POROUS CARBON ANODES FOR THE SUPPLY OF METHANE DURING ELECTROWINNING OF ALUMINIUM

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Abstract

One of the major downsides of the current aluminium production process is the high CO_2 emissions. One alternative to reduce this is to replace the consumable carbon anodes with inert anodes so that oxygen evolves instead of CO_2. Also PFC emissions will be eliminated by using inert anodes. However, so far a sufficiently inert anode has not been found. Another option is to utilize natural gas through porous anodes in order to change the anode process. This will decrease CO_2 emission remarkably and also eliminate PFC emissions and anode effect. The porous anode could be made of carbon or it can be inert. However, the as-mentioned problem still exists regarding porous inert anodes. Therefore, at the moment porous carbon anodes seem to be the best practical option. In this study, porous anodes made of different grades of graphite were used for electrolysis experiments in a laboratory cell. Also, off-gas analysis was performed to get an insight of the ongoing reactions. Our results show that for some types of graphite anodes, methane participates effectively in the anodic reaction.

Introduction

Environmental issues related to Hall-Héroult process is one of the major concerns of the aluminium industry. A large amount of CO_2 is emitted from electrolysis cells. The overall reaction is as follows [1]:

$$Al_2O_3 \text{ (diss.)} + 3/2C \text{ (s)} = 2Al \text{ (l)} + 3/2CO_2 \text{ (g)} \quad (1)$$
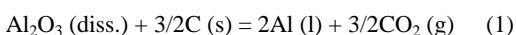
There has been a lot of research to tackle the problem of CO_2 emissions. An inert anode for the Hall-Héroult process has been called "The ultimate material challenge" [2]. It shows the high requirements of such a material. There have been only laboratory and bench scales tests to try inert anodes so far [3]. In conclusion, a prospective industrial inert anode still seems to be unreachable; at least in the near future.

Another alternative to the current industrial process is to supply a reducing gas (*e.g.* CH_4) to the anode/electrolyte interface through a porous anode. Then, the gas participates in the anodic reaction and the overall reaction changes from (1) to the following:

$$Al_2O_3 \text{ (diss.)} + 3/4CH_4 \text{ (g)} = 2Al \text{ (l)} + 3/4CO_2 \text{ (g)} + 3/2H_2O \text{ (g)} \quad (2)$$
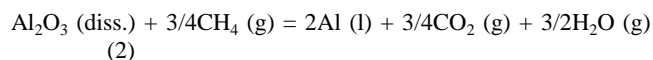
For this purpose a porous anode must be used. The porous anode could be made of carbon or an inert material. Certainly, a porous anode made of an inert material enables us to make the most of this concept; *i.e.* the amount of emitted CO_2 can be decreased to half according to the stoichiometry of reaction (2).

However, as mentioned earlier a sufficiently inert anode has not been found so far. Therefore, a porous anode made of carbon seems to be a more practical choice at the present time. When the anode is made of porous carbon, reactions (1) and (2) will be competing anodic reactions. The theoretical cell voltage of reaction (2) is 1.1 V while for reaction (1) it is equal to 1.2 V at 1233 K (960°C) [4]. This leads to a small depolarization of the cell voltage when methane is used in such a way [4, 5]. More importantly, utilizing the reducing gas, *e.g.* CH_4, results in reduced CO_2 emission. The degree of CO_2 emission reduction depends on which of these competing reactions dominates as the anodic reaction.

The concept of supplying a reducing gas to a porous anode in aluminium electrolysis has been tried before. In some studies carbon or graphite anodes were use [6-8]. A 0.3-0.4 V depolarization effect was detected when methane was used [6]. In another study porous graphite anodes showed depolarization when methane and H_2 were used. It was mentioned that due to high temperature of the process, methane decomposition occurs considerably and methane can be considered electrochemically equivalent to hydrogen. On the other hand, when hydrogen-containing fuels such as methane or hydrogen were used considerable fluoride losses from electrolyte occurred [7]. In addition, the anode might become clogged by soot when flushed by methane. When H_2 and CO were used some depolarization was observed; though the carbon consumption increased and the anodes disintegrated [8]. Inert porous anodes have also been tested in some studies. But, none of the inert anodes showed sufficient stability and were either disintegrated or dissolved to some extent after long time electrolysis [8-10]. One of the candidate inert anodes is a non-consumable gas anode based on the type used for Solid Oxide Fuel Cells (SOFC). It was reported that this anode is not suitable for the current aluminium electrolysis process, but could be utilized in a modified Hall-Héroult process [11].

