

A POROSIMETRIC STUDY OF SUB-SURFACE

CARBOXY OXIDATION IN ANODES

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Abstract

Carbon dioxide generated at the electrolytic face of operating anodes permeates the anode structure and reacts to form carbon monoxide. This gasification increases anode porosity and generates a reaction porosity profile, with internal attack decreasing to the limit of CO₂ permeation into the anode. Mercury porosimetry has been used to establish the mechanism of reaction porosity generation and to define an active pore size range within the anode structure. In all anodes studied, porosity generated by sub-surface oxidation was largely in the sub-micrometre region of the anode pore volume distribution. A model of the anode structure is proposed to account for reaction in these fine pores.

Introduction

Operating anodes in a Hall-Heroult cell are consumed by a variety of electrochemical, physical and chemical mechanisms, including the sub-surface oxidation of anode carbon by Carbon Dioxide (CO₂) gas. A number of studies (1-13) have shown that the CO₂ electrolytically generated at the working face will permeate into the anode structure and react with the anode carbon to form Carbon Monoxide (CO) according to the carboxy reaction:



In pioneering work, Barrillon (1,2) showed that internal carboxy attack produces density and surface area profiles extending up from the electrolytic face of plant butts.

More recently, Cutshall and Bullough (5) studied the properties of partially consumed plant anodes baked at two different temperatures. Anode density, permeability and surface area were affected by internal reaction to a depth of up to 100mm. Increasing anode baking temperature increased the depth of internal oxidation, however, the magnitude of attack in the zone immediately above the electrolytic face decreased.

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In a later study, Cutshall (6) used the increase in surface area (attributed to the opening of anode porosity smaller than 0.3µm) as a measure of internal reaction.

These studies have shown that porosity profiles are generated by internal reaction above the electrolytic face of anodes. Such profiles are undesirable since they are a direct source of excess anode consumption and reduce the amount of carbon available for electrolytic consumption at the working face of an anode. This increases the rate of recession of the electrolytic face and decreases the anode working life.

Anode dusting (the physical loss of carbon particles from the anode surface) is an additional source of anode consumption. Barrillon attributed dusting to internal carboxy attack above the electrolytic face. Further to this Cutshall showed that dusting was localised to the anode sides; this was associated with the preferential attack of binder coke by low current density electro-chemical oxidation.

A macrostructural study of sub-surface carboxy oxidation in anodes (12) has, however, shown that internal attack in the side of anodes is significantly greater than above the electrolytic face. This internal attack contributes to the generation of dust particles from the anode side.

Anode Porosity

The anodes used in aluminium electrolysis cells, like all carbons, have three basic structural elements: Carbon microstructure, Porosity and Impurities (14, 15). Anode properties and performance, including individual consumption mechanisms, can be related to these three fundamental components and their interactions. For example:

Sub-surface
carboxy = f (Porosity, Microstructure, Purity) (2)
oxidation

This study is primarily concerned with the role of anode porosity in sub-surface carboxy oxidation. Theoretical considerations suggest that porosity has a two-fold effect on anode internal reaction (16); fine porosity provides the internal surface area for reaction, and coarse pores provide oxidant access to this surface from the anode exterior. This simple analysis would indicate that the most reactive pores in anode carbons are those in an intermediate size range where they are sufficiently coarse to provide significant CO₂ transport rates, and yet fine enough to

Experimental

provide the surface area for reaction. Several "reactive" intermediate (e.g. in the range 0.25 - 10 μ m radius) pore size ranges for the carbon - carbon dioxide reaction in anode materials have been published (16-18).

A number of workers (10, 21, 23, 24,) have, however, stressed the importance of minimising the flow of CO₂ within anodes for reducing internal reaction. Mass transport of CO₂ through anode porosity will be largely via viscous flow and hence related to anode permeability. There have been several qualitative associations proposed between anode internal oxidation and anode permeability (10, 12, 20, 22-24). This implies that the volume of coarse pores (e.g. >10 μ m radius) should be minimised.

Other studies have shown that surface area considerations, and hence the volume of fine porosity, to be important (23, 25, 26). The importance of specific surface area, resulting from porosity finer than 6 μ m radius, in determining binder carbon reactivity has been identified (27). It was suggested that microcracks in the binder coke were in this size range. Binder microcracking has also been associated with anode reactivity by other workers (5, 8).

Carboxy attack within the anode pore structure is likely to change the pore size distribution of the reaction affected area. Although it has been suggested (8) that internal oxidation may increase pore size by gasifying pore walls, supporting porosimetry data has not been provided. Internal carboxy attack of laboratory anodes has been shown to occur by the enlargement of pores finer than 1 μ m radius (3). Cutshall (6) suggests that sub-micrometre porosity development was due to the opening of closed pores in the binder coke.

Project Objectives

This brief review of previous studies of the internal carboxy attack of anodes has identified several areas where knowledge is lacking or where clarification is required:

- (i) The mechanism of selective binder removal by carboxy attack in anodes is not well understood.
- (ii) The anode pore size range that is reactive to CO₂ has not been clearly established. This size range should be experimentally measured to determine the relative contribution of coarse and fine porosity to internal reaction.
- (iii) Further work is required to resolve the cause of anode dusting.

The objective of the present study was to contribute to the resolution of these points. It was felt that this could be achieved by undertaking a detailed porosimetric investigation of the changes in anode pore size distribution caused by sub-surface carboxy oxidation. This paper presents the results of this investigation.

Anode Butt Samples

A large number of anode butts have been studied in this investigation. Although the magnitude of sub-surface oxidation in these butts varied significantly depending on anode properties, the nature of porosity development associated with internal oxidation in each butt was very similar. This paper will, therefore, cover the work undertaken on a single butt. This butt carbon was also used in a macroscopic study of sub-surface oxidation (12).

Sample Preparation

Two core samples (45mm diameter) were extracted from the butt. One was taken through the electrolytic face at a location away from the edge of the butt. The second core was taken through the butt side, parallel to the electrolytic face, at a site that had not been exposed to air oxidation in the pot.

Each core was carefully cut into 10mm thick slices. These slices were then cut to a size (15mm x 15mm x 10mm) suitable for porosimetry. After washing in water, the samples were dried at 200°C under vacuum for 24 hours prior to porosimetric analysis.

