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Depolarised gas anodes for aluminium electrowinning

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Abstract: Consumable carbon anodes are used in the electrowinning of aluminium by the Hall-Heroult process. Emissions of CO_2 may be eliminated by introducing an inert oxygen evolving anode, which however will require a higher anode potential. An alternative approach is to use a natural gas or hydrogen gas anode to reduce the CO_2 emissions and lower the anode potential. Preliminary laboratory experiments were carried out in an alternative molten salt electrolyte consisting of $CaCl_2$-CaO-NaCl at 680 °C. Porous anodes of platinum and tin oxide were tested during electrolysis at constant current. The behaviour of inert anode candidate materials such as tin oxide and nickel ferrite were also studied.

Key words: anodes; natural gas; aluminium electrowinning

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1 Introduction

Aluminium is produced solely by the Hall-Heroult process, which was patented independently by Hall and Heroult in 1886. 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 is 689.309 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 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 kW·h/kg Al in cells running at ~300 kA or higher. The annual production of primary aluminium was about 38 million tons in 2007, making it the most important electrowinning process[2]. Although the basic principles of the process remain unchanged, great technological developments have taken place. The main improvements are related to environmental issues. Scrubbing of the exit gas has minimized the emissions of harmful and toxic gaseous and particulate constituents to the working atmosphere and to the air. Also some key performance data such as current efficiency, energy consumption and cell size (amperage) have been greatly improved. However, 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 them SnO_2 and nickel ferrites are 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 1 283.316 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 being able 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

$$\frac{1}{2}Al_2O_3(diss)+\frac{3}{8}CH_4(g)=Al(l)+\frac{3}{8}CO_2(g)+\frac{3}{4}H_2O(g) \qquad (3)$$

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having a standard Gibbs energy of 683.080 kJ/mol at 960 °C. Using a depolarising gas such as methane will also lower the anode potential and hence lower the energy consumption.

If hydrogen gas is supplied to the anode, the reaction will become

$$\frac{1}{2}\mathrm{Al_2O_3(diss)}+\frac{3}{2}\mathrm{H_2(g)}=\mathrm{Al(l)}+\frac{3}{2}\mathrm{H_2O(g)} \qquad (4)$$

In such a case, hydrogen will be produced from methane in a separate process.

The use of renewable electrical energy is of great importance, since electrolysis relies on the use of electrical energy. The total CO_2 emissions associated with electrowinning are more dependent on the source of electricity. Today, the average global CO_2 emissions coming from the generation of electricity is about 550 g CO_2/(kW·h), and this figure must be reduced considerably in the future if lowering of the CO_2 from the electrowinning process itself will be significant.

The use of gas anodes has been reported in Refs.[3−5]. CHEN et al[6] have proposed a new concept for electrowinning of 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 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 of several metals has been demonstrated in laboratory and pilot plant experiments. Other researchers have also published experimental results from similar studies[7−8].

2 Experimental

Laboratory experiments were carried out under controlled conditions at 680 °C. Model electrolytes based on molten $CaCl_2$ containing CaO were used in these experiments instead of the corrosive molten fluoride electrolyte used during aluminium electrowinning. Also AgCl was added in order to control the cathode reaction, which would be silver deposition rather than calcium formation. 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.

The experimental set-up 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 a Ag/AgCl reference electrode consisting of a mullite tube containing the molten salt electrolyte with AgCl and a Ag wire.

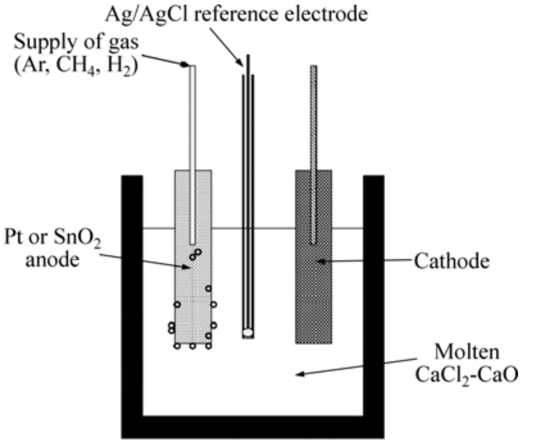

Fig.1 Schematic diagram of experimental electrochemical cell

3 Results and discussion

Several experiments were carried out by introducing methane gas to the anode during electrolysis. 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 depolarising gas.

