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CHARACTERIZATION OF CARBON CATHODE MATERIALS BY X-RAY MICROTOMOGRAPHY

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Abstract

The carbon cathode is considered as the main component of the aluminum reduction cell. It provides the electrical contact that is essential for electrolysis as a result of holding molten electrolytic bath together with aluminum. Hence, its performance is crucial in electrolysis process. X-ray microtomography was used to compare different virgin cathode materials, as well as those that had been used in laboratory-scale aluminum reduction cells. Results demonstrated significant differences in terms of bath penetration and metallic inclusions. X-ray microtomography was shown to be a powerful tool for 3-D characterization of cathode materials.

Introduction

Cathode materials are in constant improvement [1]. Their performances are one of the most important economic issues. Consequently, research on improving the cathode performance is of great interest. Erosion, chemical stability, bath percolation resistance and electrical conductivity are some examples of research subjects.

The goal of this article is to study X-ray microtomography procedure to characterize carbon cathodes. It is indeed a non destructive method to obtain 3D images of cathode samples followed by quantitative data on bath penetration and heavy metals inclusion [2,3].

The result of the porosity calculation is shown to be within the same expected range as known data. Close relationship between bath penetration and porosity is also demonstrated. A quick analysis was also carried out to investigate bath penetration front.

Methodology

Samples for analysis were taken from virgin and used rectangular cathodes. Parameters for electrolysis, samples preparation and analysis will be described in the following section.

Electrolysis parameters

Analyzed samples were taken from two different cathode materials after four different electrolysis experiments as shown in Table I and Table II.

Table I. Electrolysis experiments variables.

Experiment	Cathode material	Bath cryolite ratio
1	A	2.2
2	B	2.2
3	A	5
4	B	5

Table II. Electrolysis general settings.

Electrolysis temperature	960°C
Current density	0.9 A/cm^2
Electrolysis time	12 h*
Atmosphere	Nitrogen

* Technical issues with cathode B shortened electrolysis time to 9-10h.

Electrolysis experiments were carried out in the experimental setup shown in Figure 1.

Figure 1. Electrolysis experimental setup with (1) oven and fume hood, (2) data acquisition and (3) power supply.

Samples preparation

To extract samples from used cathodes, a first cut was done 5 mm over cathode surface. The bottom part was then cut to obtain a full vertical 12.5 mm slice and a 12.5 mm square sample as shown in Figure 2 and Figure 3.

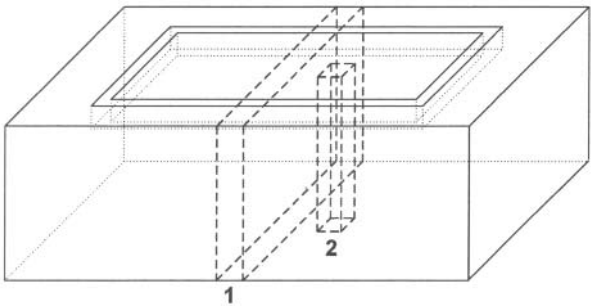

Figure 2. Lower part of cathode with (1) slice for quick measurement of bath penetration front and (2) sample for complete acquisition.

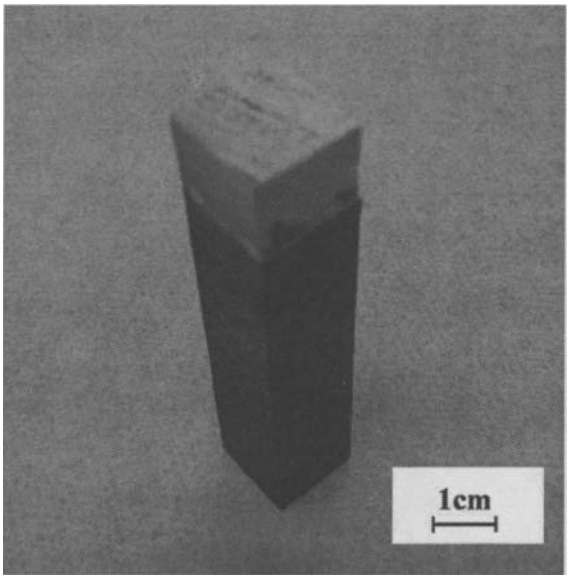

Figure 3. Sample from carbon cathode.