Mercury Porosimetry

Mercury porosimetry is an established technique for measuring the porosity characteristics of solids (28, 29). There are, however, some limitations of the technique with regard to the analysis on anode carbons:

- (i) Porosity present behind a pore neck in the anode structure will be reported at the size of the neck. For this reason it is more correct to report mercury porosimetry data in terms of a pore entrance size (e.g. Pore Entrance Radius, or PER), rather than pore size.
- (ii) Mercury porosimetry is not a sensitive technique for differentiating between the surface texture of coarse pores, and the presence of fine pores in the pore structure (30).
- (iii) Porosimetry data obtained at high mercury pressures, i.e. fine pore size data, can be subject to errors due to the opening of closed porosity by the collapse of the solid under the applied pressure. Farr-Wharton (3) has shown, however, that the opening of closed porosity was not a problem in the porosimetry of anode carbons under conditions similar to those used in this study.

These limitations must be considered when analysing porosimetry data, however, with careful interpretation valid conclusions regarding anode pore structures can be made. Although porosimetry has been used in previous studies of anode internal oxidation (3, 5), the full potential of this technique to provide information on pore development in the sub-surface oxidation zone of anode butts does not appear to have been fully exploited.

In this study, a Micromeritics Autopore 9200 porosimeter was used according to the standard method given in the operating manual (31). Pore volume distribution data was plotted as cumulative pore volume

against Pore Entrance Radius (PER) or as incremental pore volume against PER, where incremental pore volume was defined as:

$$d(V/g)/d \log PER$$

Where V = Pore volume (mm³/g)
 g = Sample mass (g)
 PER = Pore Entrance Radius (μm)

Results

Pore Volume Distribution of Anode Carbon

The incremental and cumulative pore volume distributions of bulk anode carbon (unaffected by internal attack) are shown in figures 1 and 2. These figures show that most of the measured porosity is located in the range 1-5μm PER. This porosity is attributed to the escape of pitch volatiles during anode baking. The location of the peak associated with this porosity (figure 1) is influenced by the size of the finest filler coke particles in the anode (32). The remainder of the anode porosity is distributed across the measured pore size range with a small peak at around 0.009μm, and evidence of increasing porosity at pore sizes greater than that measured (>100μm PER).

Analyses of the pore volume distribution of several core samples from one butt, and from a number of different butts have shown that:

- (i) The measured pore volume distribution of bulk anode carbon is remarkably consistent throughout an anode.
- (ii) The characteristics of the measured pore volume distribution (in the measured pore size range) of bulk carbon from various anodes are similar.

Total Porosity Profiles

The total measured porosity of each slice cut from the core taken through the electrolytic face of the anode butt was plotted against average distance from the anode exterior (figure 3). This figure shows a porosity profile through the sub-surface oxidation zone above the electrolytic face, and quantifies the increase in total measured porosity caused by carbon dioxide gasification. In the zone immediately above the electrolytic face (0-10mm slice), anode porosity is a factor of 1.4 greater than in the bulk anode carbon. This represents a loss of carbon that is equivalent to around 8% of the anode carbon consumed at the electrolytic face. Figure 3 also shows that sub-surface oxidation has penetrated to a distance of around 40mm from the electrolytic face.

Porosity Development in the Sub-Surface Oxidation Zone

To determine the effect of sub-surface on the pore volume distribution of the anode carbon, the porosity distribution within the sub-surface oxidation zone was compared to that of the unaffected bulk anode carbon. The development of reaction generated porosity in each core slice was examined, starting at the unaffected region of the reaction porosity profile and moving toward the electrolytic face.

The incremental pore volume distribution curve for the 40-50mm slice and the unaffected bulk anode carbon are shown in figure 4. As would be expected from figure 3,

the two distributions are very similar. The 40-50mm slice has a small volume of additional porosity in the 1-4μm PER range, a slight loss of very fine porosity (0.003 - 0.007μm PER) and a small porosity increase in the range 0.007 - 0.009μm PER.

The 30-40mm slice would be expected to contain greater reaction porosity development. This is confirmed in figure 5, which shows pore development of greater magnitude, but with the same trend as found in the 40-50mm slice. There is clearly a loss of very fine porosity (<0.009μm PER) and an increase of porosity in an immediately larger size range of 0.01-0.1μm PER.

The pore volume distribution of the 20-30mm slice shows the development of reaction porosity in the range 0.01 - 0.2μm PER (figure 6). When compared to the 30-40mm slice, the reaction porosity peak in the 0.01 - 0.2μm PER is larger and better defined. The pore volume at 2μm PER has also increased slightly compared to the previous slice.

Moving closer to the electrolytic face where sub-surface oxidation is of greater magnitude, sub-micrometre pore development in the 10-20mm slice (figure 7) has increased further and shifted to larger pores. The pore volume in the range 0.03 - 0.9μm PER has increased, with the enlargement of finer pores into this size range resulting in a further loss of porosity smaller than 0.03μm PER.

The 0-10mm slice, which includes the electrolytic face, shows a bimodal pore volume distribution (figure 8) with porosity peaks at 2μm PER and at around 0.3μm PER. This reaction porosity peak is larger and shifted to a coarser pore size than in the 10-20mm slice. The loss of porosity finer than the reaction porosity peak is most apparent in the 0-10mm slice.

The overall characteristics of the reaction porosity development process are shown in figure 9 which superimposes the cumulative pore volume distribution curves for each slice. This figure indicates that pore development at the coarse end of the distribution (i.e. >5μm PER) is not significant. The volatile release porosity at 1-2μm PER is increased slightly by sub-surface oxidation. Most of the reaction porosity is generated by the enlargement of very fine pores in the distribution (i.e. <0.007μm PER). Porosity in this range is lost as the pores are enlarged into the range 0.1-1μm PER. This pore development would appear to cease at around 1μm PER.

These porosimetry results suggest that the measured anode pore volume distribution may be divided into four ranges of interest:

- 0.002-0.01μm PER Reaction porosity development from sub-surface carboxy oxidation originates in pores finer than 0.01μm PER.
- 0.01 - 1μm PER This "active" range contains most of the reaction generated porosity.
- 1 - 5μm PER The original volatile release porosity is affected by internal reaction to a lesser degree than the 0.01 - 1μm PER.
- 5 - 100μm PER Little porosity development.

