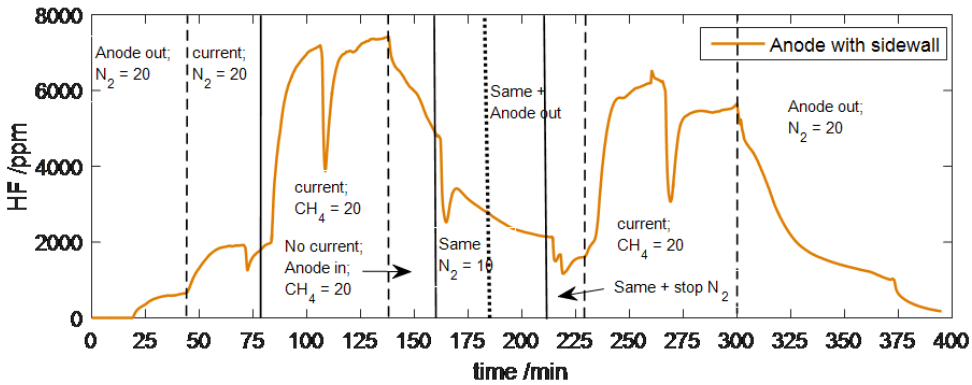

Figure 9: Changes in HF level of the off-gas during aluminium electrolysis when supplying N_2 + CH_4 to the porous anode. i = 0.5 A.cm^{-2}, T = 970 °C. The values in the figure are flow of the gas in ml.min^{-1}.

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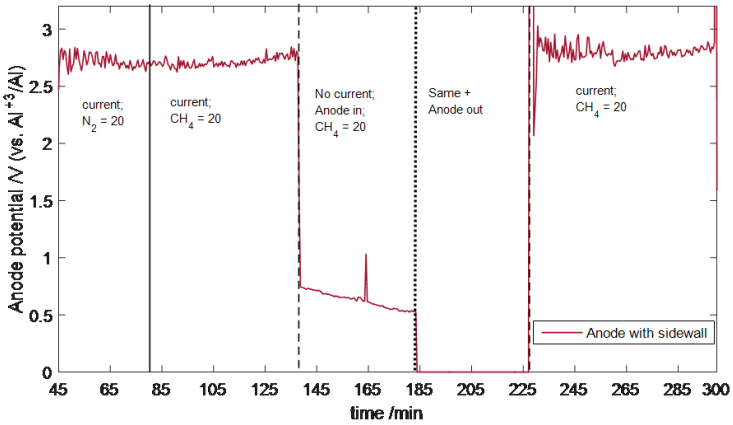

Figure 10: Anode potential changes during aluminium electrolysis when supplying N_2 + CH_4 to the porous anode. i = 0.5 A.cm^{-2}, T = 970 °C. The values in the figure are flow of the gas in ml.min^{-1}.

Conclusions

Porous carbon anodes made from different graphite grades were studied in controlled laboratory experiments. The anode potential, the anode carbon consumption, the anode pressure build up and the level of HF gas above the electrolyte were measured during electrolysis. In some cases it was found that the methane oxidation was effectively participating in the anode process. The main challenges in promoting the methane oxidation reaction during electrolysis are related to optimising the anode porosity and graphite structure and the gas flow including the methane content as well as to minimise the cracking of methane. The isotropic graphite grade (G347) showed a better performance as a gas anode compared to the moulded and extruded grades. The best results so far showed that the methane oxidation reduced the anode carbon consumption to 56 % of the theoretical carbon consumption during electrolysis for 4 hours.

Acknowledgements

The authors gratefully acknowledge financial support from the Research Council of Norway in the project NOVAL (grant number 224985) of the GASSMAKS program.

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