We have reported our studies on this concept using both inert (*e.g.* SnO_2) and graphitic porous anodes. Aluminium electrolysis experiments were carried out at 850°C in a modified electrolyte where methane and hydrogen, in separate experiments, were used as reducing gases [5, 12, 13]. In a recent work different graphite grades were tested as anode material and one showed better results [14]. In this paper the continuation of our previous studies are presented. It was revealed that the previous results were not always reproducible. So, we started to look at the other parameters which might play a role. Establishment of the three-phase boundary between the gas, anode and electrolyte is crucial for the accomplishment of this process [5]. In addition, it was observed earlier that cracking of the methane during the electrolysis leads to partial or even complete clogging of the anode which is detrimental for this process [6, 14, 15]. In order to establish the

three-phase boundary and to prevent the clogging of the anode, the flow of the gas from top and the flow of the electrolyte from the bottom through the porous structure of the anode must be considered. Also, the flow properties of the porous graphite such as permeability, porosity and pore size are of great importance. Usually the electrolyte in the lab experiments is almost stagnant. They hydrostatic pressure of the electrolyte is negligible and therefore, the main factor causing the electrolyte to penetrate the anode is the capillary pressure. On the other hand, the fluid flow through a porous medium is described by Darcy's equation:

$$V = -\frac{K}{\mu}(\nabla P - \rho g) \qquad (3)$$

Where V is the average fluid velocity, K is permeability of the porous material, μ is the fluid viscosity, P is the pressure, ρ is the density of the fluid and g is the gravitational acceleration [16]. The three-phase boundary might be established on the outer surface of the anode or inside the porous structure of the graphite. This depends on the properties of the porous graphite as well as the flows of the gas and electrolyte.

In a similar study Namboothiri *et .al* made pressure calculations in order to find the suitable permeability for the porous material to be used as the gas anode [17]. Between four different carbon materials which were candidates for anode the one with 30 % porosity and average pore diameter 10 μm gave the best performance. The permeability of this sample was measured and it was equal to $1.30 \times 10^{-14} \pm 0.200 \times 10^{-14}$ m^2. Recalling that 1 darcy is equivalent to 9.8692×10^{-13} m^2 [18], then the permeability was equal to 13.2 md (millidarcys). The air permeability of industrial carbon anodes typically varies from 2×10^{-14} to 20×10^{-14} m^2 (20 -200 md) [19]. In our previous studies inert anodes based on tin oxide were used. The porous tin oxide-based anodes were supplied with methane and hydrogen and depolarisation was observed [5, 13]. The porosity of the inert tin oxide anodes used was approximately 28%. The gas permeability of anodes was in the range of $3-13 \times 10^{-13}$ m^2 (300 to 1300 md). The gas permeability increased slightly with increasing particle diameter. This was attributed to enhanced gas transport due to larger pore sizes [20]. However, a much denser graphite grade in comparison to these anodes (see grade 1/G347 in Table I) was the most efficient in our previous study [14]. Though, we did not carry out any fluid flow and pressure balance calculations.

Experimental

Mercury porosimetry was used to characterize the graphite grades. This technique is based on the intrusion of mercury into a porous structure under stringently controlled pressures [21]. A Micrometrics Autopure IV 9500 Mercury Porosimeter was used. This instrument can determine a broad pore size distribution (0.003 to 360 micrometres) [21]. The graphite samples were ~ 2 g. The graphite samples had fractured surfaces in order to have a more accurate measurement since when graphite is cut it might end up with smeared surfaces. The permeability of the graphite samples was measured by Carbon R&D RDC-145 Air Permeability apparatus. This apparatus has been designed for measuring baked carbon electrodes. Therefore, the sensitivity of the detectors, the maximum possible vacuum and the units of measure has been selected accordingly. So, the samples having permeability in the range of 0.1 to 30 nPm (10 to 300 md) can be measured [22]. The electrolyte composition was chosen similar to the modern industrial cells except that it was saturated with alumina. The electrolyte composition was 9.3 wt % AlF$_3$ (Noralf,

