A CONCEPT FOR ELECTROWINNING OF ALUMINIUM USING DEPOLARIZED GAS ANODES

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Abstract

Aluminium is today commercially produced by the Hall-Héroult process using consumable carbon anodes. Consumable anodes have some concerns such as CO_2 emission, continuous anode-cathode distance adjustments and replacements of anodes. Replacing the consumable anodes with inert anodes has been a topic for many decades without commercial success so far. Using porous inert anodes where natural gas or hydrogen take place in the anode reaction has been shown in laboratory tests to reduce the anode potential and reduce the CO_2 emission. However, formation of water results in evolution hydrogen fluorides which must be solved. Laboratory experiments using porous depolarized SnO_2-based anodes with CH_4 and H_2-gases have been performed with off-gas analysis and with special attention to hydrogen fluoride evolution. Some ideas of how the additional HF evolution is presented.

Introduction

Aluminium is today produced by Hall-Héroult process where Al_2O_3, dissolved in cryolite melt at 960 °C, is reduced and deposited as metal at the aluminium/carbon cathode, while CO_2 is evolved at the consumable carbon anode. The overall reaction of the process is given in reaction (1).

$$Al_2O_3 \text{ (s)} + 3/2 \text{ C (s)} = 2 \text{ Al (l)} + 3/2 \text{ } CO_2 \text{ (g)} \qquad (1)$$
$$\Delta G°_{960°C} = 690 \text{ kJ}$$
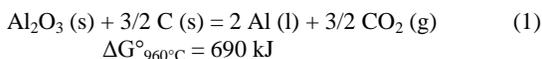
During electrolysis the anode is consumed and the anode-cathode distance must continuously be adjusted before finally being replaced. By using an inert anode both the replacement and CO_2 emission can be eliminated. However, as seen from the overall reaction in (2) $\Delta G°_{(2)} \approx 2 \cdot \Delta G°_{(1)}$, corresponding to 1 V, is necessary for the reaction using inert anode and so far no inert anode withstanding the corrosive environment has been developed for commercial use.

$$Al_2O_3 \text{ (s)} = 2 \text{ Al (l)} + 3/2 \text{ } O_2 \text{ (g)} \quad \Delta G°_{960°C} = 1284 \text{ kJ} \qquad (2)$$
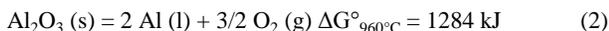
By applying an inert gas anode, where a reducing gas such as CH_4 and H_2 is fed through the anode, some of the issues above can be resolved. The overall reaction (3) reduces the CO_2 emission and since $\Delta G°_{(1)} \approx \Delta G°_{(3)}$ the theoretical energy consumption is similar to electrolysis with a consumable carbon anode.

$$Al_2O_3 \text{ (s)} + 3/4 \text{ } CH_4 \text{ (g)} =$$
$$2 \text{ Al (l)} + 3/4 \text{ } CO_2 \text{ (g)} + 3/2 \text{ } H_2O \text{ (g)} \qquad (3)$$
$$\Delta G°_{960°C} = 683 \text{kJ}$$
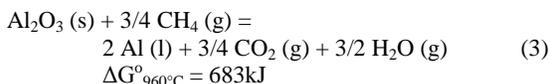
Few works, studying the effect of reducing gas for electrowinning of different materials with some success, have been published [1-3]. The challenges have been clogging of porous carbon by CH_4 and carbon oxidation competing with CH_4 oxidation. Recent thermodynamical analysis and experiments have shown a depolarization of nickel based anodes using hydrogen in aluminium electrowinning [4-6]. Preparation of SnO_2 based inert gas anodes and their use in electrowinning of aluminium and silver has demonstrated the effect of H_2 and/or CH_4 in the anode reaction [7-11]. Even though there are several challenges related to e.g. stability of anode and gas distribution, the main challenges are related to the formation of HF by reaction (4)

$$2 \text{ } AlF_3 + 3 \text{ } H_2O = Al_2O_3 + 6 \text{ HF} \qquad (4)$$
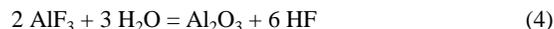
However, measurements of the HF and H_2O species have not been reported using a gas anode concept. Here we present quantitative gas analysis during electrowinning of aluminium using SnO_2 based inert gas anodes. A thermodynamical calculation of the formation of HF and a proposed solution to the HF challenges are described together with new gas anode designs.

