— Light Metals —

INFLUENCE OF INTERNAL CATHODE STRUCTURE ON BEHAVIOR DURING ELECTROLYSIS PART II: POROSITY AND WEAR MECHANISMS IN GRAPHITIZED CATHODE MATERIAL

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Abstract

Graphitized cathode samples with varying formulations to give varying internal structures were tested under laboratory electrolysis conditions to find the effect of internal structure on cathode wear.

It was found that porosity does play an important role in cathode wear with increased porosity adversely affecting the wear characteristics of graphitized materials. Sub-surface aluminium carbide formation was found to increase with increasing porosity and this exaggerated degradation by particulate detachment. Also analysis of wear rates found that porosity, current density and bath chemistry had the greatest impact on cathode wear.

Introduction

Increasing life and reliability of cathode blocks are the two major issues faced by cathode developers and smelters. The life of a cathode block is determined by a number of factors from the raw materials used to operating procedures and practices. Use of graphitic and graphitized cathode blocks has been increasing in modern cells as they have demonstrated superior thermal and electrical properties, and sodium intercalation resistance compared to anthracitic materials. However, higher costs and increased wear rates are characteristics of cathodes with a higher degree of graphitization [1]. Understanding the wear mechanisms involved with these cathode blocks is paramount in order to increase their cell life.

Porosity plays a very important role in the final mechanical and operational properties of cathode materials. For graphitized and graphitic cathodes it was generally found that denser materials are desirable. With respect to mechanical properties graphitic samples show superior properties to graphitized samples [2]. This "denser is better" theory is also applied to the operating properties of cathode blocks during electrolysis with denser products expected to have greater resistance to degradation due to reduced bath penetration and aluminium carbide formation resistance.

Sodium and Bath Penetration

In general, according to Haupin, Na^+, F^-, AlF_4^-, AlF_5^{2-}, AlF_6^{3-}, $Al_2O_2F_4^{2-}$ and $Al_2OF_6^{2-}$ ions are found in molten bath during electrolysis [3]. From these ions, the positive Na^+ ions formed from the equilibrium reaction between liquid aluminium and NaF are the major charge carriers in the bath and will migrate towards the negatively charged cathode creating areas of increased sodium concentration at the cathode. Metallic sodium will penetrate into the cathode block and form large intercalation compounds within the basal planes of the carbon material leading to swelling and

expansion which can in extreme circumstances lead to catastrophic failure. This phenomenon can be somewhat reduced with the use of cathode blocks with a higher degree of graphitization.

Carbon is poorly wetted by liquid aluminium and bath components, however, in all cases bath will penetrate into the pores and cracks of a cathode material. It has been suggested that the intercalation compounds formed during in sodium uptake will increase the carbon hosts wetting ability and will therefore help facilitate bath and aluminium penetration [4,5]. Also Kvande et al, suggested that increasing current density will increase the wettability of molten bath on cathode materials [6]. This phenomenon has become increasingly more important with reduction cells operating at high current densities.
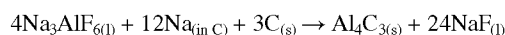
Aluminium Carbide Formation

It is believed that aluminium carbide formation and subsequent dissolution is one of the primary mechanisms involved in the degradation of cathode blocks. The formation of aluminium carbide through molten aluminium metal contact with carbon occurs via the following net reaction:

$$4Al_{(l)} + 3C_{(s)} \rightarrow Al_4C_3$$

This reaction is thermodynamically favoured at electrolysis temperatures and will occur at the carbon-molten metal interface in aluminium reduction cells. However it is has been found that the quantity of aluminium carbide suggested by the reaction's thermodynamics is not readily formed through shear contact between carbon and aluminium. With this in mind the quantities of aluminium carbide formed during electrolysis suggest the presence of alternate carbide forming mechanisms. It is believed the formation of aluminium carbide is enhanced by the presence of cryolite-containing bath which probably acts as a wetting agent for aluminium on carbon [4].

