

DIRECT OBSERVATION OF THE ANODE EFFECT BY RADIOGRAPHY

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The gas generated at the anode during electrolysis, was studied using a X-ray radiographic technique. The events occurring in a laboratory cell were visualized by means of a X-ray source and an image intensifier. Real time video-recordings of the anode gas generation were obtained both during normal electrolysis and during the anode effect.

During electrolysis, a series of small gas bubbles were formed along the vertical side of the graphite anode while larger and fewer bubbles were formed under the base of the anode. The specific area of the gas bubbles increased with increasing current density and increasing alumina concentration. During the anode effect, the anode was completely non-wetted by the electrolyte. The base of the anode was covered with a gas layer of thickness up to 3 mm while the vertical side of the anode was covered with a very thin gas film. Reversal of the cell polarity lead to the instantaneous termination of the anode effect.

INTRODUCTION

In a Hall-Heroult cell for the electrolysis of alumina, gas is continuously evolved at the anode. This gas consisting mainly of CO_2 and CO , is typically generated at a rate of $0.2 \text{ cm}^3/\text{s}$ per square cm of anode surface. Due to the limited penetration depth of the gas into the electrolyte, rapid horizontal movements of the gas must occur in order for the gas to escape. Since the visualization of these phenomena is extremely difficult, the behavior of the anode gas beneath the anode surface is not fully understood.

Most investigations(1,2) concerned with the wetting behavior at the anode have been carried out by placing a drop of liquid electrolyte on top of a graphite or carbon surface. To obtain a more realistic representation of the phenomena occurring at the anode during electrolysis, it was decided to use X-ray radiography to observe the continuous evolution of gas during the electrolysis.

EXPERIMENTAL

The experiments were carried out in graphite crucibles with an ID of 2.5 cm and a height of 8 cm. A BN liner was fitted inside the crucible to insulate the crucible walls. An inconel cylinder was connected to the upper section of the crucible and used as the cathode connector. The graphite anode was connected to a stainless steel tube and immersed into the electrolyte as shown in Fig. 1. The graphite anode had typically a diameter of 0.9 cm and was machined from graphite with a density of 1.68 g/cm^3 . The crucible was placed in a gas-tight vertical quartz tube and heated in a graphite resistor furnace(3). Images of the cell were formed on a photographic film by a horizontal beam of X-rays. At 50-55 kV and 150 mA, the exposure time was between 1/10 and 1/60 s when an intensifying screen was employed. Using the equipment shown in Fig. 2, real-time video recordings were taken. All salts were dried at 420 K before being added to the crucible together with high purity aluminum.

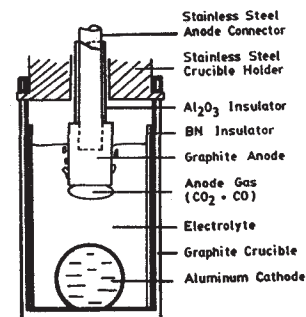


Figure 1. Crucible assembly.

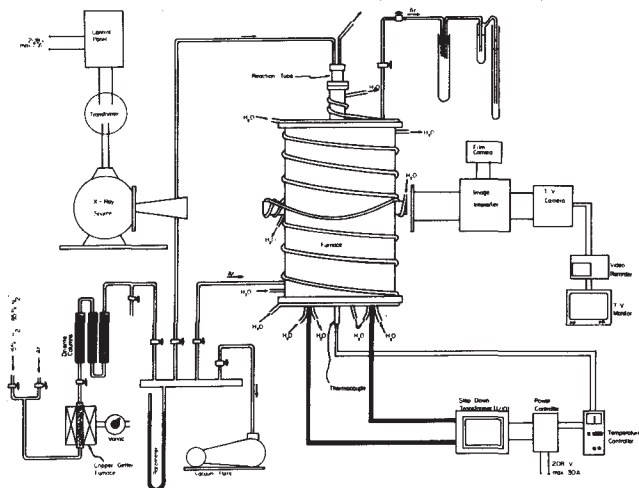


Figure 2. Experimental apparatus.

RESULTS AND DISCUSSION

During electrolysis, gas evolved over the entire anode/electrolyte interface. The gas evolution appeared to occur along the lower vertical section of the anode base due to a partial blockage of the anode base by a large single gas bubble. The bubbles which formed on the side of the anode varied in size with a maximum diameter being approx. 3 mm. The bubble generated under the base of the anode penetrated a maximum of approx. 5 mm into the electrolyte. This is in good accordance with that calculated based on the electrolyte surface tension(3). A typical gas configuration is shown in Fig. 3.

