DEPOLARIZED GAS ANODES FOR ELECTROWINNING OF ALUMINIUM FROM CRYOLITE-ALUMINA MELTS IN A LABORATORY CELL

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Keywords: Aluminium, gas anodes, anode depolarization
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Abstract

Consumable carbon anodes are used in the electrowinning of aluminium by the Hall-Heroult process and in other proposed processes for electrowinning in molten salts. Emissions of CO_2 may be eliminated by introducing an inert oxygen evolving anode, which however will require a higher anode potential. By introducing natural gas or hydrogen to the anode the CO_2 emissions can be reduced and the anode potential can be lowered. Laboratory experiments were carried out in a modified Hall-Heroult electrolyte with excess AlF_3 at 850 °C. Anodes of platinum, tin oxide and graphite were tested during electrolysis at constant current, with the supply of argon, methane and hydrogen through or at the anodes.

Laboratory studies showed that by introducing both hydrogen and methane separately through a porous SnO_2 anode in molten Na_3AlF_6-AlF_3-Al_2O_3 (4.5 wt.%) at 850 °C the anode potential was found to be lowered by several hundred millivolts for a limited time during electrolysis.

Introduction

Aluminium is produced by the Hall-Heroult process, where the overall primary cell reaction is:

$$\frac{1}{2} Al_2O_3 (diss) + \frac{3}{4} C(s) = Al(l) + \frac{3}{4} CO_2(g) \qquad (1)$$
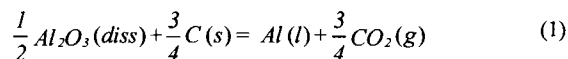
The standard Gibbs energy of reaction (1) being 345 kJ/mol at 960 °C. Pure anhydrous solid alumina is dissolved in a molten fluoride electrolyte based on cryolite (Na_3AlF_6) containing some AlF_3 as well as CaF_2 [1]. Modern cells are equipped with so called prebaked carbon anodes and operating at ~ 955 - 965 °C. The current efficiency with respect to aluminium can be as high as 96 % and the corresponding energy consumption may be ~14 kWh/kg Al in cells running at ~ 300 kA or higher. The process still suffers from the use of consumable carbon anodes, which leads to emissions of CO_2 of about 1.5 kg per kg Al in addition to the extra cost and labour for producing and replacing anodes. Considerable research efforts have not led to the development of an inert oxygen evolving anode, although some candidate materials have been identified. Among these are SnO_2 and nickel ferrites considered promising. By using an inert anode the cell reaction becomes:

$$\frac{1}{2} Al_2O_3 (diss) = Al(l) + \frac{3}{2} O_2(g) \qquad (2)$$
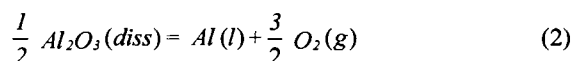
with a standard Gibbs energy of 642 kJ/mol at 960 °C. Hence the decomposition voltage will increase by about 1 V when using an inert anode. This increase may be compensated by making it possible to redesign the cells to reduce the ohmic voltage drop in the electrolyte.

An alternative way of reducing the anodic CO_2 production is to use an oxidizable gas to depolarise the anode process. By introducing methane gas to the anode the reaction can change to the following:

$$\frac{1}{2} Al_2O_3 (diss) + \frac{3}{8} CH_4(g) = Al(l) + \frac{3}{8} CO_2(g) + \frac{3}{4} H_2O(g) \qquad (3)$$
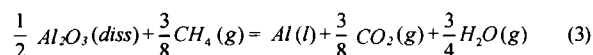
having a standard Gibbs energy of 342 kJ/mol at 960 °C. This will also lower the anode potential and the energy consumption.

If hydrogen gas is supplied to the anode the total reaction will become:

$$\frac{1}{2} Al_2O_3 (diss) + \frac{3}{2} H_2(g) = Al(l) + \frac{3}{2} H_2O(g) \qquad (4)$$
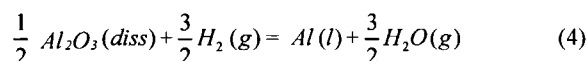
In such a case hydrogen may be produced from methane in a separate process.

The total CO_2 emissions associated with electrowinning are strongly influenced by the source of electricity. Today the average global CO_2 emissions coming from the generation of electricity is about 550 g CO_2/kWh, and this figure must be reduced considerably in the future to make the CO_2 emissions from the electrowinning process itself significant.

The use of gas anodes have been reported in the literature [3-5]. Fray et al. [6] have proposed a new concept for electrochemical production of attractive metals and alloys from molten salts. Molten calcium chloride can dissolve large amounts of calcium oxide, while the solubility of other oxides may be low. By attaching a solid metal oxide to the cathode oxide ions will dissolve in the electrolyte whereas the metal is reduced without going into solution. By using an inert oxygen evolving anode this concept is potentially very interesting for industrial use. The production small amounts of several metals has been demonstrated in laboratory and pilot plant experiments. Other researchers have also published experimental results from similar studies [7, 8].