Boliden Odda AS), 5.0 wt % CaF$_2$ (Merck, > 97 %), and 9.0 wt % Al$_2$O$_3$ (Merck, > 98 %) and the remaining Na$_3$AlF$_6$ (natural cryolite, Greenland). The cryolite ratio was 2.3. Figure 1 illustrates the schematic of the experimental set-up. A graphite crucible contained the electrolyte. The walls of the crucible were lined with alumina and its bottom served as the cathode. A hollow steel tube screwed to the porous carbon anode was used as current collector. The anode and cathode were positioned horizontally in respect to each other. The crucible containing the bath was dried in air at 120°C overnight. After the crucible was put inside the furnace, the furnace temperature was set to 200°C and N$_2$ was flushed into the furnace. And the furnace containing the crucible was dried overnight at 200°C. The next morning the furnace was heated up to the working temperature equal to 980°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.

Galvanostatic electrolysis experiments were performed using porous anodes made of different graphite grades (supplied from different companies). Some of the properties of graphite grades used for preparing anodes are given in Table I. Each experiment was started by applying a constant current of 2.5 A to the cell while N$_2$ was passed through the porous anode for the first 40 min of the electrolysis time and afterwards changing the gas to CH$_4$ and continuation of the electrolysis for 216 min (total time: 256 min).
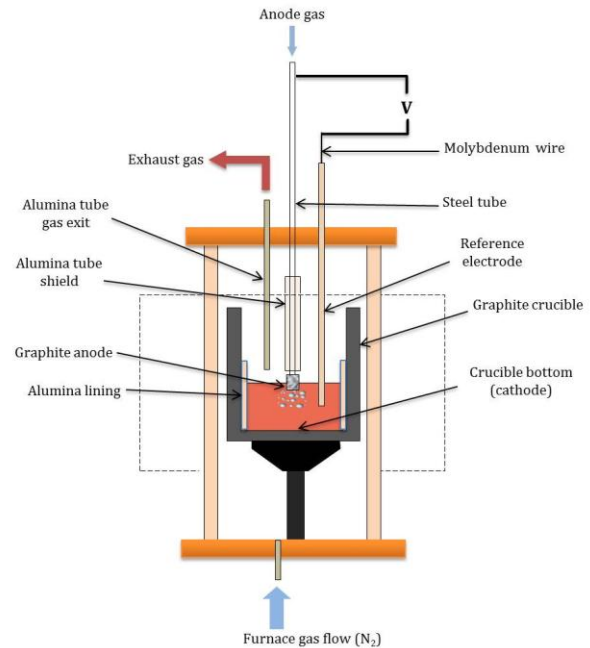

Figure 1: Schematic of the electrolysis cell.

This procedure enabled us to detect if there is any depolarization upon introduction of the CH$_4$ to the anode. Also another series of electrolysis experiments were carried out without using methane for comparison and in order to have a better insight of the process and for comparison. Different current densities were set by dipping the anode into the bath deep enough to have the desired current density while the current and electrolysis time was same for all experiments. 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.

Table I summarizes some of the properties of the graphite grades used in this study.

Table I: Typical properties of different graphite grades[23, 24]

Grade No.	Grade name	Specific gravity (g/cm^3)	Porosity (%)	Grain size (μm)	Supplier
1	G347	1.85	12	11	Tokai
2	EG-92E	1.75	16	800	Tanso
3	TM	1.82	20	10	POCO
4	G140	1.7	20	1000	Tokai

Figure 2 illustrates the anode assembly used for electrolysis experiments. Threads were made inside the graphite and the steel tube was screwed into the graphite. This made a firm connection between the steel tube and the anode.