Bath penetration into the porous cathode will allow sub-surface aluminium carbide formation to occur leading to degradation. Rafiei et al. suggested that aluminium carbide formation occurs at the bath-carbon interface within pores filled with electrolyte [7].

Aluminium carbide formation through bath penetration is thought to occur by either chemical or electrochemical means [8]. Chemical aluminium carbide formation due to bath penetration will occur through the following reaction:

$$4Na_3AlF_{6(l)} + 12Na_{(in\ C)} + 3C_{(s)} \rightarrow Al_4C_{3(s)} + 24NaF_{(l)}$$

As can be seen from the above reaction, the formation of aluminium carbide through chemical means will be limited by the amount of bath (Na_3AlF_6) penetrated into the cathode and the amount of intercalated sodium in the carbon. With the use of graphitized and graphitic cathodes this reaction will not be as important as it would be in anthracitic cathode blocks where sodium uptake occurs to a greater extent [8].

Cathode wear is generally accepted to be a function of current density, therefore it can be concluded that electrochemical degradation reactions are likely to be occurring. Keller et al. proposed that electrochemical carbide formation will occur due to the penetrated bath and sludge in the cathode having to come into equilibrium with the cathodes more negative potential. In order for a state of equilibrium to be reached, electrochemical reactions will have to take place, with one of these reactions being the formation of aluminium carbide through the following reaction [9].

$$4Al^{3+} + 3C + 12e^- \rightarrow Al_4C_3$$
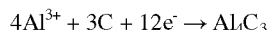
For this reaction to proceed, a supply of Al^{3+} is required. This supply is generated through the anodic dissolution of aluminium metal at the metal/electrolyte interface.

$$4Al(metal\ pad) \rightarrow 4Al^{3+} + 12e^-$$
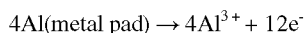
This dissolution reaction allows for current flow through the penetrated electrolyte to be sustained and is enhanced with increasing potential gradient in the system. Therefore increasing the current density in the system will mean that there will be a greater potential gradient in the system and will increase the driving force for the formation of Al^{3+} and Al_4C_3 [7]. Recent work carried out by Wilkening et al. has confirmed the effect of current density on graphite samples with erosion rate increasing with increasing current density. Thus, proving that electrochemical reactions contribute heavily to cathode wear [10].

Following the formation of aluminium carbide a dissolution mechanism occurs which leads to the carbon loss observed in cathode materials during electrolysis. Dissolved aluminium carbide can be found in both the molten aluminium and in particular cryolitic bath of aluminium smelting cells. The degree of dissolution of aluminium carbide in the bath is a function of bath chemistry and temperature. The solubility of aluminium carbide increases with increasing cryolite ratio (up to CR =1.8), decreasing temperature and decreasing alumina concentration [4]. The following equilibrium was postulated by Ødegård et al. for the dissolution of aluminium carbide in cryolitic melts:

$$Al_4C_{3(s)} + 5AlF_{3(diss)} + 9F^-_{(diss)} \rightarrow 3Al_3CF_8^{3-}_{(diss)} \ [11]$$
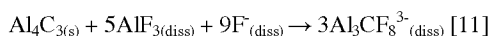
Electrochemical formation of aluminium carbide is more favoured in disordered carbons such as the binder pitch. This will cause the binder phase to dissolve in the electrolyte through the dissolution mechanism outlined above. However, once the solubility of aluminium carbide in the electrolyte (within the pore) is reached, growth of solid aluminium carbide will take place within the pores. Dissolution and growth of aluminium carbide in the pores of the cathode will lead to structural weakness and particulate detachment. Particle detachment will create uneven wear on the cathode surface and could be a possible initiator for pot-hole formation [7].

Investigation into electrolytic aluminium carbide formation is becoming more important in recent years with the use of high amperage cells in modern aluminium production.

Experimental

As described in the preceding paper [1], graphitized and graphitic samples were produced with varying open porosities and pore size distributions. Four core formulations were developed from which both isotropic coke and graphite samples were produced via extrusion.

