

ELECTROCHEMICAL BEHAVIOUR OF CARBON ANODES IN Na₃AlF₆-K₃AlF₆-BASED LOW-MELTING ELECTROLYTES FOR ALUMINIUM ELECTROLYSIS

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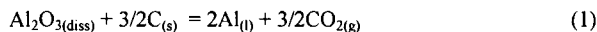
Keywords: Carbon anodes, Low-melting electrolytes, Electrochemical behaviour, Perfluorocarbons

Abstract

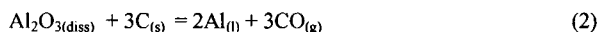
The anode processes of carbon electrodes in 49 wt% Na₃AlF₆ - 21 wt% K₃AlF₆ - 30 wt% AlF₃-Al₂O₃ (saturated or free) melts were studied in a wide range of potentials by cyclic voltammetry. Two electrolysis processes were observed on the cyclic voltammogram traces. It is considered that the first process corresponds to the discharge of oxide ions (or residual oxide ions), and the discharge of fluoride ions occur after the discharge of oxide ions, leading to the anode effect. As the potential increases, the second process occurs with the emission of Perfluorocarbon (PFC) gases. Compared to the cyclic voltammogram trace obtained from the traditional electrolyte for aluminium industry 84 wt% Na₃AlF₆ - 11 wt% AlF₃ - 5 wt% CaF₂ - Al₂O₃ (saturated), it can be seen, as the addition of a large amount of AlF₃ and the decrease of electrolysis temperature, the current density of the second process increases obviously. The performance of low temperature aluminium electrolysis increases the risk of a larger emission rate of PFCs.

Introduction

The principal basis for production of aluminium metal by the Hall-Héroult process with a consumable carbon anode can simply be described in terms of the following reactions:



and



Consumable carbon anodes have long been used and have become of major significance in the technology of aluminium production practice. When a carbon anode in a molten fluoride melt is subjected to a gradually increasing anode potential, the current will eventually reach a maximum, and then drop abruptly to a very low value, signaling the beginning of the anode effect. In industrial cells, when anode effect occurs, the voltage of the cell increases sharply, which causes the waste of electricity; at the same time, a large amount of perfluorocarbons (PFCs) is generated, mostly CF₄ and C₂F₆. These gases have been implicated in climate change owing to their high global warming potentials [1-4]. In spite of the fact that over the years many investigations have been conducted in cryolite-alumina melts, neither the mechanism of the initiation of the anode effect nor the mechanism of the reactions occurring during the anode effect has been clearly established [5-7].

On the other hand, the possibility of using inert or so-called 'non-consumable' anodes has become attractive for the concerns of energy and environment. In the case of inert (non-consumable)

anodes, the production of aluminium would be represented formally by the equation:



Over the years, many types of inert anodes have been tested for the aluminium industry [8-11]. However, development of a 'non-consumable' anode for the aluminium industry with an acceptable corrosion rate is made difficult by the aggressive nature of the cryolite electrolyte towards most metals, refractory hard metals and ceramic oxide composition.

Since low temperature electrolysis can offer a friendly operating environment for both carbon anodes and inert anodes, a large amount of research has been carried out [12-19]. In our previous work, we showed that a multi cryolite low-melting electrolyte system had potential interest for further electrolysis tests [20]. In the present work, we selected low-melting 49 wt% Na₃AlF₆ - 21 wt% K₃AlF₆ - 30 wt% AlF₃ (saturated or free) electrolytes to perform further investigation on the underlying kinetics of PFCs generation, and the nature of the reactions at the carbon electrodes. This will also help us understand the electrochemical behavior of inert anodes under similar conditions, which is still being carried out in our lab and will be discussed in a subsequent paper.

Experimental

All experiments were carried out in an alumina tube reactor, which was filled with high purity argon atmosphere. Spectrographic graphite crucibles were used for container and counter electrode as well. Na₃AlF₆, K₃AlF₆, AlF₃ and Al₂O₃ were all analytical grade chemicals. The fluorides were mixed according to the demands, and placed in a graphite crucible, heated to 110 °C, dehydrated under vacuum for 24 h. Then the temperature was increased slowly to the melting point 818 °C [21] under argon, kept for two hours, then increased to 830 °C. This temperature was maintained for electrochemical measurements.