Acquisition parameters

In order to obtain best results in terms of contrast between phases [4], X-ray microtomography was performed with a Skyscan 1172 with parameters shown in Table III.

Table III. X-ray microtomography acquisition parameters.

Voltage	50 kV
Amperage	200 µA
Filter	0.5 mm Al
Exposure time	590 ms
Rotation step	0.4°
Number of scans per step	10
Scanned angle	180°

Images reconstruction

Image reconstruction was performed using Skyscan software NRecon. General parameters used in this study are shown as follow. A few thousand cross section pictures were obtained and used for phase segmentation and quantification.

Table IV. Parameters for image reconstruction.

Min. dynamic range	0
Max. dynamic range	0.18
Ring artifact correction	6
Beam hardening correction	40 %

Phases segmentation

Details on phase segmentation and image treatment, which mainly consist of establishing threshold values for each phase followed by removing of small objects in order to reduce noise and partial volume effect, have already been described elsewhere [4]. Table V gives employed threshold values to separate each phase.

Table V. Grayscale thresholds for phase segmentation.

Phase name	Threshold min. value	Threshold max. value
Porosity	0	9
Carbon	10	42
Bath	43	105
Bath crystals	106	150
Heavy metal[1]	151	255

1: heavy metals refers to metals that have higher atomic number than aluminum.

Results

Quick determination of bath penetration front

To acquire a good picture of bath penetration, the vertical slice from the cathode was cut to four equivalent parts. Cutting was necessary to insert samples into the sample chamber. An example of bath penetration front in cathode A is illustrated in Figure 4. Electrolysis parameters used for this experiment are the same as experiment 1, except for electrolysis time that was 14 h instead of 12 h.

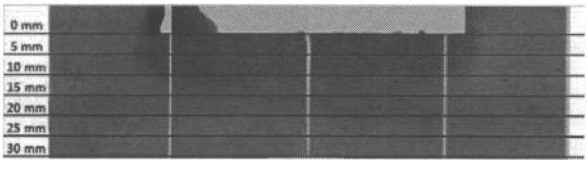

Figure 4. Bath penetration front.

The penetrated depth was measured to about 15 mm. The penetrated bath was easily observed due to high contrast. However, there is no contrast associated with sodium. Its concentration appears to be too low to be measured by this method.

The picture shown in Figure 4 is actually a fusion of four images acquired separately. These images were taken from print screens

of crude scans used to choose acquisition areas in Skyscan acquisition software. Image extraction and reconstruction with picture edition software was required to obtain such result.

Phase quantification of virgin cathode materials

Virgin cathode materials were analyzed to precisely study the phase quantification according to the defined thresholds. Results are presented in Table VI.

Table VI. Characteristics of virgin cathode material.

	Cathode material			
	A		B	
	m[1]	sd[2]	m	sd
Porosity	25.7	0.7	23	1
Bath	0.27	0.07	2.5	0.3
Bath crystals	0.02	0.01	0.06	0.02
Heavy metals	0.02	0.01	0.01	0.01

1: mean volume %; 2: standard deviation.

Porosity may have important implication on cathode behavior [5,6]. However, its amount is not typically measured by microtomography [7]. Nevertheless, data obtained by this method are in line, within a 2 % range, with those given by the cathode provider. Small discrepancies can be explained by the fact that small pores (smaller than 100 voxels, 100 000 μm^3) are not taken into account in the present calculation.

As shown in Table VI, mean volume % associated to bath in sample B is abnormally high for a virgin material without any contact with bath. This implies that an overestimation of about 2% in bath quantification is expected. In this cathode material, an unknown phase was observed with an X-ray linear attenuation coefficient higher than that of carbon. In addition, cathode B material cutting released sulfur-like smell. However, elemental analysis carried out by EDS-MEB and by Leco did not identify a significant difference for sulfur concentration between the two materials. Figure 5 compares a binary image of the bath associated phase for cathode B in virgin and after bath impregnation process.