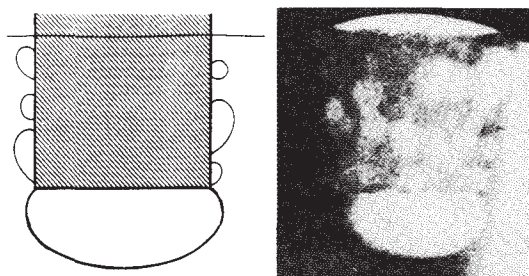


Figure 3. Schematic illustration of gas generation on a graphite anode during electrolysis.

During the growth of a single bubble under the anode base, the electrolyte was pushed away from the surface. In these cases, the electrolyte formed contact angles less than 30°. In some experiments, the gas formation started with a whole series of small bubbles under the anode. These bubbles would gradually grow together and form a thin continuous gas film. The thickness of the gas film would gradually grow and contact angles up to 160° were observed. This demonstrates that depending on the electrolyte/gas movement a wide variety of contact angles could be observed. Such a contact angle hysteresis has been observed in many other situations and is probably the main source of the discrepancies between different investigators(4).

In some experiments, external gas was bubbled into the electrolyte through a vertical hole located in the centre of the anode. No significant difference in behaviour was observed between the different gases used (Ar, CF₄, CO₂ and 15% H₂-85% N₂ mixture). As the gas flowed into the cell, it was noticed that each bubble grew in size under the anode in a manner similar to that observed when electrolysis was performed. After reaching the maximum penetration depth, the bubble separated from the anode. With increasing gas flow, the bubbles became smaller and were released more frequently.

Bubble Surface Area

The reoxidation mechanism of aluminium with anode gas is still being investigated. The rate of dissolution of CO₂ gas in the electrolyte depends to a large extent on the surface area of the anode gas. In this study the bubble diameter was measured both as a function of current density and of the alumina concentration(5). By assuming a gas temperature of 970 °C and a current efficiency of 90 percent, the specific surface area was calculated. As shown in Tables 1 and 2 and in Figs.4 and 5, the specific surface area increases both with increasing current density and with

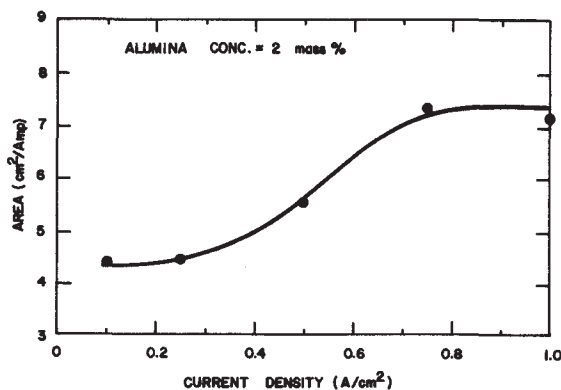


Figure 4. Specific surface area versus current density at 2 mass % Al₂O₃.

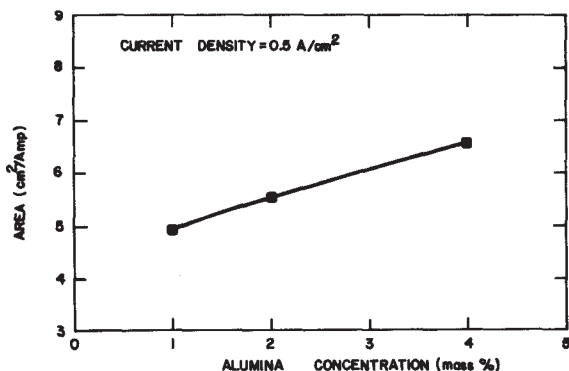


Figure 5. Effect of Al₂O₃ concentration on specific surface area at a current density of 0.5 A/cm².

increasing alumina concentration. A regression analysis resulted in the following equation:

$$\text{Area}(\text{cm}^2/\text{Amp.}) = 2.82 + 3.7 * I(\text{A}/\text{cm}^2) + 0.5 * \text{Al}_2\text{O}_3$$

Table 1. Effect of current density on the bubble area (Al₂O₃ = 2 mass%).

I (A/cm ²)	bubble d(cm)	cm ² /Amp.
0.1	0.179	4.43
0.25	0.177	4.47
0.50	0.143	5.55
0.75	0.108	7.34
1.0	0.110	7.19

Table 2. Effect of alumina concentration on the bubble area (I = 0.5 A/cm²).

