

## ELECTROLYTIC DEGRADATION WITHIN CATHODE MATERIALS

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### Abstract

There are two generally accepted electrochemical processes involving the carbon of cathode blocks, these being sodium uptake and aluminium carbide formation. Both processes occur at or below the potential required for aluminium deposition, and therefore can occur at all times in blocks permeated with electrolyte - as does occur with modern cell designs and operation. Then, since the cathode carbon is at a more cathodic potential than the molten aluminium metal pad, the electrolyte filled material can sustain the electrochemical reactions, even though the rate may be very low.

A special laboratory test has been developed to identify and ascertain the extent of the carbide forming reaction within the carbon matrix of laboratory cathode specimens. Results show that this reaction is dependent on the carbon binder pitch, the carbon filler material and the cathode heat treatment. This electrochemical reaction is expected to become more prevalent at higher current densities and the growth of the carbide can potentially contribute to accelerated wear in cathode blocks.

### Introduction

In general there are two important electrochemical reactions which contribute to cathode failure, sodium penetration and aluminium carbide formation. The extent of these reactions depends on many factors such as bath chemistry, carbon material, current density, length of electrolysis etc.[1] Sodium is known to be the primary penetration agent and its penetration depends on the cryolite ratio and the carbon cathode materials structure[2]. Sodium penetrates into carbon through an intercalation mechanism[3] and sodium uptake is smaller for graphitic and

especially graphitized cathode blocks. This uptake causes cathode swelling and positive volume change [4]. Whilst this explanation has some validity, it fails to explain the total wear since in some cathodes that are well covered with metal pad, the wear rate exceeds the possible saturation solubility of the metal pad. This is accentuated in zones during special operating processes such as metal tapping. Furthermore, such a mechanism does not explain the extensive pitting that is observed in many modern blocks as illustrated in Figure 1.

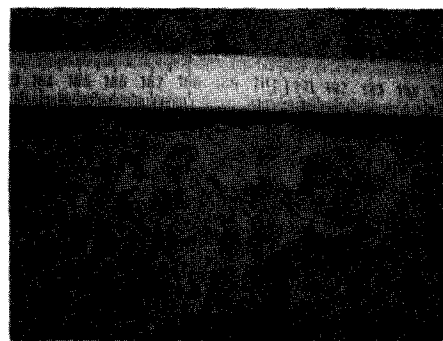


Figure 1- Extensive pitting in blocks

This pitting suggests there may be particulate detachment or sub surface processes occurring simultaneously. In addition to carbide formation, it has been suggested that there is also physical wear. However since it has been shown the total wear on a cathode increases with current density[5], [6] further explanation is required.

There are a number of factors influencing cathode wear that have

not been satisfactorily explained. Most laboratory studies have demonstrated either sodium expansion or surface wear, yet both of these are likely to occur simultaneously. Furthermore these studies are of a limited duration. Some of these processes continue at significant rate until the carbon cathode is saturated.

In another paper[7] it has been demonstrated that the pitch carbon has differing properties to the filler aggregate of cathodes, whilst there are also indications that some of the failure may be though particulate degradation. Accordingly, the study of different formulations with different pitches has been extended to include long term electrolysis under controlled conditions. As described below, a new test procedure was developed and applied to the same matrix of specimens described in another paper[7]. By extending the test to approximately 100 hours, with modern and surface sensitive techniques, very slow processes within the cathode can be studied.

**Experimental Set Up And Procedure:**

As the electrolysis process reaches the steady state, electrolyte has penetrated and filled the pores. The process causes weakening of the material and eventually leads to spalling of the cathode. Accordingly a process has been developed which involves:

- Electrolysis in excess of 96 hours.
- Specimen immersion to a depth of 45mm
- Cathode specimen to be hung in the bath so any aluminium formed drains.
- Anode-cathode distance for the bottom of the specimen to be less than the upper part so there is high and low current density regions.
- The average current density applied during the electrolysis to be 0.75 A/cm<sup>2</sup>.
- A positive flow of N<sub>2</sub> gas to be maintained during the electrolysis.

The cathodes to be electrolysed are chosen from the cathode matrix from the previous paper [7] . The apparatus is shown in Figure 2.

The cathode samples were cylindrical cores, 30x110 mm. The carbon crucible had external diameter 150mm, inside diameter 90mm, height 140mm and depth of 110mm. The anode crucible was filled with saturated bath with the following compositions:

- AlF<sub>3</sub> 10%
- CaF<sub>2</sub> 5%
- Cryolite 63%
- Alumina 22%

Bath was saturated with alumina at the start of the electrolysis to avoid anode effect during the electrolysis period. The crucible and the aluminium product were at anodic potential. The bath temperature was kept at 975°C during electrolysis.