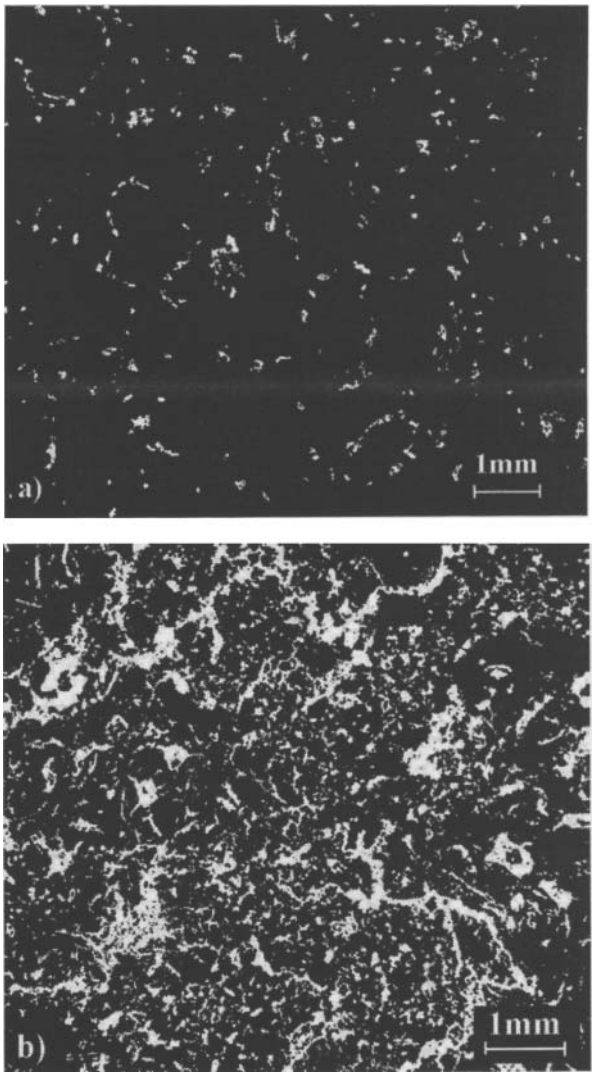

Figure 5. Binary images of cathode B in (a) virgin and (b) bath impregnated conditions. White areas are related to bath according to determined thresholds from Table V.

Phase quantification of used cathode materials

For each experiment, a square sample was analyzed using parameters described in the previous section. Results of the phase quantification, shown in Figure 6, clearly indicate that cathode B is noticeably prone to bath penetration compared to cathode A.

Bath reaches a depth of 25 mm from the surface of the cathode B which is about twice deeper than the cathode A even though the electrolysis time is about 25 % shorter. For the cathode A, concentration drops under 1 % at a depth of 13 mm, which is in line with bath front shown in Figure 4. Furthermore, the bath-free porosity in the first 10mm from the sample surface is significantly lower in cathode B, implying a significant presence of open porosities in this material. In addition, results show that the bath volume % drops as the porosity rises at nearly the same rate. That

clearly demonstrates that electrolytic bath follows porosity network to penetrate carbon matrix.

It is also observed that the bath acidity has no significant influence on bath penetration based on the cryolite ratio range of the studied baths. For each cathode material, the bath reached approximately the same depth.

Table VI indicates similar mean volume % of heavy metals inclusion associated with both virgin materials. However, graphical trends from Figure 6 show significant differences. Contrary to cathode B, concentration peaks are clearly observed for cathodes A. Figure 7 shows presence of a 400 µm heavy metal inclusion in cathode A. This inclusion size is commonly observed in material A, contrarily to material B which shows much smaller but more evenly distributed inclusions.