Experimental

Preparation of gas anodes

Porous inert anodes were prepared using crushed SnO_2 (Stannex ELR, Dyson Thermal Technologies) and screened to different fractions. The powder fractions were coated with fine mixture of 96 wt% SnO_2 (Sigma Aldrich 99.9%), 2 wt% CuO (Sigma Aldrich, 98.5%) and and 2 wt% Sb_2O_3 (Merck, "rein"). The mixtures with added binder carboxymethylecellulose (CMC) were rammed into alumina tube and sintered at 1330 °C for 3 hours. To tailor the pore size in the porous gas anodes, three different size fractions of Stannex materials were manufactured; 45-90, 90-180 and 180-355 µm. A detailed description and characterization is given by Mokkelbost et al. [9].

Electrolysis

The bath composition was Na_3AlF_6 (natural cryolite, Greenland) and AlF_3 (Noralf, Boliden Odda AS) in a cryolite ratio of 1.59 with 4.5 wt% Al_2O_3 (Merck, >99 %) Operating temperature was 850 °C during electrolysis. The bottom of a carbon crucible, lined with alumina tube was used as cathode. A hollow steel tube compressed to the porous anode inside the alumina tube was used as current collector. Inside the current collector a thinner hollow steel tube was used for transporting gas to and through the anode. Furnace and bath was dried at 250 °C in N_2 over night prior to experiments. 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 outlet gas directly above the bath close to the anode was analysed with respect to water and hydrogen fluoride. A more detailed and schematic description of the electrochemical cell is was given by Xiao et al. [11].

For galvanostatic electrolysis a constant current of 0.2 A was used corresponding to an apparent current density of 0.25 A cm^{-2}.

The anodes were characterized using scanning electron microscopy (Hitachi -3400 N).

Results

Prior to the experiments using reducing gas, both dense and porous SnO_2 based anodes were tested. The dense anode was stable for 6 hours except for a shift in cell voltage from 2.3 to 2.5 V. Prior to the increase in cell voltage an increase in the HF emission (~5000 ppm) was observed but a plateau was reached during the increase in cell voltage. Experiments with a porous SnO_2 anode with and without gas demonstrated also relatively stable, but more scattered, cell voltage.

Depolarization of SnO2 anodes

Figure 1 shows cell voltage, gas flows of N_2 and H_2, gas pressure to anode and HF and H_2O measured directly above the bath close to the anode during aluminium electrolysis using a SnO_2 based anode prepared from size fraction 180-355 μm coarse SnO_2 particles. Changing the supply gas through the anode from N_2 to H_2 results in a decrease in cell voltage from 2.3 to 2.1 V. After continuous decrease in cell voltage the voltage gradually returned back to approximately 2.3 V, however a more unstable cell voltage than prior to the drop in cell voltage was recorded. A significant increase in HF was observed during reduction of cell voltage. During the increase in cell voltage a increase in pressure was recorded. A magnification of the pressure and cell voltage is shown in Figure 2. A systematic increase in cell voltage together with an increase in pressure was observed. Both pressure and cell voltage dropped every 6-10 minutes for ~1 hour before the cell voltage stabilized at 2.4 V and slightly increased to 2.5 V although H_2 was fed through the anode.