Table 1: Core formulations for sample production

CL	Coarse granulometry, Low porosity
CH	Coarse granulometry, High porosity
FL	Fine granulometry, Low porosity
FH	Fine granulometry, High porosity

30mm diameter x 110mm length samples were cut for laboratory electrolysis testing. Samples were cut in directions parallel and perpendicular to the extrusion direction so the influence of grain orientation could be measured. With the use of a second order factorial experimental design the effects and interactions of multiple variables were able to be investigated in respect to cathode wear. Six key variables ranging from cathode characteristics to cell operating parameters were assessed.

Table 2: Key variables assessed

Variable	Variance 1	Variance 2
Filler type	Isotropic coke	Graphite
Granulometry	Coarse	Fine
Flour content	Low	High
Cut direction	Parallel	Perpendicular
Bath acidity	10% excess AlF_3	5% excess AlF_3
Current density	1 A/cm^2	0.6 A/cm^2

Half-fraction factorial statistical analysis was used to determine samples required for electrolysis testing. Factorial analysis resulted in the deliberate selection of 32 graphitized and graphitic formulations for laboratory electrolysis and analysis. The following laboratory electrolysis configuration was used.
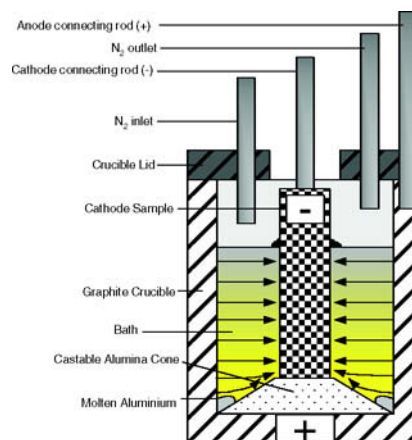

Figure 2: Laboratory electrolysis configuration

Cathode samples were tested using an inverted cell configuration. A graphite crucible was used to hold the molten bath and act as the anode. Inconel rods were used to connect the anode and cathode to the DC power source from which a constant current was supplied to the samples. A constant electrolysis time of 96 hours was used for all samples electrolyzed. This duration allowed enough time for measurable wear to be observed and allowed time for reactions to proceed to a sufficient extent for reliable measurements to be made.

A castable alumina cone on which the cathode sample rested was placed on the bottom of the graphite crucible to help improve the electrolysis process. The cone firstly was used to drain molten aluminium away from the cathode. This allowed molten aluminium to come in contact with the positively charged anode and re-oxidise back to alumina (Al_2O_3), thus replenishing the bath. Over time, the alumina cone will slowly deteriorate and release alumina into the bath. This degradation also helped to replenish the bath and kept the bath in the saturated alumina state. However, the most beneficial use of the cone was to improve current distribution. Furthermore, the cone acted as an electrical insulator, restricting current flow from the bottom of the crucible and concentrating it through the sides of the crucible. This allowed for a more uniform current distribution over the cathode surface to be reached which led to greater uniformity in cathode wear. In all cases the cell was purged with nitrogen gas to prevent any air burning and sample hydrolysis.

Following electrolysis, samples were carefully cleaned to remove any bath from the cathode surface. Direct dimension difference measurements and volumetric difference measurements using mercury displacement were used to determine the extent of wear. Volumetric difference measurements proved to be more substantial as final surface topography of the samples had a great impact on the wear results. Scanning electron microscopy, EDAX and polarized light microscopy was also used to analyze various aspects of cathode wear.

Results and Discussion

Results shown only reflect the findings of graphitized isotropic coke samples. Graphitic samples previously discussed are currently in early stages of testing so will not be discussed in detail.

Sixteen electrolysis experiments were conducted using the graphitized isotropic coke samples. The following four core formulations were tested:

1. ICL- Isotropic coke, coarse grained, low porosity
2. ICH- Isotropic coke, coarse grained, high porosity
3. IFL- Isotropic coke, fine grained, low porosity
4. IFH- Isotropic coke, fine grained, high porosity

From these formulations samples were taken parallel and perpendicular to the extrusion direction and tested under the various electrolysis conditions as stated in table 2.