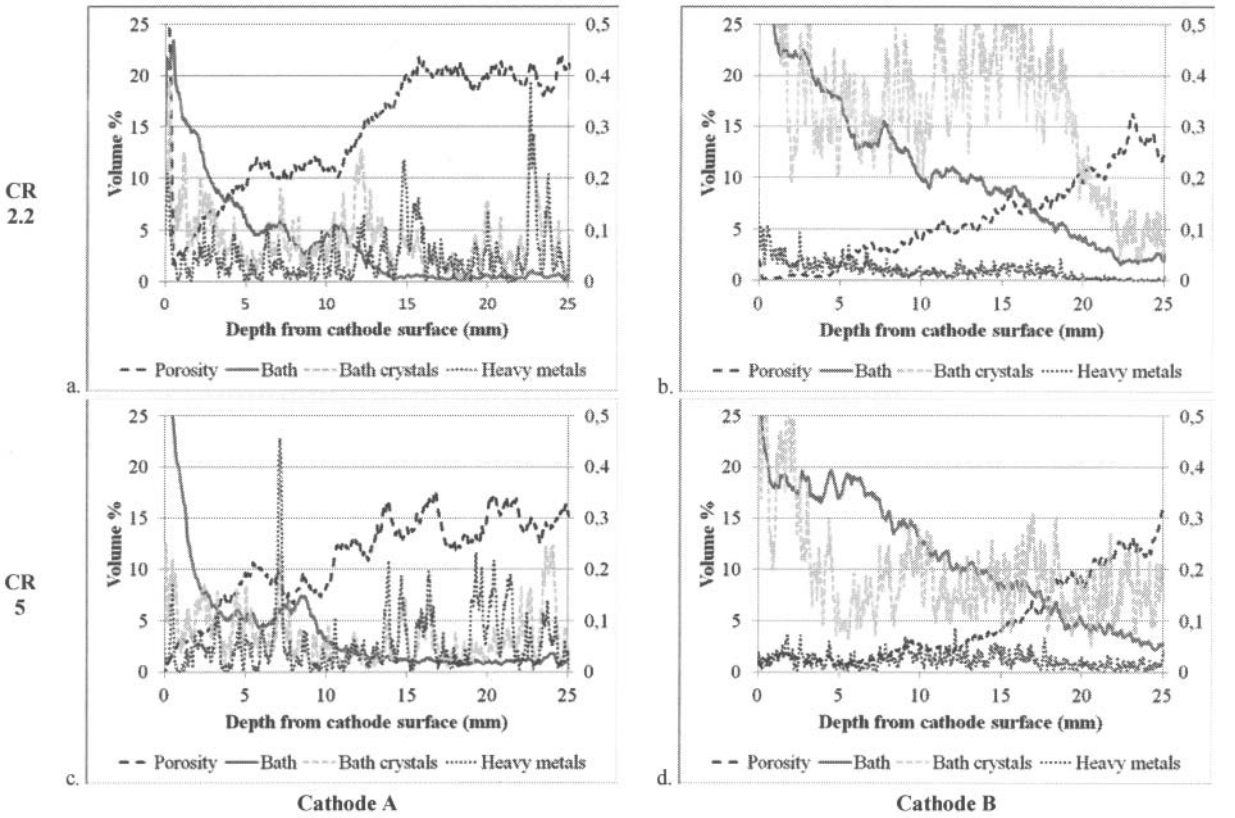

Figure 6. Phase quantification of (a) experiment 1, (b) experiment 2, (c) experiment 3 and (d) experiment 4. Left scale refers to porosity and bath. Right scale refers to bath crystals and heavy metals.

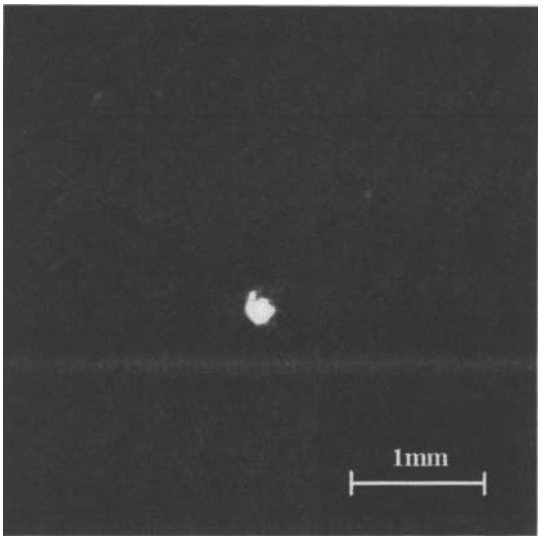

Figure 7. Example of a heavy metal inclusion (bright spot) in cathode material A.

Phase related to bath crystals is more represented in cathodes B than in cathodes A. The reason of a significant presence of that particular phase in cathode B is still unclear. It can be possibly related to the higher concentration of calcium cryolite in pores of cathode B. Further analysis is required to explain the mechanism of this phenomenon.

Conclusion

A quick X-ray micro tomography scan of cathode materials used in electrolysis experiments showed the position of penetrated bath. However, the position of sodium penetration was not visible. Values of quantification of porosity on virgin materials are in line, within 2 % range, with data indicated from cathode provider. Small discrepancies are probably due to smaller porosity that is not taken in account in this study. Phase quantification carried out on four electrolysis experiments demonstrated significant differences in bath penetration related to cathode material. On the other hand, no significant difference was observed in bath penetration with different cryolite ratio. Future is promising for applications of X-ray microtomography as a qualitative and quantitative method in aluminum electrolysis field.

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