Before running experiment the flow of the gas through the porous anode was tested inside ethanol at room temperature. In case of some of the graphite anodes there was a flow of the gas from the connection area. This is shown in Figure 2 by red arrows. However, as it will be addressed later this connection became sealed as the temperature was increased to electrolysis temperature in most cases.
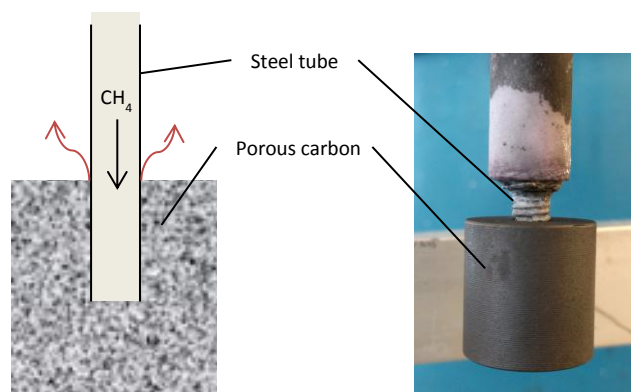

Figure 2: Anode Assembly. On the right hand side a schematic of the anode assembly is shown and on left a photo of the real anode assembly. The arrows show the place where anode gas might escape from the system.

Results and Discussion

The result of mercury porosimetry is shown in Figure 3. The differential intrusion of mercury is plotted vs. pore size distribution. This method only gives the open porosity which is of course important considering the fluid flow in the porous structure of the graphite. Besides, it gives the "minimum pore size" since it measures the pressure needed to penetrate into the pore [25]. Therefore, the pore sizes measured by this method might be underestimated to some extent. As can be seen the grades with larger grain size such as number 2 (EG-92E) and 4 (G140) have larger pores as well. And the pore size distributions are also broad. While in case of grades number 1 (G347) and 3 (TM) the pore size distribution is quite narrow.

The permeability of grade 2 (EG-92E) was measured and it was equal to 0.79 nPm (nanoPerm). This is equal to 0.79×10^{-13} m^2 or 80 md. But, the permeability of grade 1 (G347) was not in the range of the apparatus and the measurement failed. This grade is

denser and considering the range of the apparatus its permeability must be lower than 10 md.
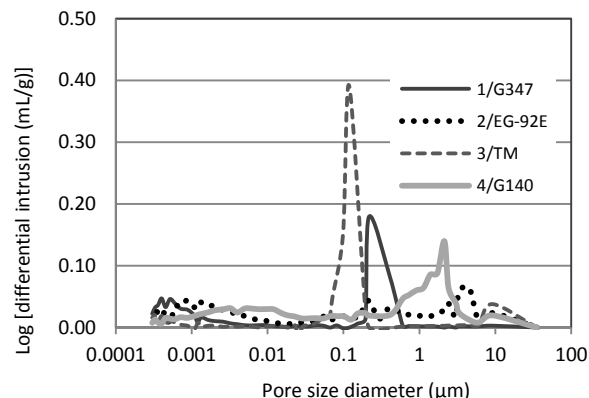

Figure 3: Differential intrusion of mercury into pores vs. pore size distribution for different graphite grades. The graphite grades are depicted by grade numbers given in Table I.

Table II summarizes the consumption of the porous graphite anodes in electrolysis experiments. The anodes were made of three different grades: grade 1 (G347) and grade 2 (EG-92E) and grade 3 (G140); see Table I. The theoretical consumption of the graphite anode is 1.2 g. This is based on reaction (1); *i.e.* with assumption that CH_4 does not take part in the anodic reaction and therefore, the whole weight loss is due to reaction (1). Of course, when CH_4 is used as gas anode reactions (1) and (2) are competitive anodic reactions.

Table II: The consumption of graphite anodes under different experimental conditions. Electrolysis was run in cryolite-based electrolyte at 980°C for 265 min. The theoretical consumption is 1.2 g. Experiments 3 and 6 are some earlier results: [14, 15].