Electrolysis Results

After 96 hour electrolysis testing a significant amount of wear was observed. Wear rates were measured using both dimensional changes and volume changes during electrolysis. Using 2nd order

half factorial analysis the effects and interactions of five key variables were found. These were:

1. Bath Chemistry
2. Granulometry
3. Porosity (Flour Content)
4. Cut Direction
5. Current Density

Analysis showed that no single variable contributed solely to cathode wear. It was found that interactions between combinations of variables were responsible for the wear of the cathodes. Important interactions are stated in table 3.

Table 3: Relative impact of variable interactions on wear

VARIABLE INTERACTION	EFFECT
1, 2	3.37
1, 3	7.14 *
1, 4	3.28
2, 3	3.28
2, 4	-0.217
3, 4	0.793
1, 5	6.77 *
2, 5	1.00
3, 5	8.46 *
1, 3, 5	9.05 *

Note: Values marked with an asterisk (*) indicate the interactions that had the greatest impact on wear rates of graphitized cathode samples.

Table 3 shows the results of key 2nd order and 3rd order interactions. The variable interaction column lists the specific variable interaction being looked at and the effect column shows the relative increase/decrease on cathode wear that altering these specific variables from their variance 2 state to their variance 1 state as outlined in table 2, whilst all other variables are maintained in their variance 2 states. Values marked with an * indicate the interactions that had the greatest impact on wear rates of graphitized cathode samples.

Results showed that all variables of interest had some type of effect on the wear rates. However, some interactions had more of an effect than others. It was found that the three major variables that had the most influence of the cathode samples were bath chemistry, porosity and current density. The interactions between these three variables showed to have the greatest impact on the wear of cathodes, with results showing that increasing AlF_3 content, increasing porosity and increasing current density will increase the wear rate considerably more than any other combination of variables. These three variables were considered to be the three main variables that will affect the wear rate as increasing porosity will increase bath penetration into the sample and therefore lead to a higher degree of degradation reactions occurring. Increasing current density will have the effect of increasing electrolytic aluminium carbide formation as this is an electrochemical reaction so is highly dependant on current density. Increasing excess AlF_3 content increases aluminium carbide solubility in the melt and therefore will dissolve more

cathode material. These three variables coupled together will cause the most damage to cathode materials.

Table 4 shows an example of typical wear rates found for graphitized samples tested at a current density of 1 A/cm^2 and 5% excess AlF$_3$ content in the bath. This example shows that as open porosity increases wear rate also increases. This was also found to be true by analysis of wear rates using 2nd order factorial analysis of all data.

Table 4: Wear rate examples at 1 A/cm^2 and 5% excess AlF$_3$

SAMPLE	WEAR RATE
IFL Parallel	24.64 cm/year
ICL Perpendicular	21.99 cm/year
IFH Perpendicular	36.03 cm/year
ICH Parallel	24.92 cm/year