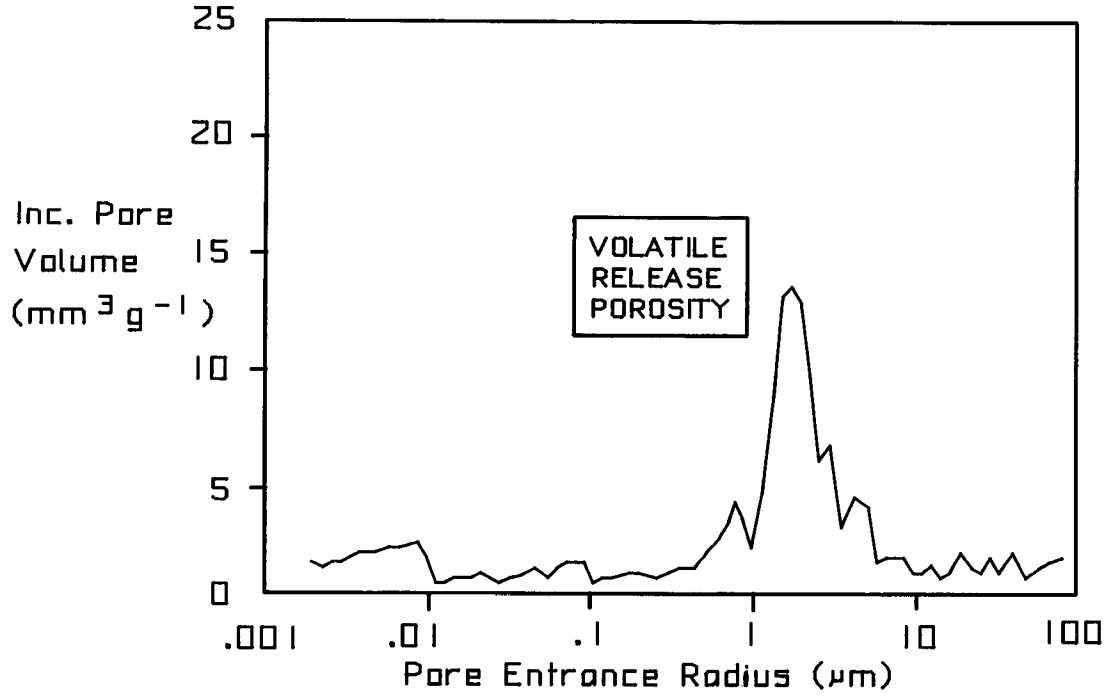


Figure 1: Incremental pore volume distribution of the bulk carbon in an anode butt.

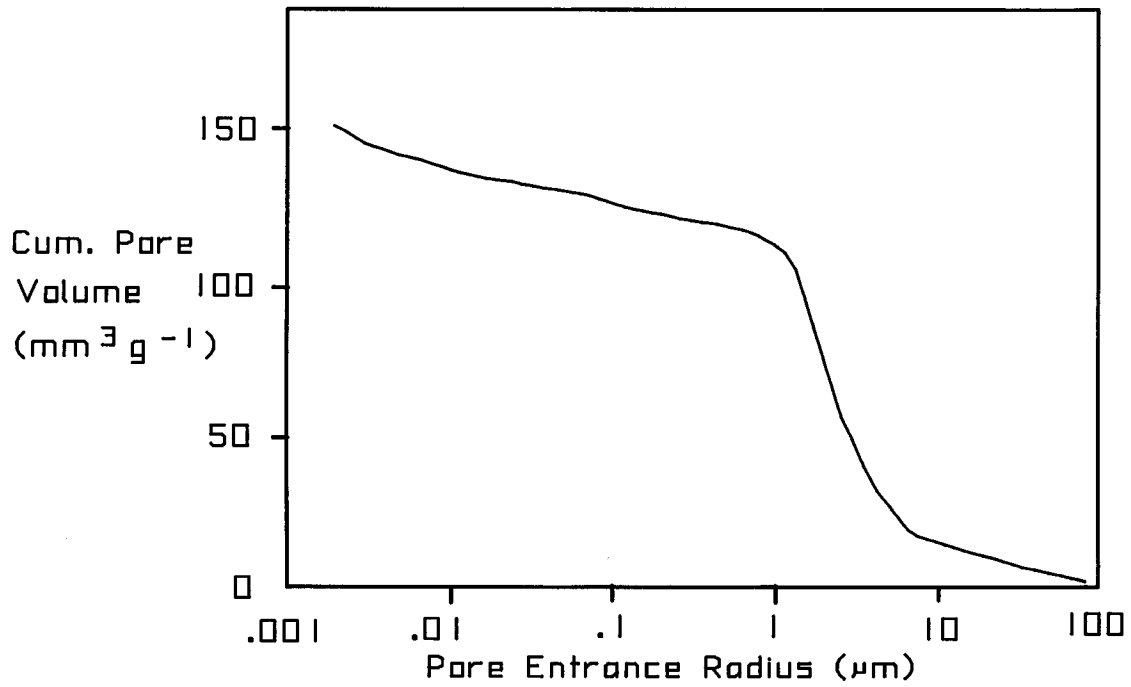


Figure 2: Cumulative pore volume distribution of the bulk carbon in an anode butt.

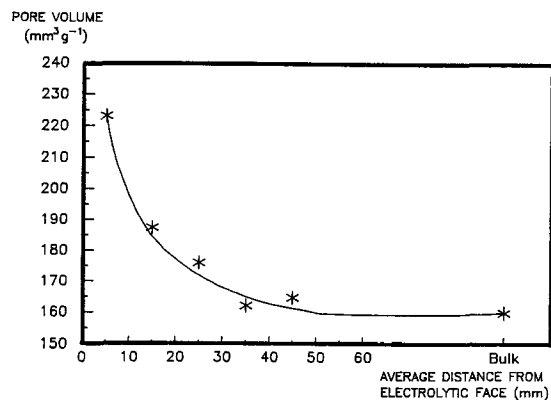


Figure 3: Total measured pore volume profile through the electrolytic face sub-surface oxidation zone of an anode butt.