Electrochemical studies confirmed that O_2(g) was evolved on both Pt and SnO_2 anodes. Fig.2 shows the

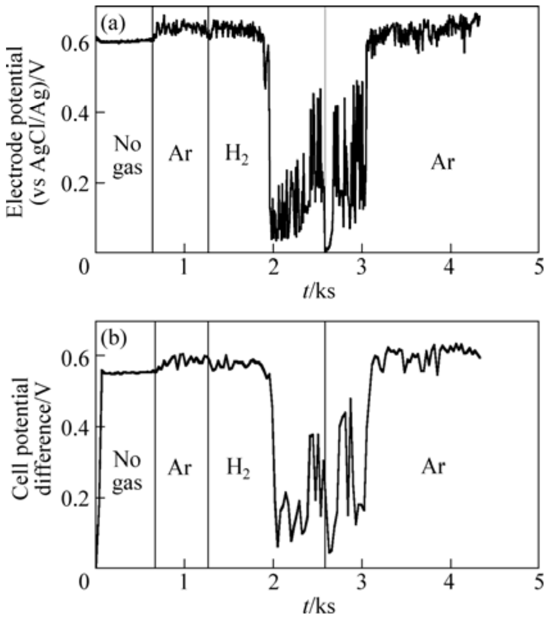

Fig.2 Time dependencies of anode potential (a) and cell potential difference (b) during electrolysis at 0.1 A (25 mA/cm^2) with Pt anode in $CaCl_2$-NaCl(70%−30%)-CaO(15.4%)-AgCl(3.6%) melts at 953 K and gas flow rate of 10 cm^3/min

anode potential and cell voltage during galvanostatic electrolysis in molten $CaCl_2$-NaCl-CaO-AgCl using a Pt anode. 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, with the potential change being about 0.3−0.5 V. A certain delay time for the action of hydrogen of about 10 min was observed. This is due to the rather slow gas flow rate through the anode.

Fig.3 shows the anode potential and cell voltage during galvanostatic electrolysis in the molten $CaCl_2$-CaO based electrolyte using a SnO_2 anode. The anode potential was found to be fairly constant during argon supply through the anode. After a delay of about 15 min, the anode potential was found to decrease by about 0.1 V. The anode potential was unaffected by doubling the flow rate of hydrogen. It is not clear why the response of the SnO_2 anode was less pronounced than the Pt anode. However, changes in the active electrode area due to different wetting properties of the two anode materials may be an explanation.

Other candidate inert anode materials were also tested in molten $CaCl_2$-CaO based electrolytes. Nickel ferrites have been proposed for aluminium electrowinning. $NiFe_2O_4$ anodes with addition of NiO, Ni and Cu were prepared and tested during electrolysis. The metal phase of the anodes corroded badly, but NiO seemed to give a better performance of the anodes. Pre-electrolysis using the anodes led to better behaviour and less corrosion. The results from these studies have been published[9].

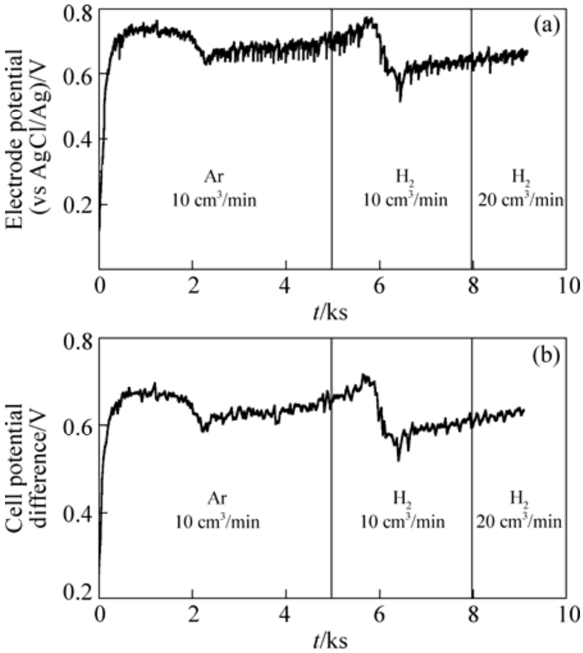

Fig.3 Time dependencies of anode potential (a) and cell potential difference (b) during electrolysis at 0.06 A (15 mA/cm^2) with porous SnO_2-based anode in $CaCl_2$-NaCl (70%−30%)-CaO(16%)-AgCl(4.5%) melts at 953 K

4 Conclusions

1) Laboratory studies showed that by introducing hydrogen to the anode during constant current electrolysis in molten $CaCl_2$-CaO based electrolytes, the anode potential was significantly lowered (0.3−0.5 V) using a platinum anode. Using an inert tin oxide anode, the potential was lowered by about 0.1 V.

2) 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 using hydrogen or methane gas.

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