Figure 3 a to d shows general surface topography of the four different formulations after electrolysis experiments.
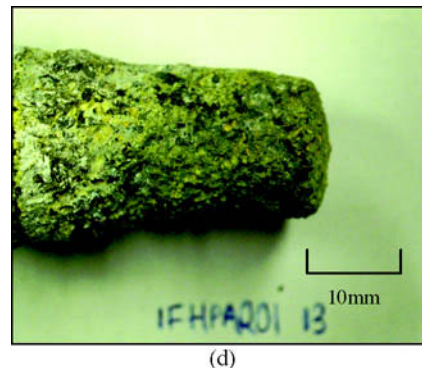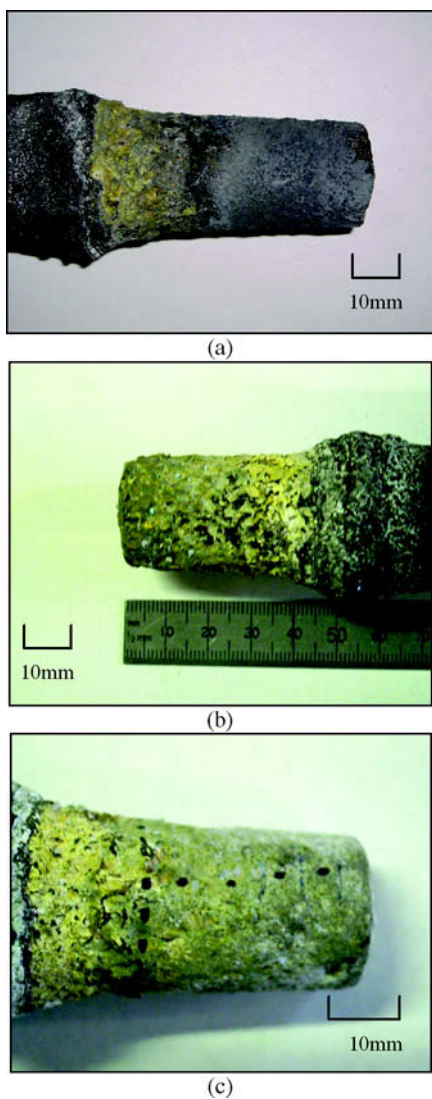

(a)

(b)

(c)

(d)

Figure 3: General topography of electrolyzed graphitized isotropic coke cathodes after 96 hours. a) CL, b) CH, c) FL, d) FH

All samples showed different wear rates which were dependant on the operating conditions used during electrolysis. Though different wear rates were found, samples with similar formulations showed consistent surface topographies and patterns.

Porosity was the main factor that differentiated the four core samples. After electrolysis both coarse grained and fine grained high porosity samples had a considerably roughened surfaces as shown in figure 3b and d. This rough surface is probably a direct result of particle detachment which has led to a pitting effect on the surface. With high porosity samples a greater degree of bath penetration will occur within the cathode leading to a greater chance of aluminium carbide forming. With greater open porosity there will naturally be a greater total pore surface area which will also increase the amount of internal carbide formation. Due to aluminium carbide formation, dissolution and growth (once solubility limit in bath is reached) weakening of the cathode material will take place and particle detachment will occur. High porosity samples naturally have weaker structures than low porosity samples due to less contact between particles, thus reducing the binding strength of the material. This coupled with aluminium carbide formation will promote degradation through particle detachment.

Low porosity samples on the other hand exhibited much different behavior. Figures 3a and c shows the surfaces of both ICL and IFL samples respectively. Low porosity samples showed little to no surface pitting. This indicates that particle detachment is not occurring in dense samples. This will be due to less carbide formation within the pores of the cathode and the greater binding strength between particles in the bulk. With the smooth nature of the surfaces produced, aluminium carbide formation and dissolution would predominately occur at the cathode surface.

The yellow compound found on the surface of the cathode samples shown in figure 3 is the aluminium carbide formed and not dissolved into the bath. It was noticed that low porosity samples showed less build up of aluminium carbide on exposed surfaces. One possible reason for this phenomenon is that the low porosity samples may have a total surface area lower than the high porosity samples. Total aluminium carbide formation maybe a function of the surface area exposed to bath materials. Therefore with greater surface area, greater aluminium carbide formation would likely occur. Removal of aluminium carbide to the bath is dependant on its solubility limit in the bath. However, in the experimental set-up used, dissolved aluminium carbide will likely be oxidised at the anode. Therefore saturation will be probably not

be achieved in the bath. In the pores, however, limited diffusion may lead to formation and growth of an aluminium carbide layer.

With high porosity samples with expected high degrees of aluminium carbide formation the solubility limit of the bath could possibly be reached, resulting in the aluminium carbide growth mechanism becoming dominant over the dissolution mechanism. This growth will lead to a solid carbide layer forming on the surface of the cathode as seen on the high porosity samples in figure 3. This process will probably be enhanced within cathode pores due to carbide solubility limits of electrolyte trapped in the pores being low and limited diffusion of carbide through the pores. Growth of aluminium carbide will occur in the pores and will not be able to be dissolved until particle detachment occurs and the solid aluminium carbide layer is exposed to the bulk bath.