A three-electrode system was used for the electrochemical measurements. A carbon anode (6.0 mm in diameter) was used as the working electrode. The working electrodes were dipped about 5.0 mm into the molten salts. The actual immersed height was determined at the end of the run. The graphite crucible was used as the counter electrode, and an aluminum electrode was used as the reference electrode [22]. All potentials in this paper are given with reference to this Al³⁺/Al electrode. Cyclic voltammetry [23] was performed using a universal potentiostat/galvanostat, Model 273, controlled via a personal computer executing the electrochemical software Echem M270. The collected data were further analyzed with KaleidaGraph 4.0 (Synergy Software) and the thermodynamic parameters were calculated with HSC 5.0 (Chemistry Software).

Results and Discussion

Cyclic Voltammetry was performed firstly on the melts saturated with alumina. Figure 1 shows the example of the voltammograms of one cycle (forward sweep and reverse sweep). For an anodic potential scan starting at 1.2 V, the current increases at 1.3 V to reach a peak at 5.0 V, and drops sharply. In this case, the peak potential is called critical potential, E_c , and the peak current density is called critical current density, j_c . Right after the sharp drop, the current increases continuously as the potential increases. When the potential sweep is reversed at 8.0 V, the current follows the previous profile in the anodic direction. The anodic peak at 5.0 V, however, is retraced with some offset to more cathodic potential (~ 3.6 V). No cathodic current ever appears during the cathodic sweep.

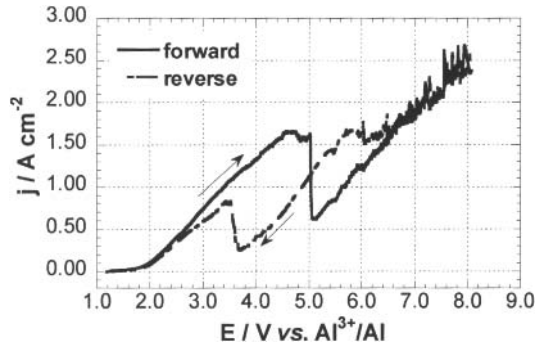


Figure 1. Cyclic voltammograms of carbon in 49 wt% Na_3AlF_6 - 21 wt% K_3AlF_6 - 30 wt% AlF_3 - Al_2O_3 (saturated) melt. Temperature, 830 °C; Sweep rate, 0.05 V s^{-1} .

In order to assign reactions to this oxidation process, the reversible potentials of some reactions related to the present study were calculated according to equation (4) and tabulated in Table I, where all the activities were assumed to equal unity.

$$\Delta_r G_m^0 = -zFE^0 \quad (4)$$

Since the measured potentials are expressed vs. the Al^{3+}/Al reference, the appropriate cell reactions lead to the formation of the anodic products and aluminium as cathodic product.

Table I. Calculated reversible potentials for reactions at 830 °C

Possible reactions	$\Delta_r G_m^0$ /kJ mol ⁻¹	$E(\text{vs. Al}^{3+}/\text{Al})$ / V
$\text{Al}_2\text{O}_3(\text{diss}) + 3\text{C}(\text{s}) = 2\text{Al}(\text{l}) + 3\text{CO}(\text{g})$	639.6	1.104
$\text{Al}_2\text{O}_3(\text{diss}) + 3/2\text{C}(\text{s}) = 2\text{Al}(\text{l}) + 3/2\text{CO}_2(\text{g})$	1347	1.164
$2\text{Al}_2\text{O}_3(\text{diss}) = 4\text{Al}(\text{l}) + 3\text{O}_2(\text{g})$	2535	2.189
$3\text{C}(\text{s}) + 4\text{AlF}_3(\text{diss}) = 4\text{Al}(\text{l}) + 3\text{CF}_4(\text{g})$	2615	2.258
$2\text{C}(\text{s}) + 2\text{AlF}_3(\text{diss}) = 2\text{Al}(\text{l}) + 3\text{C}_2\text{F}_6(\text{g})$	1427	2.465
$2\text{AlF}_3(\text{diss}) = 2\text{Al}(\text{l}) + 3\text{F}_2(\text{g})$	1228	4.242