A photograph of a used, vertically cut SnO_2 based gas anode cut vertically is shown in Figure 3 (a) with corresponding micrographs (b-d) from different sections of the anode. Elemental analysis was performed using EDS (energy dispersive spectroscopy). In the top Sn metal is observed and magnified in (b). Micrograph (c) is from the middle of the anode, but above the bath. Dark areas are evaporated bath, the small spherical bright particles are Sn metal and the large bright particles are coarse SnO_2 particles. The interface where bath was immersed into the anode is observed as an interface from dense to porous seen in d).
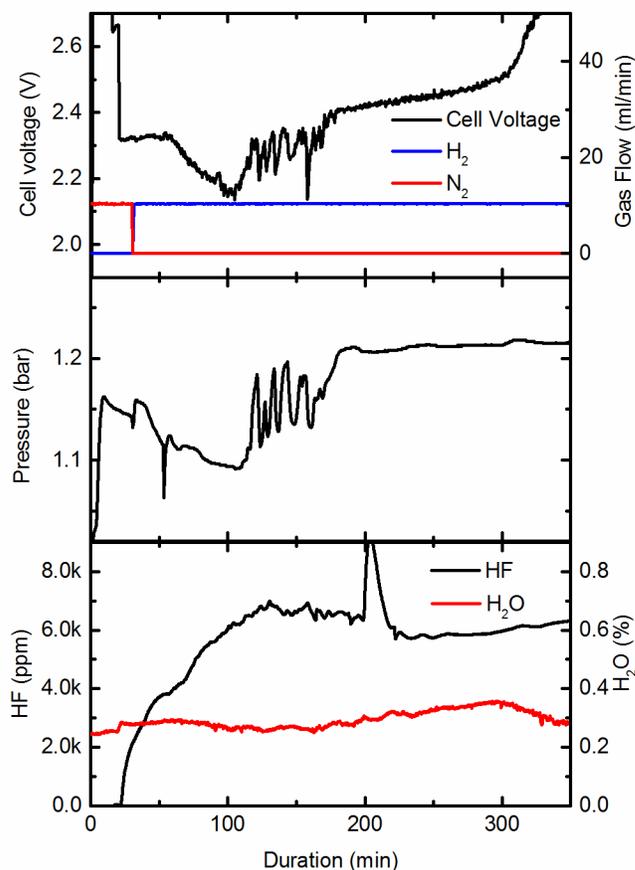

Figure 1 Cell voltage, H_2 and N_2 gas flow (top), pressure (middle) and HF and H_2O amounts versus time during constant current electrolysis (0.25 A cm^{-2} using SnO_2 based gas anode with initial particle size 180-355 μm.
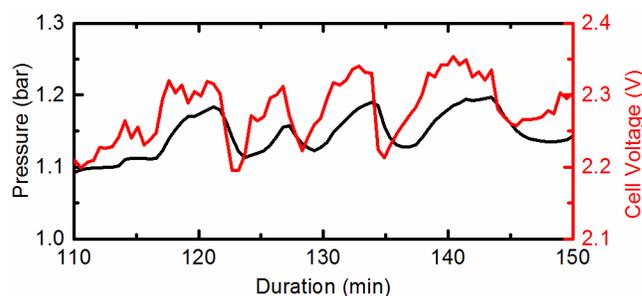

Figure 2 Cell voltage and pressure versus time (110-150 min.) from Figure 1.
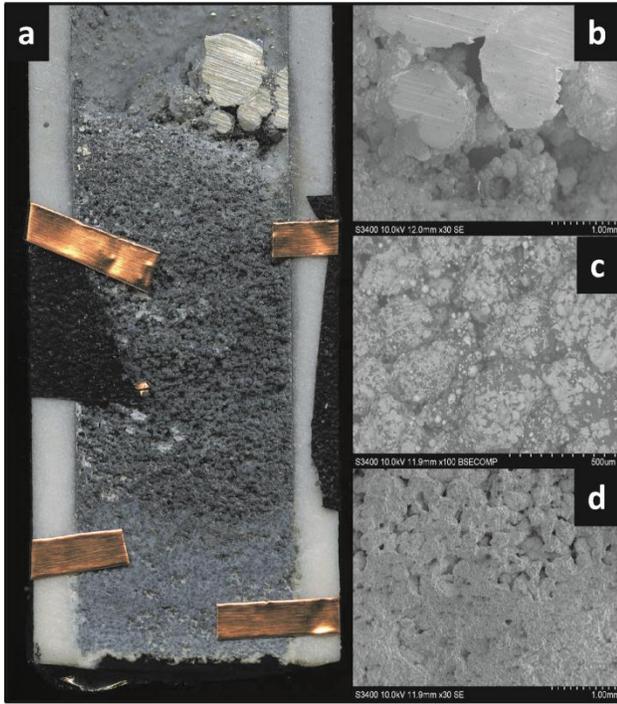
Figure 3 Photograph and micrographs of used SnO$_2$ based gas anodes. a) Anode rammed inside alumina tube b) Top section, c) Middle section and d) Interface bath. (The Cu and C tape is for the SEM analysis).