Experimental

Laboratory experiments were carried out under controlled conditions in molten fluoride electrolytes.

Experiments were carried out in an atmosphere of dry argon to avoid the introduction and contamination by moisture and oxygen from the air. Supply of pure methane gas and hydrogen gas was

made during electrolysis to study the effect of depolarising the anode process using oxygen evolving anodes of platinum and SnO$_2$. The behaviour of inert anodes of tin oxide and nickel ferrite was studied in separate experiments.

Porous SnO$_2$-based anodes were made from Stannex ELR (Dyson Thermal Technologies). The Green body was a mixture of coarse grains of 180-355 μm from Stannex ELR and fine SnO$_2$/CuO/Sb$_2$O$_3$ powders, which was rammed inside alumina tubes and then sintered at 1300 °C for 3 hours.

Na$_3$AlF$_6$-AlF$_3$ (Cryolite Ratio=1.59, determined as the molar ratio of NaF and AlF$_3$)-Al$_2$O$_3$ (4.5 wt %) was chosen as the electrolyte. Na$_3$AlF$_6$ was natural cryolite from Greenland and AlF$_3$ (Noraulf, Boliden Odda AS) was with 12 wt% alumina contained. All the compounds were dried at 200 °C in air for at least 48 hours.

The experimental cell used in cryolite based electrolytes is shown in Fig. 1. The anode was porous with a gas tight seal to the inlet tube so that the gas was forced through the anode. The desired anode process should take place at the three phase boundary between gas, anode and electrolyte. The anode potential was recorded by using an aluminium reference electrode consisting of an alumina tube containing liquid Al in contact with electrolyte.
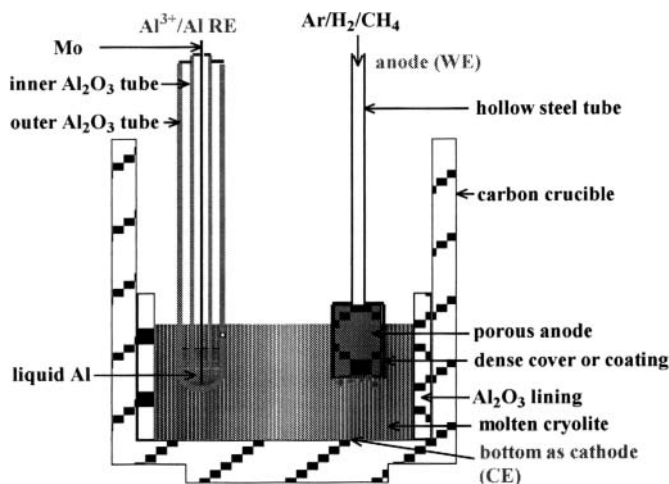

Figure 1. Experimental electrochemical cell for cryolite based electrolytes.

Results and discussion

Preliminary experiments were carried out by introducing methane gas to the anode during electrolysis in molten chloride electrolytes. However, no change in the anode potential was observed, and it was concluded that the kinetics of the methane oxidation reaction must be very slow. Therefore, methane was replaced by hydrogen as the depolarizing gas. Electrochemical studies, mainly cyclic voltammetry, suggested that O$_2$ (g) was evolved on both Pt and SnO$_2$ anodes. The anode potential was found to be stable and constant in argon atmosphere and during argon supply. A significant depolarisation was observed after

hydrogen supply, the potential change being about 0.3 - 0.5 V. A certain delay time for the action of hydrogen of about 10 minutes was observed. This is due to the rather slow gas flow rate through the anode. It is also possible that HCl (g) may be formed instead of H$_2$O (g) during the hydrogen supply, which will also give a depolarisation of the anode potential.

Figure 2 shows the measured anode potential during galvanostatic electrolysis in the molten Na$_3$AlF$_6$-AlF$_3$ (CR = 1.59) - Al$_2$O$_3$ (saturation, ~4.5 wt %) using a porous SnO$_2$ anode. Also the plot of the measured cell voltage versus time is shown. The introduction of hydrogen was found to cause a significant lowering of the anode potential after a certain delay time. However, the lower anode potential was maintained only for about 30 minutes. After introducing argon the anode potential went back to near the original value. Problems with successfully establishing the three phase boundary (gas, electrolyte, electrode) may account for the limited depolarising effect during hydrogen supply.
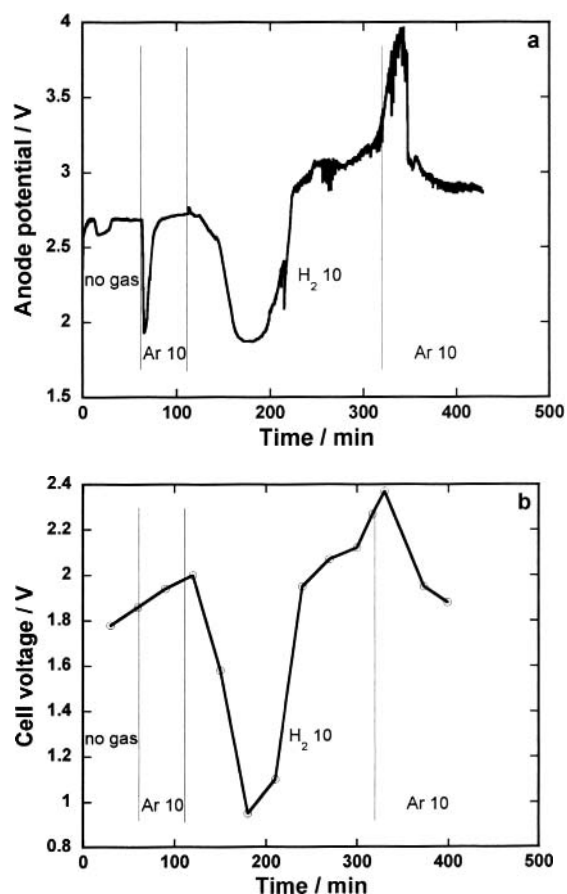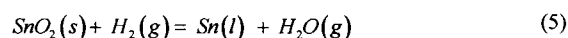