Electrolytic Aluminium Carbide Formation in Pores

Confirmation of aluminium carbide formation within the pores of the graphitized material was made through SEM and EDAX analysis after electrolysis.

Figure 4 shows typical micrographs of low and high porosity graphitized isotropic coke samples after electrolysis. Light areas indicate pores and cracks filled will bath whilst dark areas represent the cathode material. Figure 4a and b clearly shows filler material grains surrounded by penetrated bath. These sites are where sub-surface aluminium carbide formation is likely to occur. It can also be seen that there is a higher degree of bath penetration (indicated by the light areas) in the high porosity samples (Figure 4b).
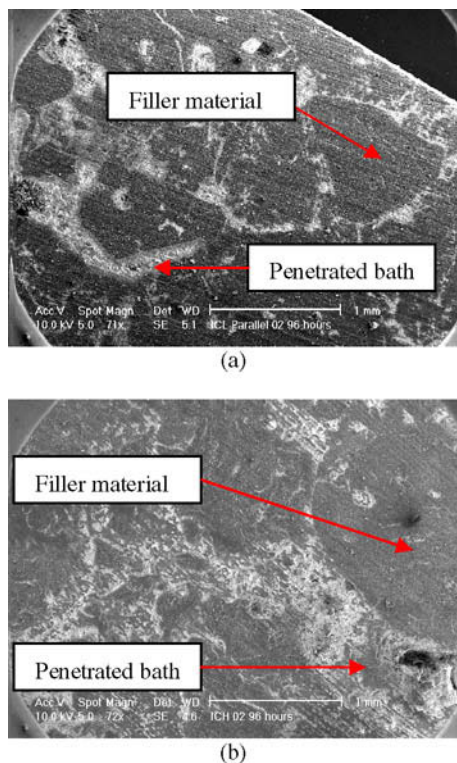

(a)

(b)

Figure 4: Typical micrographs of a cathode material penetrated with bath material a) Low porosity b) High porosity

Taking a closer look at the pores present in the cathode samples shows more meaningful information. Figure 5 shows typical x-ray maps of aluminium and sodium in a bath-filled pore.
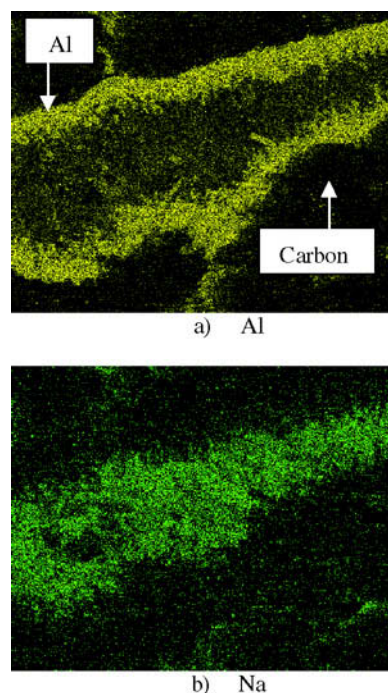

a) Al

b) Na

Figure 5: X-ray mapping of bath filled pore. a) Aluminium b) Sodium

All cathode samples tested showed evidence of aluminium carbide formation in the pores.