Grade	Anode gas	gas flow (ml min^{-1})	Current density (A cm^{-2})	Weight loss (g)	Consp. (%)	No.
1/G347	N$_2$→CH$_4$	20	0.35	1.16	97	1
			0.29	1.11	93	2
			0.26	0.87	73	3
		10	0.35	1.18	98	4
	N$_2$	20	0.35	1.23	103	5
			0.35	1.28	107	6
	No gas	-	0.35	1.25	104	7
2/EG-92E	N$_2$→CH$_4$	20	0.35	1.10	92	8
			0.29	1.07	89	9
		10	0.31	1.13	94	10
	N$_2$	20	0.35	1.22	102	11
	No gas	-	0.38	1.27	106	12
4/G140	N$_2$→CH$_4$	10	0.27	1.12	93	13

0.40	1.21	101	14

Thus, oxygen-containing ions dissolved in the bath might react with methane which leads to lower consumption of the anode and smaller weight loss. By comparing the weight loss in experiments with CH_4 with those without CH_4 the degree of CH_4 participation in the anodic reaction can be identified. As can be seen, the consumptions of anodes were lower in all experiments when CH_4 was used as the anode gas. This suggests that in all of these experiments CH_4 was involved in the anodic reaction; at least to some extent. However, the difference in weight loss and consumption is very small in most cases and it implies that CH_4 involvement in anodic reaction was not significant. Though, this is in contradiction to some of our earlier findings [14, 15] where in case of graphite grade 1 (G347) the consumption was much lower; experiment 3 in Table II.

Figure 4 shows the variation of cell voltage during galvanostatic electrolysis using gas anodes made of graphite grade 1 (G347) for experiments 1, 2, 3 and 5; see Table II. The vertical dashed line corresponds to anode gas shift from nitrogen to methane only in experiment 1, 2 and 3. In experiment 5 only nitrogen was used as anode gas and here it is illustrated only for comparison.

The current density was equal to 0.35, 0.29 and 0.26 A.cm^{-2} in experiments 1, and 3, respectively. The current was same in all experiments and different current densities was established by dipping the anode in the bath to different depths. So, the wetted surface area was different. It seems that when the current density was low enough the cell voltage variation showed a different behaviour. During experiment 2 and 3 the cell voltage was almost constant and stable. This cannot be only due to the supply of methane since in experiment 1 also the anode was supplied with methane. But, in experiment 1 the cell voltage variations was quite similar to the case where there was no supply of methane; experiment 5. It implies that when the anode was dipped sufficiently in the bath and/or current density was low enough the methane became involved in the anodic reaction much more efficiently. However, the weight loss changes in experiment 2 and 3 are not very close. And there must be other factors influencing the results. One apparent observation is that in experiment 2 the cell voltage fluctuations were more intense during the first 100 min of electrolysis.
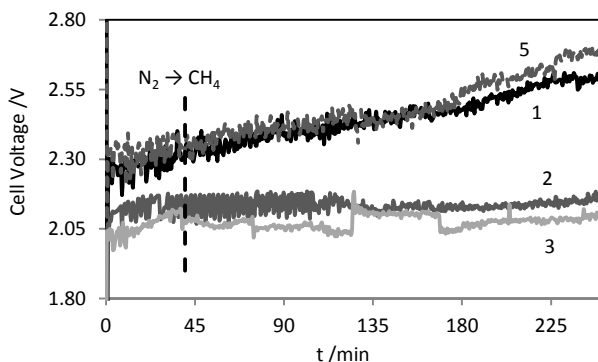

Figure 4: The variations of cell voltage during galvanostatic electrolysis of aluminium for experiments 1, 2, 3 and 4. In experiment 1, 2 and 3 anode gas was N_2 (for the first 40 minutes) followed by CH_4 (until the end of electrolysis). In experiment 4 the anode gas was N_2. Anodes were identical and were made of graphite grade 1 (G347), i = 2.5 A, T = 980°C. <mark>Comment: 1, 2, 3 and 5 are given in the figure and the text?</mark>