Figure 4 shows the same as Figure 1 but using an anode based on smaller SnO$_2$ particles (90-180 μm) and using CH$_4$ instead of H$_2$. As in the previous experiment a initial drop in cell voltage (2.3 to 2.0 V) was observed when introducing CH$_4$ through the anode followed by a gradual increase to 2.3 V. During the reduction in cell potential more HF was formed while H$_2$O drops until the cell voltage went back to 2.3 V. Then the water increased and HF decreased. After ~1.5 hours a sudden drop in gas flow and increase in pressure was observed. Changing the gas from CH$_4$ to N$_2$ resulted in a drop in pressure and switching back increased the pressure again as seen after 250 minutes.

Discussion

Depolarization of SnO$_2$ anodes

From Figure 1and Figure 4 it is clear that a depolarization of the anode occurred when introducing H$_2$ and CH$_4$ through the anode and the anode reaction in Equation (3) clearly took place. However, the reduction in cell voltage is not as high as theoretical (1 V). Unfortunately the depolarization only lasted for a short period of time before the cell voltage slowly increased back to values as before the depolarization of the anode took place.

The increase in HF, due to reactions between H$_2$O and AlF$_3$, is measured to several thousand ppm. These are very high values, but it must been taken into account that the measured gas was located directly above the bath and close to the anode. Formation of HF will decrease the AlF$_3$ in the bath. By purpose extra AlF$_3$ was added compared to the Hall-Héroult process to lower the liquidus temperature reducing the possible cracking of methane during the experiments. Using the porous SnO$_2$ anodes the reaction is most probably taking place inside the anode. From the

micrographs in Figure 3 it is shown that the bath wets the porous anode well and a clear interface is observed inside the anode. The distance from the bottom on the anode to the interface agrees well with the experimental measurements when lowering the anode into the bath. Thus, a depletion of fluoride ions inside the anode will result in a higher liquidus temperature, in agreement with the phase diagram of NaF-AlF$_3$, and possible frozen bath inside the anode. The pressure increase observed in the experiments is also an evidence of frozen bath. Comparing the two different SnO$_2$ based gas anodes with different particle size composition an alternating pressure increase/decrease followed by cell voltage increase/decrease was observed in the anodes with the largest particle size (thus pore size), while this was not observed for the anodes with smaller particles. This is most probably due to removal of frozen bath which is believed to be ??easier in a more porous structure. Another explanation can be the difference in size of molecules (H$_2$ less than CH$_4$) where H$_2$ will easier be transported through a porous material.
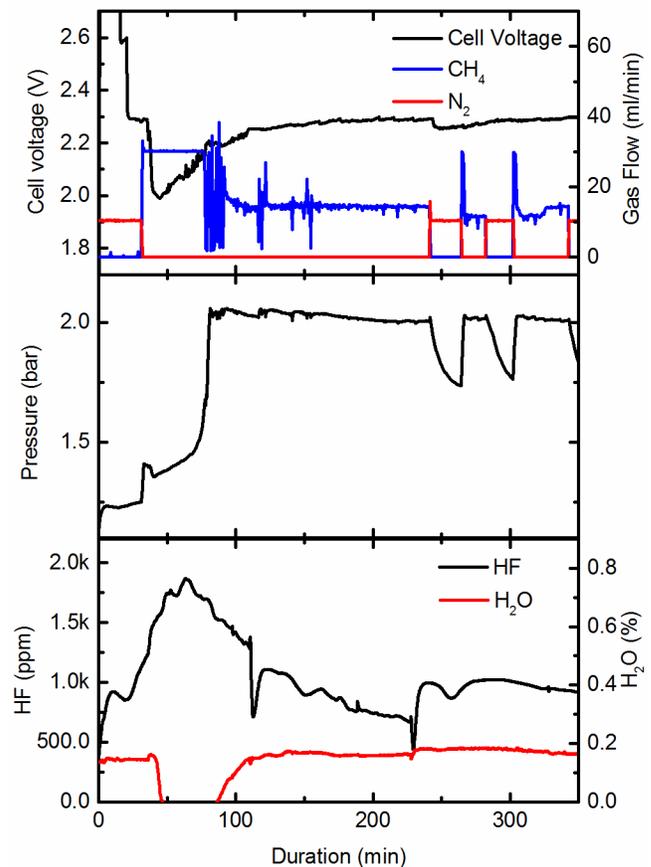