Porosity development in each of these PER ranges is shown in figure 10, which confirms that 0.01 - 1 μm PER porosity provides the greatest contribution to the reaction generated porosity. This range is, therefore, of prime importance to this study.

Reaction Porosity Development in the Side of Anodes

The core taken through the side of the anode butt was analysed in the same way as the electrolytic face core. The mechanism of reaction porosity development was found to be identical at both locations. Sub-surface oxidation of the anode side was, however, of greater magnitude and penetrated to a greater depth than above the electrolytic face. This is evident in figure 11, which shows the relative increase in porosity in the range 0.01 - 1 μm PER plotted against the distance from the butt surface. Figure 11 indicates that in the zone immediately above the electrolytic face of the anode, the volume of porosity in the 0.01 - 1 μm PER range has increased by a factor of 3 compared to the unaffected bulk anode carbon. Porosity in the same size range in the zone just in from the anode side has increased by a factor of 4.

Reaction Porosity Development in Other Anodes

In all the other anode butts examined in this study, the characteristics of reaction porosity development were virtually identical to those outlined. Anode properties such as permeability, total porosity and baking temperature (up to the filler coke calcination temperature) and pot operating parameters (cell design, current density, etc.) did not influence the way in which reaction porosity developed.

Sub-surface oxidation due to airburn was also found to occur predominantly in the 0.01 - 1 μm PER size range.

Discussion

The results of the porosimetric analysis of anode sub-surface carboxy oxidation may be summarised:

- (i) Sub-surface carboxy oxidation generates porosity profiles above the electrolytic face and in from the side of anode butts.

- (ii) The depth and magnitude of sub-surface carboxy oxidation is greater in the side of anode butts than above the electrolytic face*.

- (iii) Reaction porosity is generated by the enlargement of very fine pores (i.e. <0.007 μm PER) in the anode structure. These pores are lost from the distribution as they are enlarged into the 0.01 - 1 μm PER range.

Anode Dusting

As noted previously, anode dusting is normally confined to the side of anodes. Porosimetry has confirmed the results of an earlier macroscopy study (12), supporting the conclusion that this side dusting is largely due to sub-surface oxidation.

Mechanism of Reaction Porosity Development

The changes in anode pore volume distribution resulting from sub-surface oxidation are consistent with a pore enlargement mechanism whereby the walls of very fine pores are selectively attacked by sub-surface carboxy oxidation. The size and volume of the affected pores are increased, i.e. the fine porosity becomes coarser, the corresponding pore volume increases and a porosity deficit is left in the very small pore size range.

Porosity development in fine porosity (i.e. <0.01 μm PER) was not expected, however, given the two prerequisites of internal reaction: mass transport and surface area. These considerations suggest that reaction would not be significant in such fine porosity due to mass transport limitations. The flow rate of CO_2 and CO gases in these pores would be via Knudsen diffusion. This would be too slow to sustain a significant reaction rate if the surface area and mass transport necessary for internal reaction were required in the same pores. This is the basis of the "tree" pore structure model.

Tree pore structures (figure 12) contain large feeder pores than can transport CO_2 by viscous flow. These pores branch out into increasingly smaller pores, eventually becoming the fine porosity that contribute the bulk of the surface area in anodes. According to this model, the transport of CO_2 to the surface area required for reaction is along a relatively long and tortuous path through increasingly finer pores. The most reactive pore size in a tree pore structure will be the intermediate range where pores are large enough to provide sufficient CO_2 flow rates, and yet small enough to provide the specific surface area required for reaction.

The tree pore model is clearly not consistent with the results of this study on anode carbon. This model may be adequate to describe porosity in carbons such as filler cokes and the intermediate reactive pore size range may be applicable to sub-surface oxidation in these carbons. The tree pore model does not, however, appear to describe the pore structure of anode carbons.

*This greater attack of the anode side is due to the limit imposed on porosity development above the electrolytic face by the retreat of this face resulting from electrochemical attack (12).

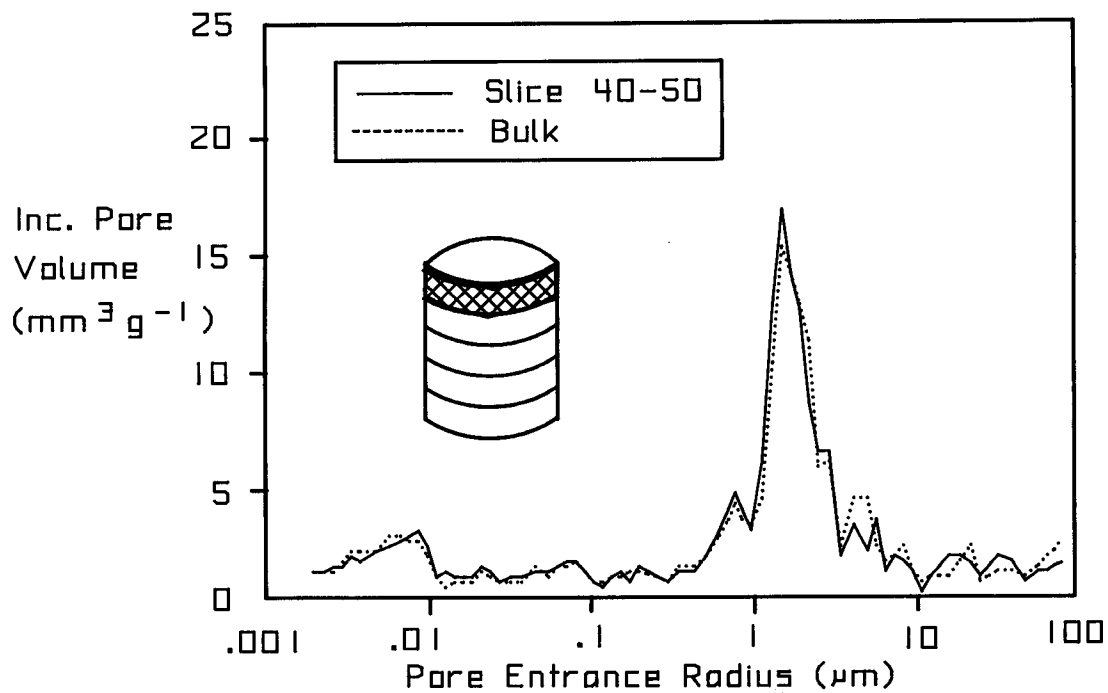


Figure 4: Incremental pore volume distribution, 40-50mm above the electrolytic face of an anode butt. (Bulk anode carbon shown for comparison)