X-ray mapping showed some interesting phenomena within the pores. Elemental mapping of aluminium and sodium showed a definite segregation of species within the pores. Figure 5a shows that aluminium had a tendency to segregate from the bath material and line the pore walls. The intensity of the aluminium at the pore edges could suggest that there electrolysis occurring within the pores and therefore forming aluminium from the bath penetrated into the pores. Results have also shown the presence of oxygen in areas coinciding with the aluminium lining the pore edges. Maps at the edge of the pore compared to that in the center of the pore suggest that an aluminium-oxygen compound is lining the edge of the pore. This phenomenon was more evident closer to the cathode surface than in the bulk and the compound could possibly be Al_2O_3 formed through the hydrolysis of aluminium carbide. Aluminium carbide will readily hydrolyze into Al_2O_3 via one of the following reactions.

$$Al_4C_3 + 6O_2 \rightarrow 2Al_2O_3 + 3CO_2$$

$$Al_4C_3 + 6H_2O \rightarrow 2Al_2O_3 + 3CH_4$$
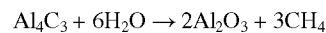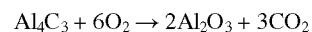
This phenomenon was more evident closer to the cathode surface due to the greater supply of Al^{3+} in this region from the dissolution of aluminium metal at metal/electrolyte interface on the cathode surface. If this is indeed true, this will support the theory of electrochemical aluminium formation within the cathode pores, which was further supported by the increase in wear rates with increased current density.

EDAX line scans were also conducted and a typical line scan of a filled pore is shown in Figure 6.
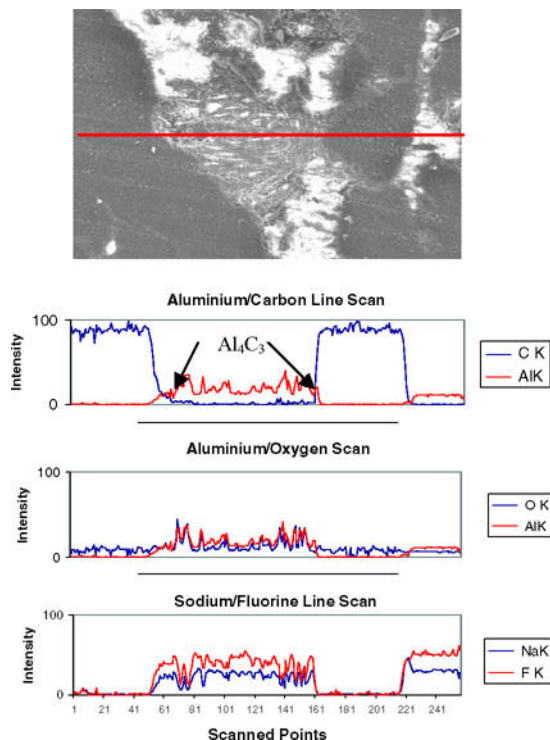

Figure 6: Line scan of bath filled pore

The EDAX line scan shows the definite presence of aluminium carbide at the edge of the pore by the coinciding aluminium and carbon scans at the pore bath interface. Also the above EDAX scan shows the presence of an Al-O compound throughout the pore which may indicate the possible hydrolysis of aluminium carbide.

As mentioned earlier, aluminium carbide can be formed by either chemical or electrochemical means. In the case of these laboratory experiments it is believed that the electrochemical formation of aluminium carbide is the dominant carbide forming mechanism. With the upside down cell configuration any aluminium formed on the cathode surface will flow away from the cathode and therefore limit the ability of aluminium carbide formation through simple aluminium-carbon contact. This is however only correct if it is assumed that aluminium carbide is not formed instantaneously on contact.

The chemical mechanism where the amount of bath and sodium penetration is the limiting factor will also be less of a factor in these trials as the samples used have been graphitized and will have greater sodium penetration resistance. Therefore, reducing the chance of this reaction occurring. However, this experimental set-up allows the effect of electrochemical aluminium carbide formation to be measured and results showed that this is a dominating wear mechanism with current density playing a significant role in the wear of the cathodes.

Conclusions

- Aluminium carbide formation has been found to occur within cathode pores.

- It is proposed that increasing open porosity will increase bath penetration and subsequent aluminium carbide formation.

- Highly porous samples show uneven wear probably due to particulate detachment which arises from the formation, dissolution and growth of aluminium carbide in the pores.

- Porosity, bath composition and current density, especially in combination, were found to have the most pronounced effect on cathode wear.

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