Figure 4 Cell voltage, CH$_4$ and N$_2$ gas flow (top), pressure (middle) and HF and H$_2$O amounts versus time during constant current electrolysis (0.25 A cm^{-2} using SnO$_2$ based gas anode with initial particle size 90-180 μm.

Thermodynamic calculations of HF formation

Equilibrium calculations (with no voltage applied in order to shift the equilibrium) were conducted with FactSage thermodynamical software, using solution databases optimized for Hall Héroult bath.

The results are depicted in Figure 5. In general, the presence of water promotes the formation of HF. H_2O reacts with AlF_3, forming Al_2O_3 and HF in the idealized Equation (4). As an initial rough estimate, the equilibrium gas phase contains 1/3 HF, the rest being unreacted H_2O. Reactions with H_2 yields considerably less HF. The ideal reaction equation involves a red/ox reaction with cryolite, forming elementary aluminium and HF together with NaF, Equation (5):

$$Na_3AlF_6(l) \; + \; 3/2 \, H_2 \; = \; Al(l) \; + \; 3 \, NaF(l) \; + \; 3 \, HF(g) \qquad (5)$$
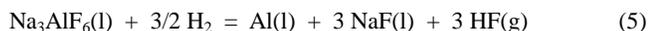
Since aluminium metal is very unstable, the resulting partial pressure of HF is low. Corresponding calculations using Hall-Héroult bath instead of gas anode bath, carried out at 960 °C, show similar results to those reported here. Hence it is possible that some of the experiences from the traditional Al-electrolysis can be applied.
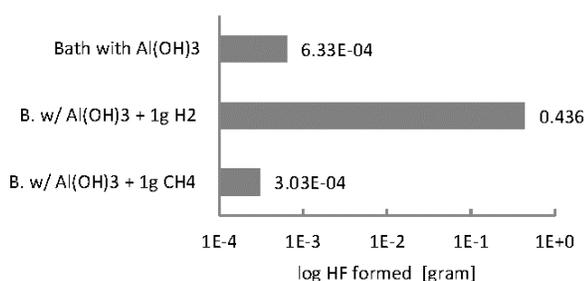

Figure 5 HF formed at equilibrium by reactions with bath Na_3AlF_6-AlF_3-Al_2O_3 (70.5 − 27.2 − 2.3 wt%) T = 850 °C, P_{tot} = 1 atm.

Closed fluoride looping

It has been argued that one of the problems with this process is that the hydrogen contained in the natural gas will generate HF in contact with the fluoride melt. This is also well documented in our experiments. This will create two problems, an accumulation of oxide in the bath and a reduction in the fluoride content. A conventional gas scrubbing system such as those used in aluminium plants today will not be able to adsorb enough HF per kg of alumina for the mass balances to work out.

A design where the off gas from the cells is fed directly into a fluorination plant reacting it with Al_2O_3 to form AlF_3, instead of just adsorbing HF on the surface of the Al_2O_3 is suggested. If HF is converted to AlF_3 the problem with alterations in the bath chemistry is avoided. This can be seen as an analogy to the Cl_2 evolution and chlorination of the Mg electrolysis technology.

If all Al_2O_3 is fed through the fluorination plant in such a way that all fluoride from HF can be recovered, then the remaining mixture will contain exactly the right ratio of Al_2O_3:AlF_3 to balance the bath chemistry.

The fluorination in itself can be done similar to what is done in commercial fluidized bed AlF_3 plants. These plants fluorinate Al_2O_3 without any significant fluoride emissions today, and there should not pose any large challenge to adapt this technology to.