These calculations were then compared to electrochemical measurements, and the first electrolysis process, occurring at 1.3 V, should correspond to the discharge of oxide ions, with

formation of CO and CO_2 [5, 7]. The discharge of fluoride ions occurs after the discharge of oxide ions, and, probably a $(\text{CF})_n$ film is formed on the electrode surface, which inhibits the electrode process and contributes to the anode effect [7]. On the basis of this work alone not much can be said about the chemistry of the film. However, in an analogous system, molten KF-HF, it is suggested that the formation of a 'CF' film will inhibit the electrode process [24-26]. As the potential increases, the current increases again. The relatively high current shows that the shielding of anode surface is not complete. In a similar system related to neodymium electrolysis, our study showed a large amount of PFC gases evolution occurs in this regime [27]. The absence of any cathodic current during the reverse scanning indicates the high degree of electrochemical irreversibility of the whole anode process.

Voltammograms at various sweep rates are compared in Figure 2. To be clear, the forward sweep and the reverse sweep were drawn respectively, which is the same to the following figures. It further shows that the voltammogram of the reverse sweep is rather similar to that of forward sweep. For the forward sweep, there appears to be some correlation between the potential at which the current drops off (or the peak current density) and sweep rate. However, on the reverse sweep, the potential at which current rises shows no dependence on sweep rate, and the peak current density as well.

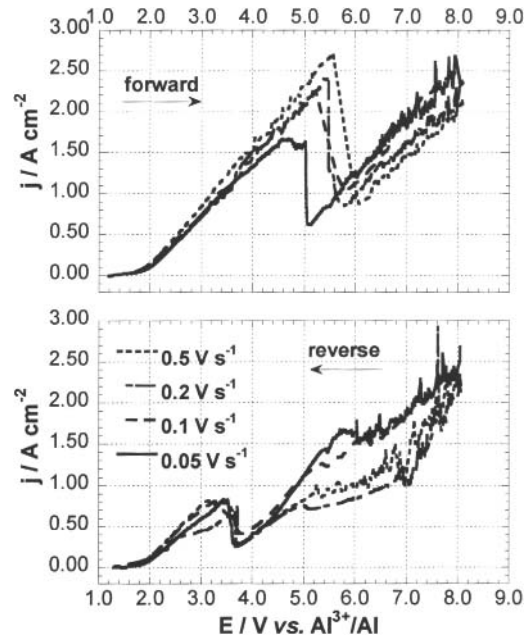


Figure 2. Cyclic voltammograms of carbon in 49 wt% Na_3AlF_6 - 21 wt% K_3AlF_6 - 30 wt% AlF_3 - Al_2O_3 (saturated) melt at 830 °C.

Figure 3 shows the effect of alumina concentration in a set of voltammograms all taken at the same sweep rate of 0.05 V s^{-1} . The current density of the first electrolysis process starting at 1.3 V increases with alumina concentration, which is consistent with the assignment of this peak to the discharge of oxide ions. In alumina free melt, residual oxide ions still remained in the melt after dehydration, which contributed to the first electrolysis

process [28]. For the forward sweep, the critical potential in the alumina saturated melt (~ 5.0 V) is much more anodic than that in alumina free melt (~ 3.7 V). However the recovery potential on the reverse scan does not depend on the oxide concentration. Thus, we expect the resistant film to be a fluorocarbon compound – formed when the discharge of fluoride ion occurs and sustained only at potentials higher than a certain value (~ 3.6 V vs. Al^{3+}/Al).

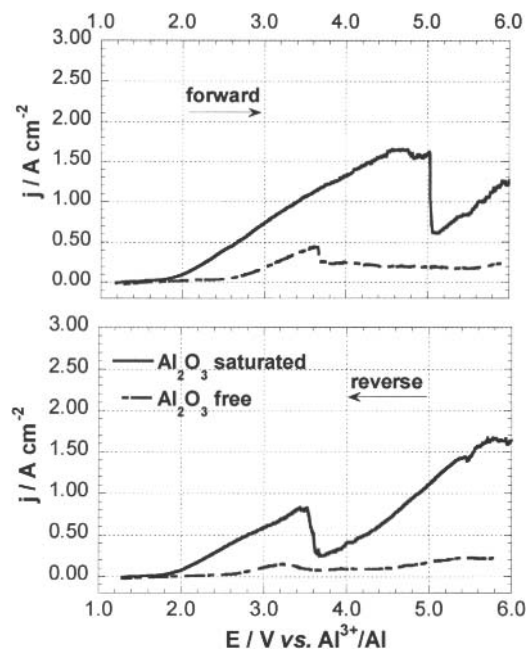


Figure 3. Cyclic voltammograms of carbon anode in 49 wt% Na_3AlF_6 - 21 wt% K_3AlF_6 - 30 wt% AlF_3 - Al_2O_3 (saturated or free) melts. Temperature, 830 °C; Sweep rate, 0.05 V s^{-1} .