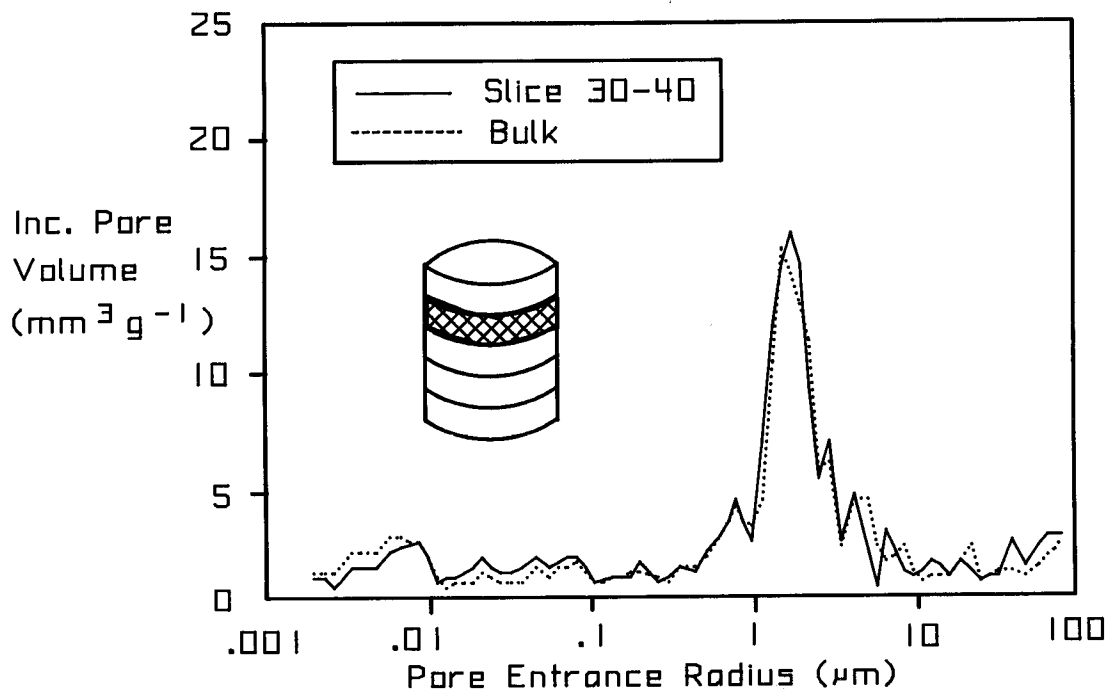


Figure 5: Incremental pore volume distribution, 30-40mm above the electrolytic face of an anode butt.

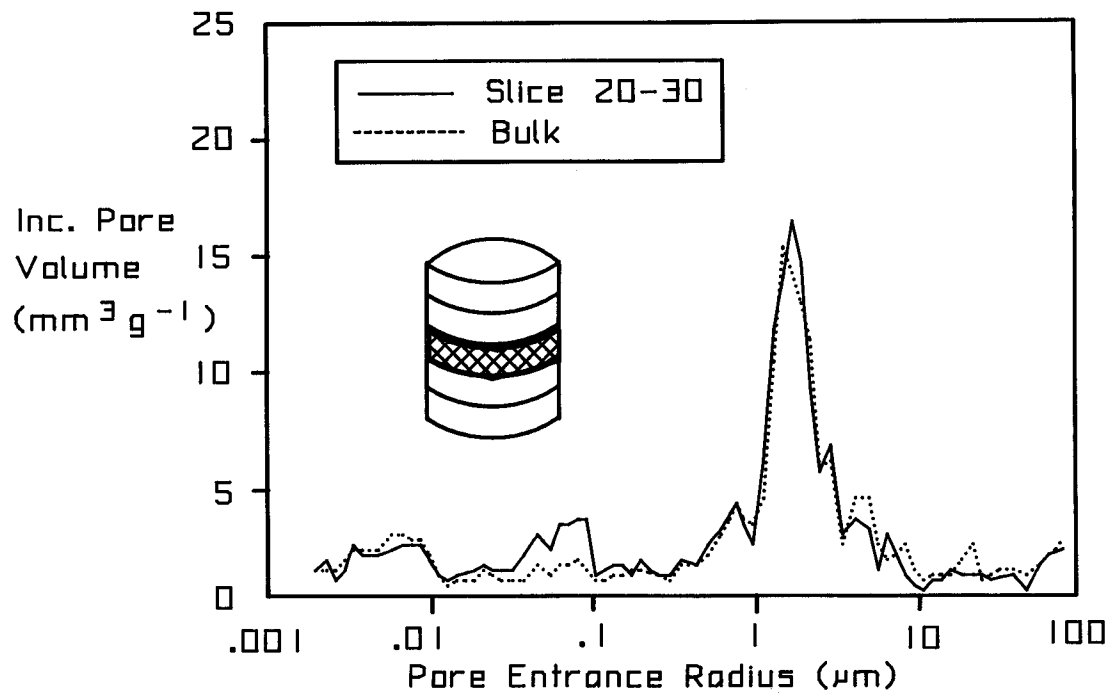


Figure 6: Incremental pore volume distribution, 20-30mm above the electrolytic face of an anode butt.