Possible new anode designs

By using natural gas as reduction medium, new anode designs have to be developed allowing long enough contact time between anode, gas and electrolyte for the gas to react with alumina. In addition it is necessary to have a circulation of the bath where the anode reaction occurs due to the depletion of fluoride from bath caused formation of HF. As described above a porous anode with stationary bath inside can not be used in this concept unless a bath circulation is established. One possible design is shown in Figure 6. The anode is made such that it is thickest at the centre of the electrolysis cell and thinnest at the outside walls. The gas is supplied to the electrolyte through the central yoke leg entering the cell at the lowest part of the anode and will ascend along the anode surface to the outer edge where it will leave the electrolyte. At this point the natural gas should have reacted completely to CO_2 and H_2O. With this cell design the aluminium will stay in the middle of the cathode where it can be collected.

Another possible design is shown in Figure 7 where the anode is thinnest along the centre-axis of the cell and thickest along the side walls. The gas enters the cell along the thickest part of the anode and will move slowly along the anode surface to the center where it leaves the cell as HF (g), CO_2, $H_2O(g)$. By this design the aluminium will flow to the side walls of the cell. Also in this design the cell have to have a gas tight to closing to allow a controlled collection of the reacted gas for further gas processing such as removal of HF and H_2O.
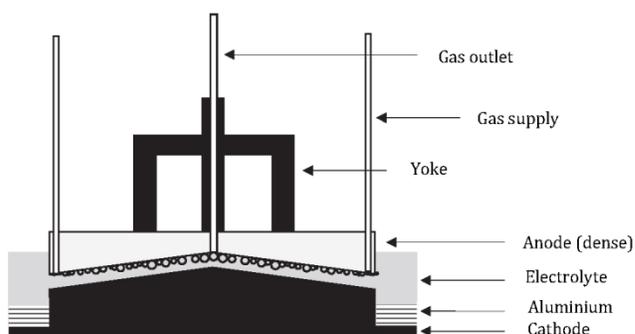

Figure 6 A proposed designs where the produced aluminium will flow to each side of the cathode. The whole assembly needs to be closed in order to prevent gas leakages and enabling treatment of the exhaust gases.
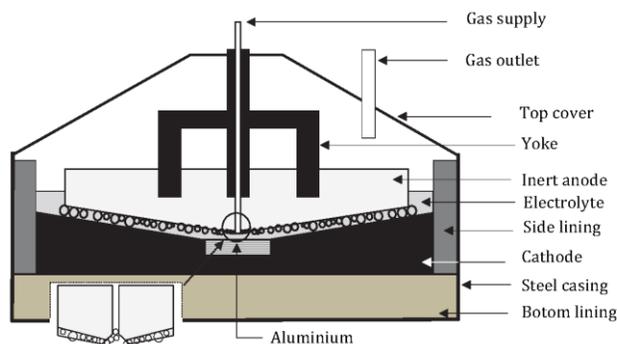

Figure 7 A rectangular anode with two sloping surfaces with the lowest part along the center-axis of the electrolysis cell. The aluminium metal is collected at the center of the cathode.

Of the two designs the simplest design is the one shown in Figure 7 since the gas is supplied only at the centre of the electrolysis cell and the aluminium flows to the centre where is easily can be collected.

Conclusion

The effect of using H_2 or CH_4 as a reducing agent to depolarize the anode in electrowinning of aluminium at 850 °C in Na_3AlF_6-AlF_3-Al_2O_3 is demonstrated using a porous SnO_2 based gas anode with different pore sizes. The short life time of the depolarization effect is most probably due to locally depletion of fluoride species inside the porous anode which are well wetted by the bath. The depletion results in frozen bath and the three phase boundary necessary for depolarization of the anode will not be available. The increase in pressure to the anode and the reduced HF formation also support the proposed explanation. The challenges can be solved using a different anode design as proposed here with sloping surfaces distributing the gas while a homogeneous bath composition is maintained.

We have proposed a solution to the main challenge, HF formation, using H_2 or CH_4 to depolarize the anode. The solution is based on a closed loop where HF and Al_2O_3 react to form AlF_3 which is fed back to the bath.

Acknowledgement

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