Al ₂ O ₃	bubble d(cm)	cm ² /Amp.
1.0	0.160	4.96
2.0	0.143	5.55
4.0	0.121	6.56

ANODE EFFECT OBSERVATIONS

Using high purity cryolite, the anode effect was initiated after approximately 0.5 to 2 s at current densities of 0.5 and 2 A/cm², respectively. Without any warning and without any gas evolution, the anode effect occurred after the voltage reached approx. 2.6 V. Simultaneously with the occurrence of the anode effect, the anode became completely non-wetted by the electrolyte. At the exact time that a thin gas film was observed covering the anode base, the cell voltage rose to a maximum of 80 V. The gas film covering the anode base

had a maximum thickness of 3 mm. When the cell polarity was reversed, rapid wetting of the anode occurred and the gas film instantaneously formed a gas bubble which was separated from the anode base by a thin layer of electrolyte as shown in Fig. 6.

When external gas was passed through the center of the anode during the anode effect, no gas bubbles were observed at the base of the anode. Instead a continuous film covered the anode base and vibrations were observed along the vertical side of the anode. This suggests that the gas flowing through the anode hole escapes through a thin gas film covering the vertical side of the anode. It has been estimated that film thickness is approx. 30 μm(3). The charge transfer during the anode effect may occur from protruding parts of the anode. However, the observed gas film and the smoothness of the anodes used for these studies, indicate that the anode was completely separated from the electrolyte during the anode effect and that the charge transfer must occur across this gas layer. Another evidence of the forces involved during the anode effect was the fact that the anode effect could be initiated using the crucible as the anode. In this configuration, the anode effect was manifested by a formation of a gas layer of approximately 1 mm which separated the liquid electrolyte from the crucible bottom.

Under constant current conditions such as in a commercial cell, the cell voltage increases slowly prior to a sudden increase in the cell voltage manifesting the anode effect. The slow increase in the cell voltage before the anode effect is due to the depletion of the alumina concentration which leads to increasing anodic voltage. However, the sudden increase in the cell voltage indicating the onset of the anode effect, is still not fully understood.

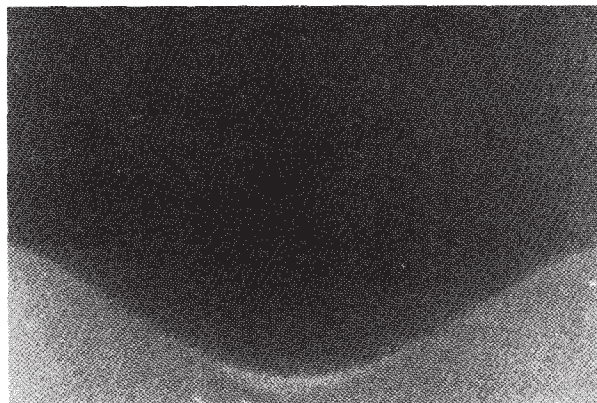


Figure 6. Separation of the electrolyte from the crucible (anode) during the anode effect.

The present experiments show the following:

1. The initiation of the anode effect occurs simultaneously with the complete non-wetting of the anode.
2. The anode is completely separated from the electrolyte by a thin gas film through which charge transfer must occur.
3. In high purity cryolite, the anode effect can be initiated without any preceding gas evolution at the anode.
4. A flow of external gas through the center of the anode did not change the appearance of the anode effect.
5. Reversal of the cell polarity leads to the immediate and complete wetting of the anode by the electrolyte.

These observations indicate that the anode effect results from the sudden occurrence of a new and different event. The determination of the existence of a thin gas film suggests that the new event is not related to the formation of a new solid compound at the anode surface. It is more likely that the anode effect is caused by an event occurring within the electrolyte at the electrolyte/anode surface. Since the anodic overvoltage increases rapidly with decreasing aluminum oxide concentrations, at alumina concentrations below 1 to 2 mass%, the energy liberated at the interface increases with decreasing concentrations. Under constant current conditions, the temperature at the bath/anode interface increases as the anode effect approaches. With the sudden initiation of the evaporation of the electrolyte, the anode effect may occur(6). Both industrial and laboratory work show that very high temperatures($T > 1800\text{ K}$) are generated during the anode effect.

CONCLUSIONS

1. The electrolysis process has been visualized by means of X-ray radiography.
2. The specific surface area of the anode gas increases with increasing current density and alumina concentration.
3. The electrolyte formed contact angles varying between 30° and 160° with the graphite anode.
4. A gas film separates the anode from the electrolyte during the anode effect and the electrolyte becomes completely non-wetted.

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