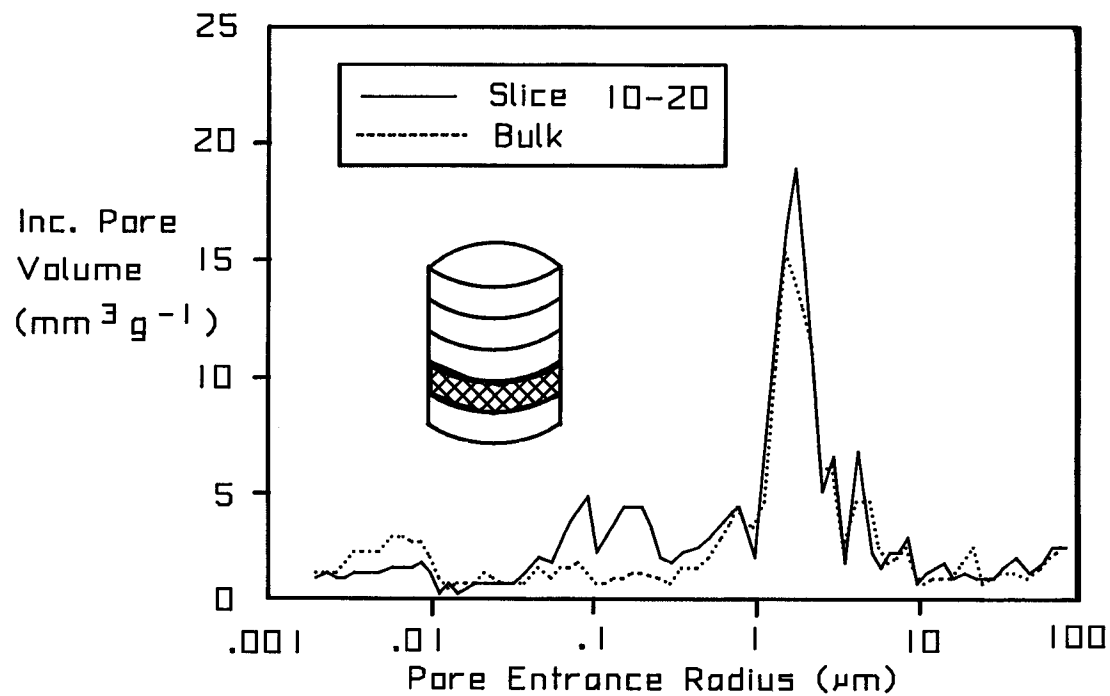


Figure 7: Incremental pore volume distribution, 10-20mm above the electrolytic face of an anode butt.

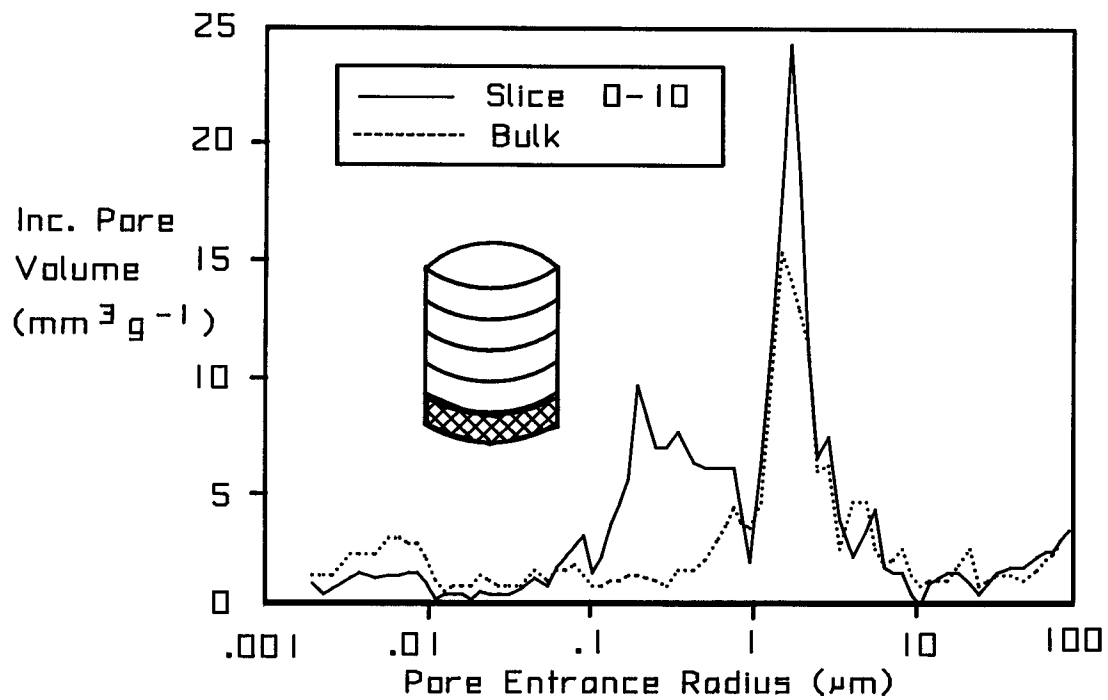


Figure 8: Incremental pore volume distribution, 0-10mm above the electrolytic face of an anode butt.

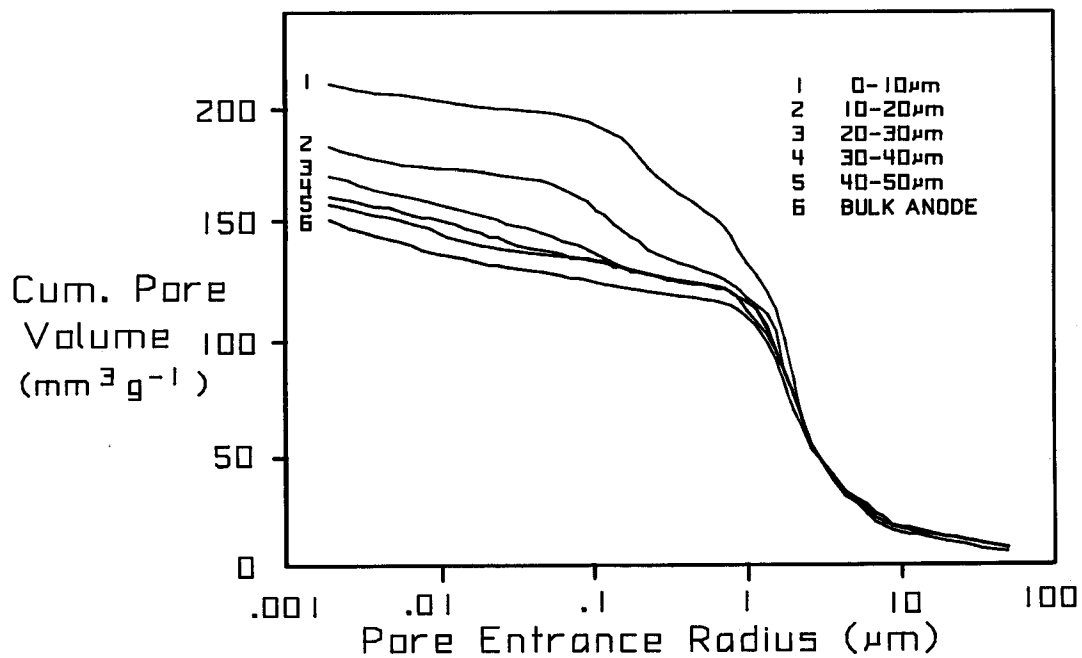


Figure 9: Cumulative pore volume distributions showing reaction porosity development above the electrolytic face of an anode butt.