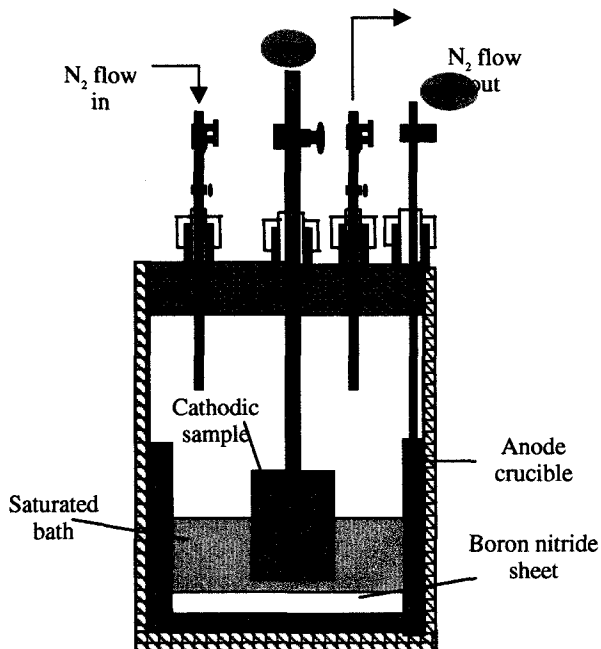


Figure 2 – Electrolysis set up

**Preliminary Specimen Evaluation:**

At the end of electrolysis the cathode specimen was removed and the adherent electrolyte was carefully removed from the specimen's surface. The specimen was examined to determine its roughness profile and new shape due to erosion and corrosion, extent of sodium swelling, volume of carbon eroded in the test period and the extent of the sub-surface degradation.

**Evaluating The Extent Of The Sub-Surface Degradation:**

After the preliminary evaluation on the electrolysed specimen, it was then cut longitudinally through its corroded section, Figure 3.

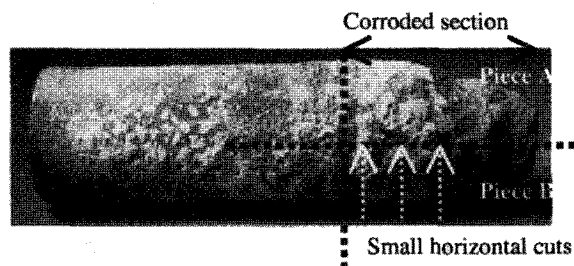


Figure 3– Cathode specimen cuts

One of the halved pieces was then cut into approximately 3mm thick semi-circular discs at 4mm intervals for the immersed section.

To determine the nature of the products within the electrolysed cathode section, X-ray Diffraction(XRD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used. The hydrolysis of the cathode sections following electrolysis was observed. Cut samples were stored in controlled temperature and humidity and photographed at 24 hour intervals.

**Preliminary Wear Results:**

The weight, diameter, surface roughness and volume was measured before and after the electrolysis period. The changes in weight, volume and diameter of the cathode specimens due to electrolysis are given in Table I. The weight gain for the anthracitic group was more than the graphitic group, and the cathode bound with pitch A seemed to have higher electrolyte penetration than the ones bound with pitch B.

Table I- Electrolysed cathode wear results.

	Coarse-anthracitic (Pitch A)	Coarse-anthracitic (Pitch B)	Coarse-graphitic (Pitch A)	Coarse-graphitic (Pitch B)
Weight change(g.)	+19.3	+16	+11.7	+9.6
Volume change(cm <sup>3</sup> )	13.73	12.48	12.96	12.36
Diameter (mm) (min to max)	19.6-32.6	20.9-32.0	22.0-32.1	19.2-32.5

**Products Analysis Within Carbon Cathode:**

X-ray diffraction was performed on the electrolysed cathodes to determine the nature of the reaction products. However only cryolite and carbon were identified. This suggested that the bulk of the reaction product was amorphous and therefore it could not be detected by XRD.