Figure 5 shows the measured pressure before the anode upon introduction of N_2 to the anodes and during heating up the furnace; the anode was out of the bath and electrolysis had not started. The data for experiment 1, 2, 3 and 5 are presented. Unfortunately the pressure data for experiment 3 was recorded only after introduction of the gas to anode at high temperature. However, based on the following discussion the pressure changes for experiment 3 upon introduction of gas and during heating can be estimated.
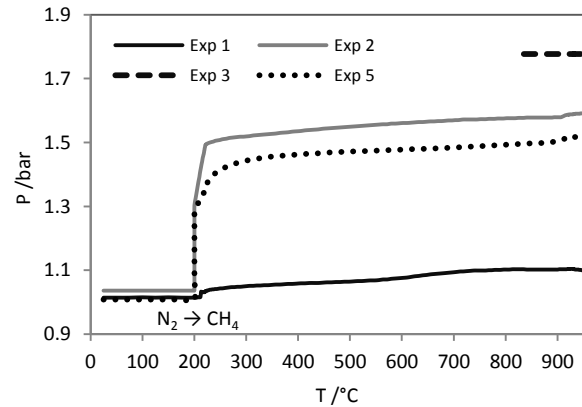

Figure 5: Measured pressure before the anode, upon introduction of gas (N_2) to the graphite anode and after increasing the temperature from 200°C to 950°C during experiments 1, 2, 3 and 5. The anode was out of the bath and the electrolysis had not started. All anodes had same dimensions and were made of graphite grade 1 (G347). The flow rate of N_2 = 20 ml min^{-1}. <mark>Comment: Where is the rest of the curve for Exp 3?</mark>

At the time of gas introduction to the anode the temperature was equal to 200°C. Introduction of the gas into the porous anode immediately caused an increase in pressure. This is due to the resistance of the porous structure against the gas flow which can be identified by equation 3. Because graphite grade 1 (G347) is not very porous and has low pore size (see Figure 3) and low permeability, the pressure increase was high. Furthermore, as the temperature inside the furnace was elevated the pressure also increased. When the temperature increased both the anode and the steel tube expanded. Since the thermal coefficient of steel is much larger than the graphite, the steel expanded more and the connection became firm and sealed at high temperature. This explains the gradual pressure increase after the initial immediate increase at 200°C.

However, it is obvious that the porous anodes behaved quite differently though they had same dimensions and were made from same graphite; grade 1 (G347).

The pressure changes in experiment 1 were quite different in comparison to the other experiments. Neither introduction of the gas to the anode, nor the following heating up made a considerable change in the pressure of anode 1. This might be due to leakage from the connection between the anode and the steel tube or a crack or fracture in anode. In any case, most likely a major part of the gas escaped from the anode assembly without passing through the porous structure and entering the bath. This explains the cell voltage variations and weight loss of this anode. For experiment 2, the pressure increase was greater than experiment 1 but perhaps not high enough. In experiment 3 the pressure increased to 1.8 bars while in experiment 2 it reached 1.55 bars. It is likely that the anode assembly in experiment 3 was

completely tight and the graphite behaved well so the methane became efficiently involved in the anodic reaction. Besides, the anode was deeper inside the bath which in turn could facilitate the methane reaction with the bath.