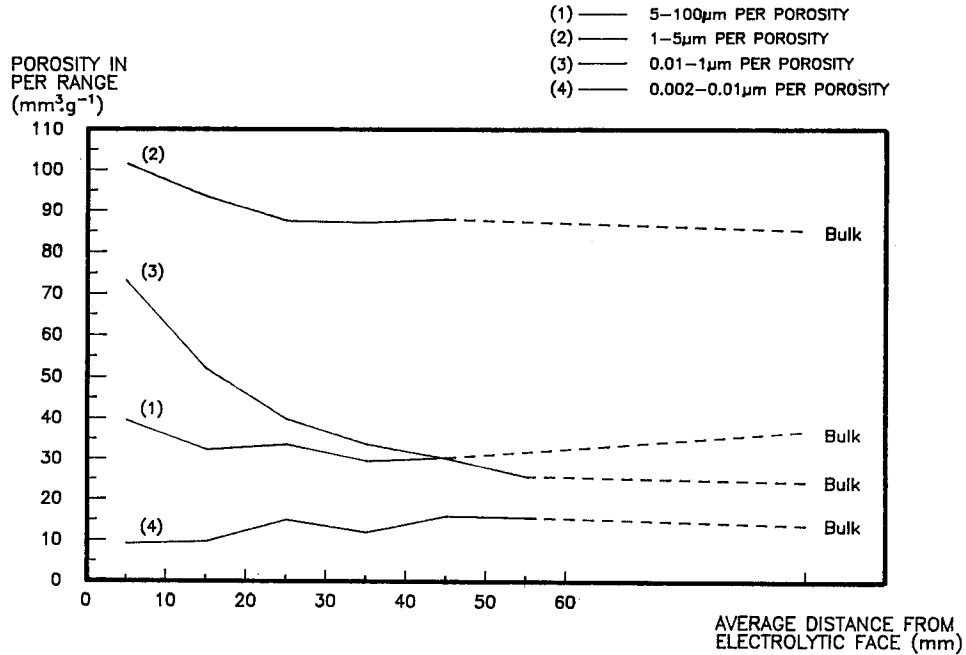


Figure 10: Porosity development profiles within particular PER ranges of an anode butt.

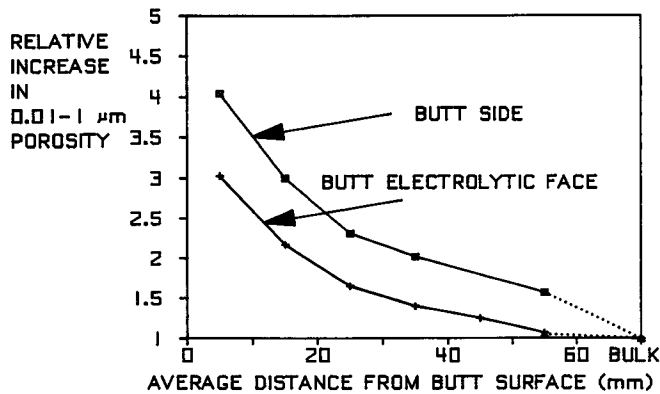


Figure 11: Reaction porosity development in the side and above the electrolytic face of an anode butt.

Consideration of the processes involved in anode production has led to the formulation of an alternative anode pore structure model.

Anode Pore Structure Model

Volatile release porosity has been identified in the anode pore volume distribution. This porosity forms within the binder/fines matrix between coke particles and is lined with binder carbon. An alternative way of viewing this pore structure would be a frame-work of coke particles coated with a film of binder with volatile release pores located in the interstices between the coke particles (figure 13). The binder film surrounding coke particles will contain fine pores

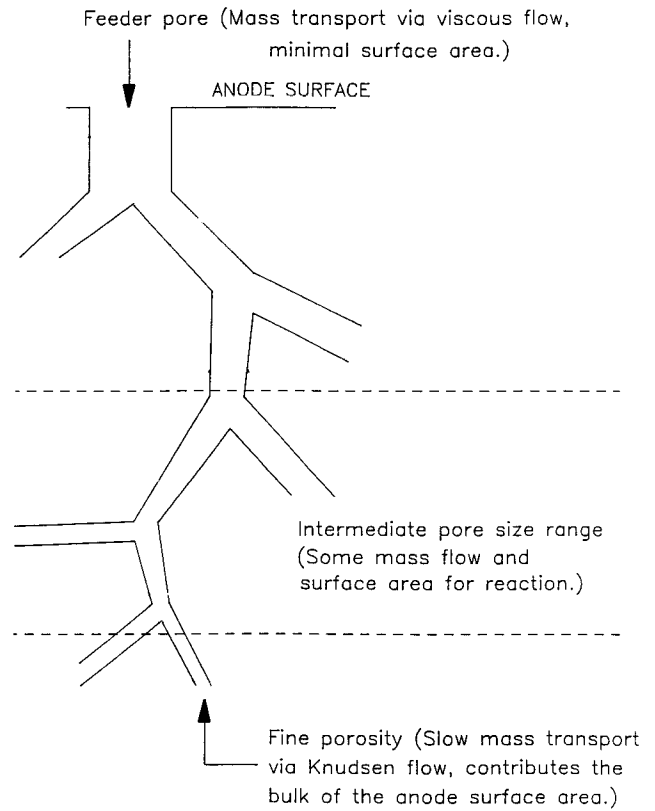


Figure 12: Tree model of anode pore structure.