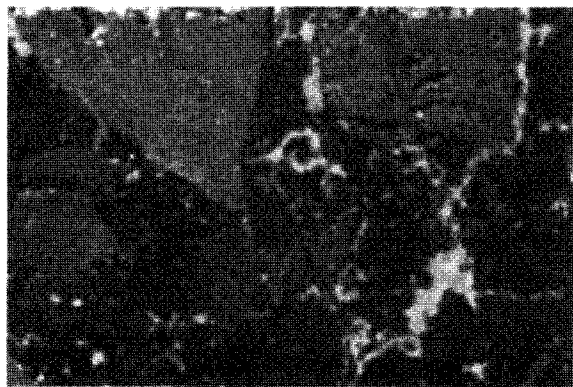


Figure 4-A close up of a piece of an anthracitic cathode after cutting.

Alternative methods such as X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were applied to determine the presence of carbide and other electrolyte elements. The wide scan from XPS analysis on the product showed the presence of Na, F, O, C and Al. To identify the chemical compounds present on the surface, such as Al<sub>4</sub>C<sub>3</sub>, narrow scans were carried out. The results of the narrow scans are illustrated in Table II.

Table II- Narrow scan results of carbon peak

Peaks	Position BE(eV)	Chemical compound
C 1s 1	285.035	Carbon
C 1s 2	290.460	Sodium carbonate
C 1s 3	282.373	Carbide
C 1s 4	288.055	Possibly carboxylic group

After each electrolysis, one of the semi-circular pieces of each sample was examined using Scanning Electron Microscopy. The piece was usually 6 to 10 mm from the immersed part of the cathode sample. The result of one of the line scans and the SEM image is illustrated in Figure 5.

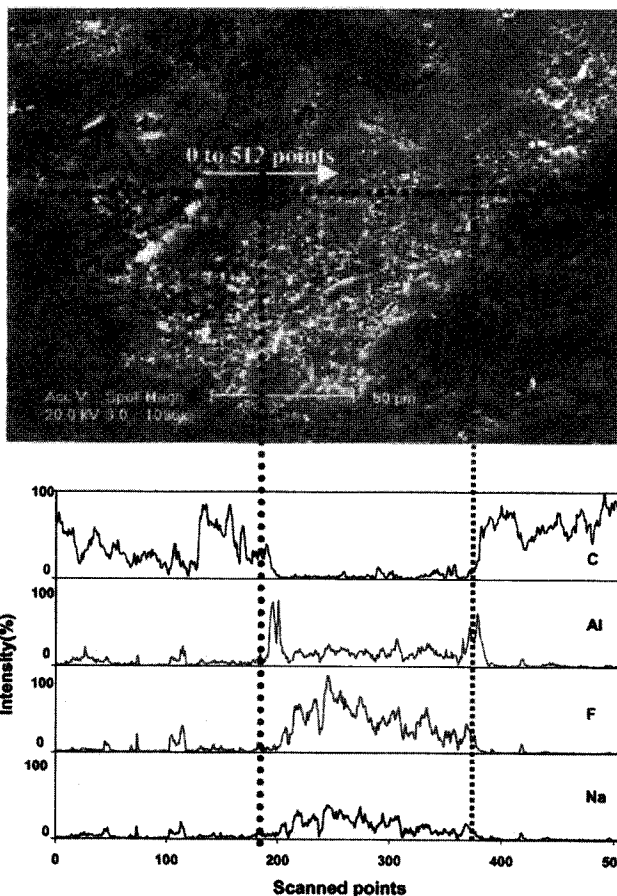


Figure 5- Line scan result of an anthracitic cathode bound with pitch B.

A pore or crack in the cathode was filled with electrolyte as evidenced from the presence of Na, Al and F. However at the interface of the pore a peak at the level of aluminium with corresponding peaks of Na and F suggested the presence of aluminium carbide. The presence of aluminium was determined in the absence of Na and F so this suggested carbide formation inside the carbon cathode.

Degradation Due To Formation Of Carbide (Baked To 900°C):

Mid-Section Hydrolysis:

The hydrolysis of the third piece and the half piece is shown in Figure-6.

	Day 2±1	Day 5±1	Day 10±1	Day 15±1	Day 20±1	Day 25+
Coarse-graphitic group (Piece3) Pitch A						
Coarse-graphitic group (Piece3) Pitch B						
Coarse graphitic group (half-piece) Pitch A						
Coarse graphitic group (half-piece) Pitch B						
Coarse -anthracitic group (piece 3)Pitch A						
Coarse -anthracitic group (piece 3)Pitch B						
Coarse -anthracitic group (half-piece) Pitch A						
Coarse -anthracitic group (half-piece) PitchB						