Figure 2. Anode potential (a) and cell voltage (b) versus time during constant current electrolysis (0.1 A; 0.1 A cm^{-2}) using a porous SnO$_2$-based anode in molten Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$ (4.5 wt%) at 850 °C. Supply of argon and hydrogen.

Figure 3 shows the recorded anode potential and the cell voltage during galvanostatic electrolysis in the molten Na_3AlF_6-AlF_3 (CR = 1.59) - Al_2O_3 (saturation, ~4.5 wt %) using a porous SnO_2 anode. The supply of methane was found to lower the anode potential by about 0.3 V. The depolarising effect was maintained for at least 60 minutes.

The formation of water caused by the reactions of hydrogen and methane at the anode, reactions (3 - 4) may lead to the formation of HF and possibly cause some operational problems. Also the wetting properties of the anode may be affected by the presence of water. However, no efforts were made to investigate the impact of moisture in these studies.

Another concern when using tin oxide anodes is the posible reduction by hydrogen to form tin metal, according to the following reaction:

$$SnO_2(s) + H_2(g) = Sn(l) + H_2O(g) \qquad (5)$$

which has a standard Gibbs energy of -30 kJ/mol. Hence it may take place except where the SnO_2 anode is protected by the potential. A similar reaction with CH_4 is also spontaneous.
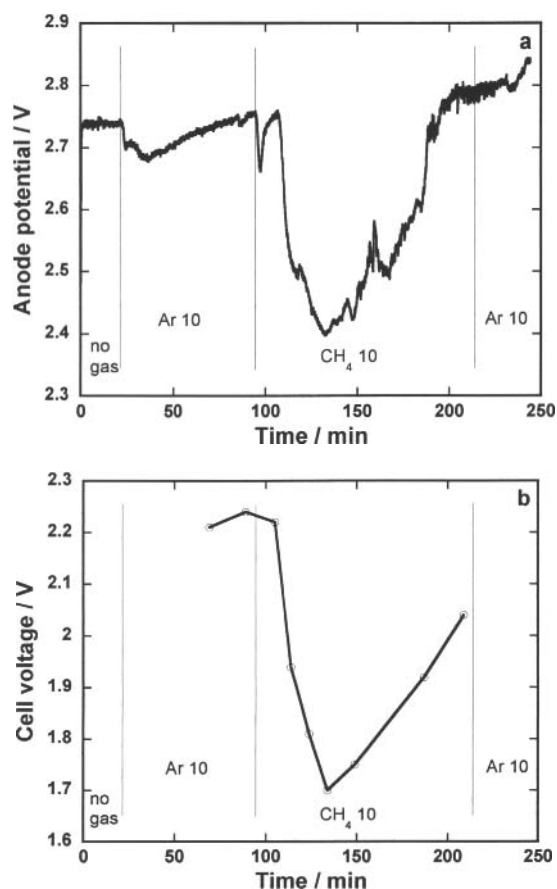

Figure 3. Anode potential (a) and cell voltage (b) versus time during constant current electrolysis (0.2 A; 0.2 A cm^{-2}) using a porous SnO_2 anode in molten Na_3AlF_6-AlF_3-Al_2O_3 (4.5 wt.%) at 850 °C. Al(III)/Al reference electrode. Supply of argon and methane.

Conclusions

Laboratory studies showed that by introducing hydrogen to the anode during constant current electrolysis in molten Na_3AlF_6-AlF_3-Al_2O_3 (4.5 wt.%) at 850 °C introduction of both hydrogen and methane through a porous SnO_2 anode was found to depolarise the anode process by several hundred millivolts for a limited time.

The results are promising for the prospects of reducing the CO_2 emissions and the energy consumption for electrowinning of aluminium by depolarising the anode process by using hydrogen or methane gas. Challenges are related to the of HF caused by water formation and the possible reduction of the unprotected parts of the SnO_2 anode.

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