On the whole, the performance of anodes made of grade 2 (EG-92E) was slightly better than those made of grade 1. The results of anodes made of grade 2 are also presented in Table II; experiments 8-12. According to Namboothiri *et al.* [17] the permeability of graphite grade 2 is more suitable than grade 1 for this process. The variation of cell voltage during electrolysis for these experiments together with the experiment where only nitrogen was used as gas anode (experiment 11) is presented in Figure 6 (a). Note that here again the vertical dashed line only corresponds to gas anode shift in experiments 8-10; and not experiment 11. As can be seen, the variation of cell voltage in experiment 10 is quite similar to experiment 11. It seems the methane was not much involved in the anodic reaction. This is in accordance with weight loss results. However, cell voltage variations in experiments 8 and 9 are different. These results can be seen more clearly in Figure 6 (b). During these two experiments cell voltage gradually increased while nitrogen was being supplied. This gradual increase continued for almost 1 hour after introduction of methane. Then the cell voltage showed a small decrease and kept almost constant until the end of electrolysis with much less pronounced voltage fluctuations. This is similar to cell voltage variations in experiment 2 and 3; see Figure 4. Though, it seems the overall participation of methane in anodic reaction in these two experiments was not very large. Nevertheless, here again the effect of larger immersion of the anode in the bath/lower current density is evident. Experiment 9 had a lower cell voltage and smaller anode consumption.
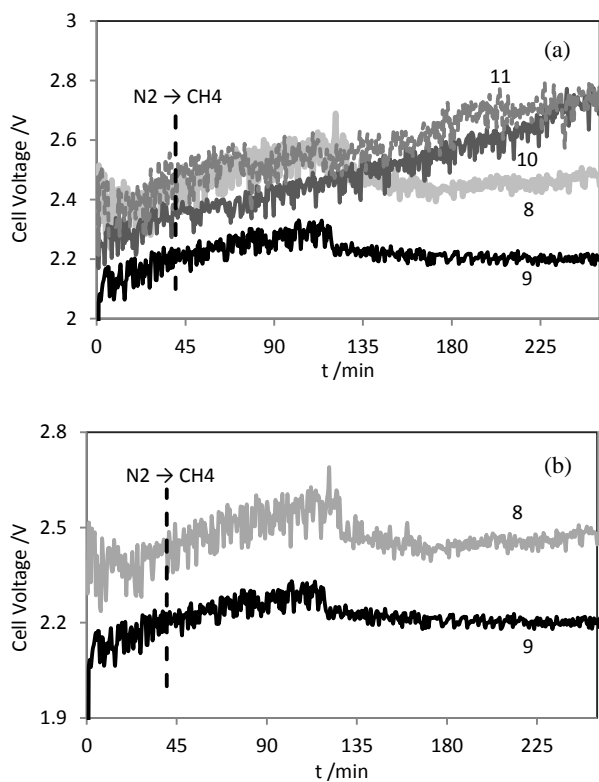

Figure 6: The variations of cell voltage during galvanostatic electrolysis of aluminium. (a) Experiments 8 - 11. (b) Experiment

8 and 9. In experiment 8-10 anode gas was N_2 (for the first 40 minutes) followed by CH_4 (until the end of electrolysis). In experiment 11 the anode gas was N_2. Anodes were identical and were made of graphite grade 2 (EG-92E), i = 2.5 A, T = 980°C.

As it was demonstrated before, the pressure changes might give an idea of how the flow properties of different anodes might influence the flow of the gas and in turn, the participation of methane in anodic reaction. However, since the graphite grade 2 (EG-92E), in comparison to grade 1, has higher porosity, larger grain/pore size and larger air permeability, the pressure changes were negligible and similar. The maximum pressure increase was equal to 0.15 bars (the results are not shown here). Similar results were observed in a previous study [14].

Two electrolysis experiments were also carried out using anodes made of grade 4 (G140); experiments 13 and 14 (Table II). Though supply of methane did not lead to a large reduction in anode consumption but, higher current density and/or depth of the anode in the bath resulted in noticeable change; see Table II.

The graphite grade 1 has low permeability and therefore, imposes high resistance toward the flow of the gas. Consequently, the anode gas escapes from the anode assembly in case of any leakage and methane does not participate in anodic reaction. Nevertheless, if the anode assembly is gas tight, supply of methane can lead to significant reduction in carbon consumption; as it was observed in experiment 3. Graphite grade 2 has higher permeability and seems to be more appropriate for this process.

In case of all graphite grades, when the anode had been dipped deeper into the bath the trend of variation of cell voltage changed and led to a more efficient involvement of methane in the anodic reaction. This might be due to the change of gas flow or/and lower current density. Further studies must be carried out to distinguish the effect of each parameter.

Conclusion

Supply of methane to porous graphite anode can lead to participation of methane in the anodic process during electrowinning of aluminium provided that the three-phase boundary is appropriately established between the gas, the electrolyte and the anode. The gas tightness of the anode assembly is of great importance and prevents the escape of the gas. Besides, inserting the anode deep enough into the bath facilitates the participation of methane in anodic reaction. Current density can also influence this process.

Acknowledgment

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