Figure-6- Mid section and the half piece degradation due to carbide formation

The amount of aluminium carbide formed was influenced by the specimen's quality. The relative amount of carbide formed was found by the time taken for hydrolysis to cause a fixed amount of degradation. This "frost heave" was more rapid for the specimens baked at the lower baking temperature. From Figure-6 it can be concluded:

- Pitch A was more reactive than pitch B. Cathodes bound with pitch A had a marginally faster degradation rate than the ones bound with pitch B. This was more obvious for the anthracitic matrix. The carbide could be observed around the grains of carbon on the second day after electrolysis.
- The graphitic group had a slower degradation rate than the anthracitic group. The anthracitic matrix degraded 5-10 days faster than the graphitic one.
- The wear for the graphitic cathode appeared to be more uniform and in the outer surface, but the anthracitic cathode showed irregular wear and degradation.

Bottom section/ higher current density zone:

During electrolysis the lower part of the cathode immersed in the electrolyte was electrolysed from two directions. This caused more aluminium carbide to form in comparison with other cut sections. The bottom pieces of four electrolysed cathode matrixes are compared in Figure 7.

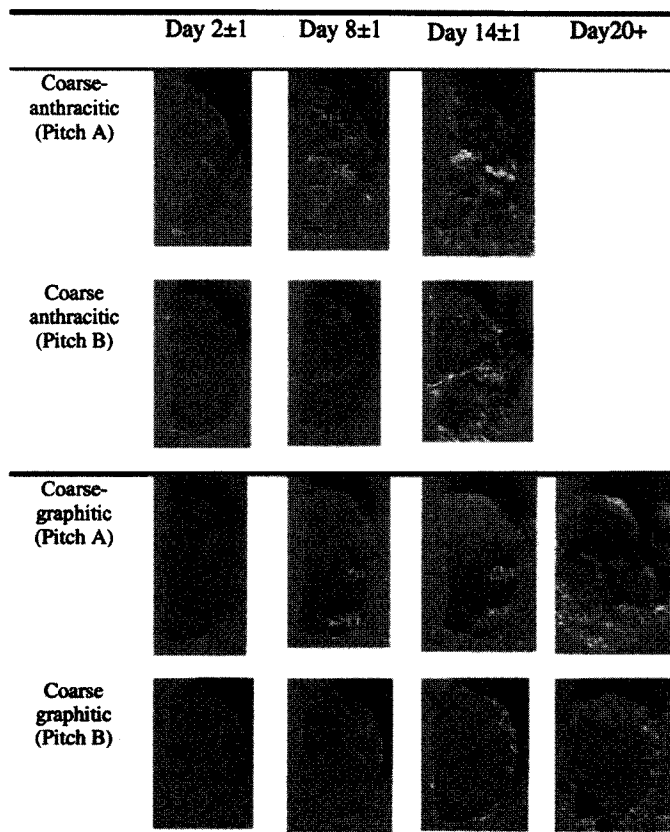


Figure 7- Bottom pieces for four electrolysed cathode samples.

The aluminium carbide around the carbon grains could be easily observed for the coarse anthracitic cathodes.

Degradation Due To Formation Of Carbide C( Baked To 1150°C)

The graphitic cathodes baked to 1150°C showed a much slower degradation rate than the ones baked to 900°C. The changes are in the order of 10 days slower than low temperature baked samples.

Conclusions:

From the results of XPS, SEM and degradation photos, it can be concluded:

- Aluminium carbide is formed within the pores and cracks of the carbon cathode specimen and it is associated with electrolyte penetration. The carbide formation is formed by electrochemical reaction since the deposited aluminium on the surface readily drains off.
- The electrochemical formation of aluminium carbide could be more favoured for disordered carbons, ( thermodynamic activity greater than 1) and therefore the aluminium carbide reaction would be more favoured for the anthracitic cathode than the graphitic one.
- In heterogeneous specimens the amount of carbide formed increases with the disorder of the carbon.
- The carbide formation is also dependant on the pitch type and the difference can not be distinguished by normal pitch characterisation methodology.
- The amount of carbide formed increases with cathode current density.
- Higher baking temperature results in cathodes with higher resistance to carbide formation. This could be due to the more ordered structured carbon due to higher baking temperature.