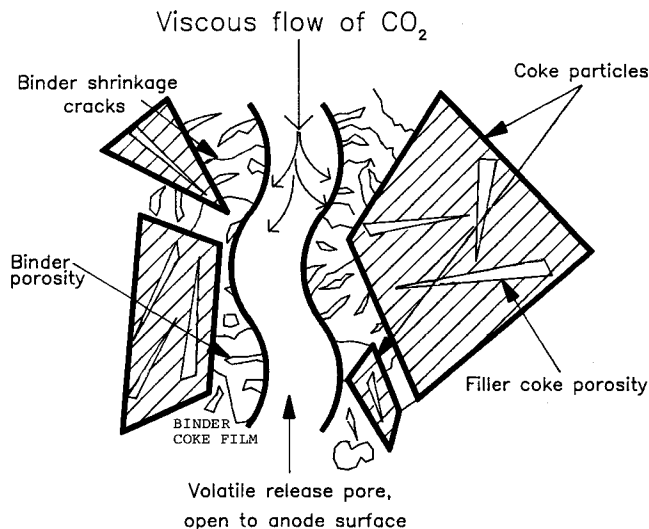


Figure 13: Model anode pore structure

(33) and microcracks (5, 34-36) that result from the shrinkage of binder around filler particles as they expand during anode baking. These microcracks and pores in the binder will be a major source of active surface area for reaction with CO_2 (5, 8).

This pore structure model (figure 13) has large feeder pores, that can provide relatively rapid mass transport rates, connected directly to microcracks and pores that provide active surface area for reaction. To reach the active surface area from the feeder pores, the CO_2 need only travel a short distance that is limited to the thickness of the binder coke film. This may be calculated to be of the order of $1\mu\text{m}$. The provision of active surface area by the surface texture of volatile release pores largely avoids the mass transport limitations normally associated with fine porosity. The pore growth and enlargement mechanism of reaction porosity development observed in this study is consistent with this model.

Binder shrinkage microcracks will be enlarged by sub-surface oxidation. As the surfaces of these cracks are gasified they increase in size and volume as identified by porosimetry. Eventually, carboxy attack may gasify all of the binder carbon lining a pore wall. This may correspond to the observed increase in volume of large pores in the 0 - 10mm slice.

Microcracks in binder coke have been associated with anode reactivity previously, however, this connection has been in general terms. The present study and the proposed model clarify this association by defining the role of binder microcracking in reaction porosity development, and quantifying the volume and size range of the pores involved.

Practical Implications of Model

The proposed model may be used to identify ways of reducing sub-surface oxidation in anodes. Any such reduction will directly reduce anode consumption rates and may also reduce anode dusting.

The model confirms that reducing anode permeability by decreasing the size and volume of the volatile release porosity will reduce sub-surface oxidation by lowering the rate of gas flow to the active surface area. The current technology used to fabricate anodes will, however, invariably result in a network of open, interconnected pores. Possible ways of reducing this porosity, and hence anode permeability, are: the use of slower heating rates during baking to reduce the rate of volatile release, a change in the size of the finest coke particles in the aggregate, by maximising the packing of the pitch wetted aggregate, optimisation of the pitch level, or by increasing the coking value of the binder pitch.

Reducing the surface area of the binder film is an alternative way of reducing sub-surface oxidation. Binder coke porosity, particularly shrinkage cracks, is central to the mechanism of internal attack. There are several possibilities for reducing this porosity, and hence anode active surface area. Binder shrinkage cracks could possibly be reduced by the selective addition of partially calcined filler coke to the aggregate. This coke will shrink with the binder during baking and lessen the shrinkage/expansion process that produces the microcracks. There is also some evidence that a lower porosity binder carbon may be achieved with the use of additives to the pitch. Heavier (i.e. higher softening point) binder pitches are being used (37, 38). These pitches have higher coking values and will shrink less during baking. This should reduce shrinkage cracking, and possibly the size of volatile release pores. Modifications to existing anode production equipment are required to use these pitches.

Summary/Conclusions

Around 8% of the carbon consumed at the electrolytic face of an anode was removed by sub-surface carboxy oxidation. The porosity resulting from this internal attack developed via a pore growth and enlargement mechanism and produced a reaction porosity profile within the anode. At the limit of CO_2 penetration, sub-surface oxidation starts by enlarging fine porosity ($<0.01\mu\text{m PER}$). The size and volume of the pores attacked by internal reaction progressively increase closer to the anode surface. This pore development occurs predominantly in an active pore size range of 0.01 - $1\mu\text{m PER}$.

Porosity development in the sub-micrometre size range was not predicted from theoretical considerations or from the published literature on sub-surface oxidation. Carboxy sub-surface oxidation in anodes requires the combination of sufficient surface area for reaction and adequate gaseous mass transport rates. The fine porosity in anodes determines the surface area, whereas coarse porosity largely controls mass transport within the anode. Assuming a "tree" model of anode porosity, in which large pores branch into successively finer pores, the most reactive porosity would be expected to be in the intermediate range (e.g. 0.25 - $10\mu\text{m PER}$). In this range mass transport and surface area could be significant. If the tree model is applicable to anode carbons, pores larger and smaller than this range would not make a significant contribution to anode internal reaction due to surface area and mass flow constraints respectively. The results of this study indicate that the tree model does not describe the pore structure of anode carbons and that the intermediate reactive porosity range is not applicable to anode sub-surface carboxy oxidation.

An alternative anode pore structure model was formulated. This model is centred on the large pores generated during anode baking by the escape of pitch volatiles. These pores can provide relatively high rates of mass flow and are lined with binder coke. This lining contains shrinkage cracks and other porosity that provides the surface area for reaction. The two factors required for sub-surface oxidation are, therefore, present with the surface area for reaction in the binder coke accessible to the CO₂ permeating through the coarse pores. The subsequent carboxy attack of the binder coke generates the 0.01 - 1µm PER porosity identified in the anode butt.

This model suggests that sub-surface oxidation can be reduced by minimising coarse or fine porosity in the anode structure.

Sub-surface carboxy oxidation is invariably greater in the side of anode butts than above the electrolytic face and contributes to the generation of anode dust from this surface.

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