In the aluminium free melt, the oxide concentration was very low, and the melts were essentially fluorides doped with a tiny amount of alumina. In spite of this, the current density of the second electrolysis process at the same potential is much lower than that in alumina saturated melt. According to this, we suppose that the electrolysis reaction associated with the second electrolysis process probably involves the formation of a second type of fluorocarbon surface species, which may be thermally unstable, leading to the emission of carbon oxides and PFCs.

These features of the voltammograms on the emission of carbon oxides and the occurrence of anode effect obtained in our low-melting electrolysis system resemble those known for molten cryolites [5-7]. These similarities are not surprising, since in both cases oxide and fluoride ions are discharged anodically. However the features of the voltammograms after the occurrence of anode effect are very different in our low-melting system compared to the traditional industrial system, which we also obtained with our experimental system for both alumina saturated and free melts. As shown in Figure 4, the potential was swept over an exceptionally wide range out to 10.0 V. Starting from 0 V, the current rises with potential up to about 6.5 V at which point there is a distinct decrease in current. However, the current remains low, all the way

out to 10.0 V. With the exception of a tiny peak around 6.0 V on the reverse sweep, there is no evidence of electrolysis activity after anode effect. There is such difference between our low-melting electrolyte system and the traditional industry system. Firstly, Na_3AlF_6 was partly substituted to K_3AlF_6 , however potassium ions could not affect anode process largely. Secondly, a larger amount of AlF_3 was added. It is proposed in literature [29] that the failure of the low current region (anode effect) to be maintained during voltammetry in AlF_3 -rich electrolyte is due to depletion of F^- ions, which are required to form and maintain a resistive or reaction inhibiting layer. Thirdly, the electrolysis temperature was much lower than the traditional aluminium industry. Although we still have not found a definite explanation to the effect of temperature, it is obvious that the performance of low temperature aluminium electrolysis with carbon electrodes increases the risk of a larger emission rate of PFCs.

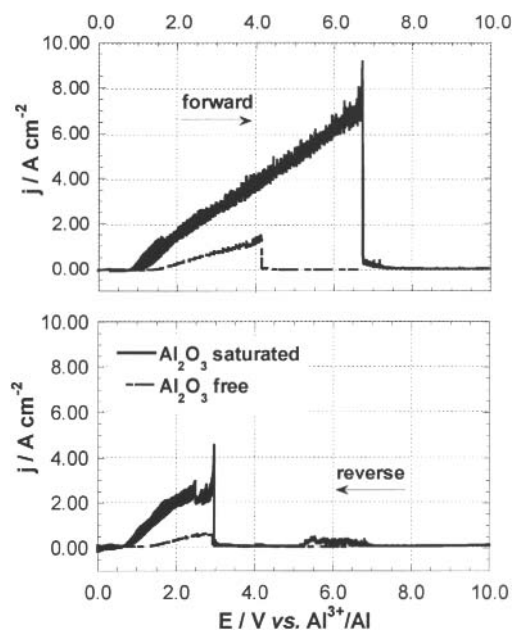


Figure 4. Cyclic voltammograms of carbon in 83.6 wt% Na_3AlF_6 - 11.4 wt% AlF_3 - 5.0 wt% CaF_2 - Al_2O_3 (saturated or free) melts. Temperature, 970 °C; Sweep rate, 0.05 V s^{-1} .

Conclusion

Comparative experiments were carried out on carbon anodes in Na_3AlF_6 - K_3AlF_6 -based low-melting electrolytes and in traditional industrial electrolytes. The results showed in low-melting electrolytes, two electrolysis processes occurred on carbon anodes, which were the emission of carbon oxides and PFCs. The performance of low temperature aluminium electrolysis increases the risk of a larger emission rate of PFCs.

Acknowledgement

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