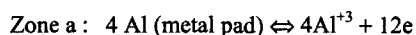
Mechanism Proposed for Degradation:

Prior to presenting a mechanistic interpretation, it should be noted several other relevant trends are well established including :

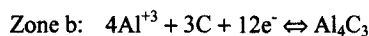
- At the start of electrolysis, sodium penetrates carbon through an intercalation mechanism.
- Bath penetration is rapid, this being favoured by the pitch generated porosity and wetting enhanced through the sodium/carbon intercalation.
- In modern cathodes, the penetrating electrolyte is more enriched in aluminium fluoride than the alkali baths used in start up of cells in earlier years.
- Thermodynamically, aluminium carbide is more favoured on cathode surfaces. It has been thought that this is limited or inhibited by mass transfer of carbon to the reaction interface or of the carbide product away.
- Aluminium carbide has a finite solubility in the electrolyte and this increases with aluminium fluoride content.
- There is always a catholyte film between the metal pad and the carbon cathode surface in normal operating cells.

- The nearer one moves towards the cathode collector bars, the more cathodic the potential is for the carbons. That is to say, there is a potential gradient from the metal pad down through to the collector bar.

The mechanistic interpretation is best envisioned by considering a metal pad overlaying the penetrated bath and the cathode carbon. (In the absence of the metal, the anodic reaction in the discussion below will be different, but not lead to any different conclusions.) While the penetrated electrolyte exhibits ionic conductivity, this presents a parallel path for current flow to the electronic conduction through the carbon, although current density will be much less because of the higher resistance of the electrolyte and its reduced cross sectional area. Current flowing through the electrolyte will be enabled by anodic dissolution of aluminium at the electrolyte metal under-surface interface and a deposition reaction involving aluminium ions at the electrolyte carbon interface. Thus, as schematically represented, we have two half reactions and the overall reaction resulting in aluminium carbide formation, Figure 8.



And on the more cathodic carbon:



Overall reaction:



It is well known that thermodynamically this reaction is favoured to its own right. Whilst this is a strong driving force, the driving force is enhanced by the potential gradient through the cathode carbon, because of its own electrical resistivity. This, therefore, gives a more favoured potential path, although it will be at a lower current density because of the high resistance of the electrolyte in the pores. The electrochemical formation of aluminium carbide is thermodynamically more favoured for disordered carbons (which have a thermodynamic activity greater than unity) and, therefore, reaction of that material would be favoured over graphite when both are present at a given location. The net effect of this is to electrochemically dissolve the binding carbon that holds the particulate material together and, simultaneously, grow a layer of solid aluminium carbide (or aluminium carbide electrolyte deposit). These two phenomena give rise to a weakening of the surface structure, making physical erosion easier, as well as potentially giving rise to ejection of particulates by the frost heave growth of the carbide layer.

At higher current densities, the potential gradient through the cathode carbon is greater. Accordingly, the rate of formation of the carbide is also enhanced. Thus, one would expect a greater weakening and particulate detachment rate at higher current densities via this mechanism. Following particulate detachment, the void generated will be partly filled with aluminium metal. Thus, the potential gradient, as a driving force for further carbide formation, is further enhanced because of the reduced distance to the cathode collector bar. This will accelerate erosion, and lead to the equivalent of pot holing.

Whilst the phenomena observed is explained by differential reactivity of carbons, the processes would occur in any porous material that has a potential gradient through it and pores filled with aluminium and an oxidisable metallic source at a more anodic potential.

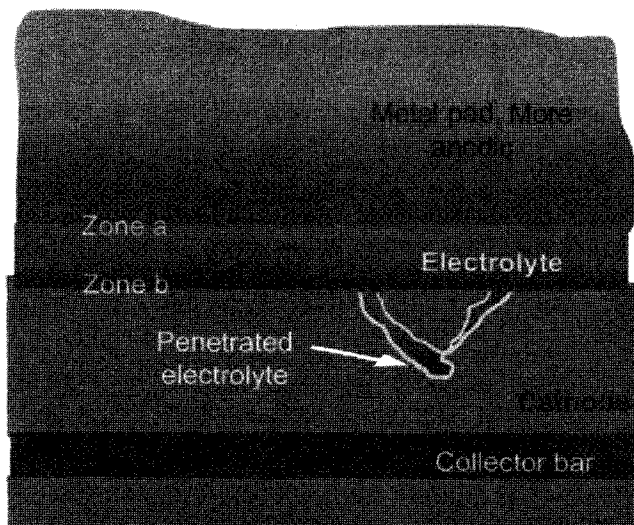


Figure 8- The proposed mechanism for aluminium carbide formation

The weakening is dependent on the bonding structure and, for graphitic materials, the interlayer bonding is weaker than the inter crystalline bonding of amorphous carbons. Thus, even wear would be expected in graphitic materials, but a more accelerated one.

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