Ageing of Carbon Materials during Electrolysis, Experience from Operation and Laboratory Tests

Eirik Hagen[1]and Hanne Keseler[2]
1. Program Manager Waste to Value
2. Product Manager High Performance Anodes
Hydro Aluminium, Porsgrunn/Årdal, Norway
Corresponding author: eirik.hagen@hydro.com

Abstract

Carbon materials (C-materials) are important lining materials in aluminium electrolysis. They undergo significant changes during operation that might affect the stability and the performance of the cell. In this paper, we describe the development of an aging test in lab scale for C-materials simulating operational conditions during aluminium electrolysis. We further present the behaviour of different materials during the test compared with real life experience. Possible ageing mechanisms are discussed in light of experimental findings and characterization methods.

Keywords: Aluminium electrolysis, Carbon materials, Lining material, Testing.

1. Introduction

Carbon materials constitute important parts of the lining in an aluminium electrolysis cell. Carbon is normally used in the cathode blocks, the rammed joints and in the sidewall as pre-shaped blocks [1]. There are different properties desired for the different usages in the lining. The cathode blocks should have low electrical resistance and high wear resistance. In the most productive lines, only graphitized materials are used as cathode blocks. Between and around the cathode block, ramming paste is used. The ramming paste consists of mainly calcined anthracite with a carbonaceous binder, either pitch- or sugar-based types. The primary purpose of the ramming paste is to seal the area around the cathode blocks to prevent bath and/or metal to leak into the lining.

The ramming paste can also be used in the sidewalls of a cell. The thermal conductivity of the sidewall material is an important property in designing the thermal balance of the cell. Instead of using ramming paste in the sidewalls, many smelters are using pre-baked side blocks. This simplifies the installation and provide a more erosion resistant material. The pre-baked side blocks are normally made of calcined anthracite with addition of 0-30 % graphite. The amount of graphite and the calcination degree of the anthracite determine the final thermal conductivity of the side block. In general, the thermal conductivity of a pre-baked side block is higher than that of a corresponding baked ramming paste.

In designing low energy cells, a low thermal conductivity material in the sidewall is desired. However, the exposure to the electrolysis conditions in a cell is known to change the properties of carbon material [1]. The present paper shows that the change in properties can be rapid and significant. Thus, a lab test with the aim of being able to screen carbon materials with respect to their aging properties has been developed.

2. Ageing of Carbon Materials in Industrial Cells

2.1 Sampling/Characterization

Larger samples or chunks of ramming paste, side- and cathode blocks were taken out during autopsies of shut-down cells of different ages, see Figure 1 for the location of the different materials in the cell. Smaller samples for analysis were then core-drilled from the large samples in dry condition. The main ageing property of interest in this work is the thermal conductivity. The thermal conductivity is measured at room temperature by the hot disk method [2]. Electrical resistivity is also measured at room temperature according to ISO method 11713:2000.

Samples of virgin materials were core-drilled out of regular deliveries to the plants and analysed in the same way as used materials.

The lattice parameters of the carbon structure as determined by XRD based on ISO 20203:2005, were analysed for selected samples.

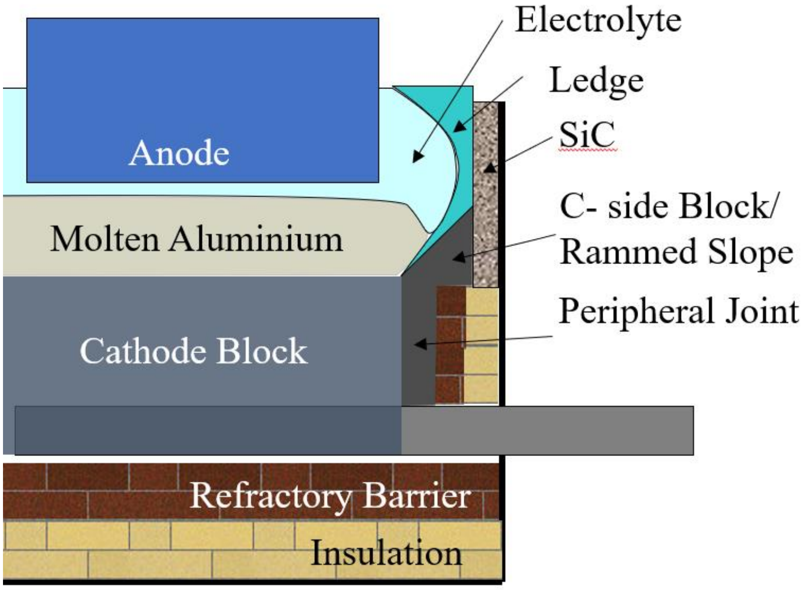

Figure 1. Sketch of one half of a cross-section of a Hall-Hérault electrolysis cell showing the location of the different materials.

2.2 Ramming Paste

Measured values of thermal conductivities of ramming paste in virgin and used conditions are shown in Table 1. Table 1 further gives the position in the cell where the paste is taken from as well as the binder type in the ramming paste. All pastes are based on anthracite as the aggregate phase. Several samples taken from the same pot, and the range of values are given in this table. The thermal conductivities of all the samples taken from only the narrow joints (between the long side of the blocks) are shown in Figure 2. Virgin baked samples of ramming paste were prepared according to ISO 20202:2004, rammed with 50 strokes.

The thermal conductivities of baked virgin ramming paste are in the range 4-7 W/mK. In operation, the thermal conductivity values increase several times and values above 50 W/mK are seen. Even after a few days in operation an increase is seen. The variation within a cell is also large. The narrow joints seem to have the largest increase, and the rammed slope and peripheral joint have normally lower thermal conductivity values than the narrow joints.

It is not possible to differentiate between the different pastes. Given the fact that anthracite is the main component in the ramming paste, it seems that the nature of the binder does not influence the aging of the ramming paste.

Table 1. Thermal conductivity of different ramming pastes, new and from different positions in the cell.

			Thermal Conductivity [W/mK]			
Grade	Binder	Cell life [days]	New	Narrow joint	Peripheral joint	Slope
RP-A	PAH-free	0	4.4			
RP-A	PAH-free	2154		27	21-26	
RP-B	PAH-free	0	6.5			
RP-B	PAH-free	3		5-13		
RP-C	Resin	0	6.3			
RP-C	Resin	1019		38-40		
RP-C	Resin	1462		44		
RP-C	Resin	1580			30-51	
RP-C	Resin	1837		29-45		
RP-D	Pitch	0	5.4			
RP-D	Pitch	3		6.8-9.7	15-33	
RP-D	Pitch	366		22-42		
RP-D	Pitch	611			8-16	
RP-D	Pitch	1066		15-28		
RP-D	Pitch	1721			35	26
RP-D	Pitch	1861		33.5	11-14	
RP-E	Pitch	0	7			
RP-E	Pitch	2019		34-44		
RP-E	Pitch	2085			13-48	
RP-E	Pitch	2528			10-37	
RP-E	Pitch	3024		33		
RP-F	Pitch	0	6.5			
RP-F	Pitch	1426		35-45		10.1-10.5
RP-F	Pitch	2164		40		4.1

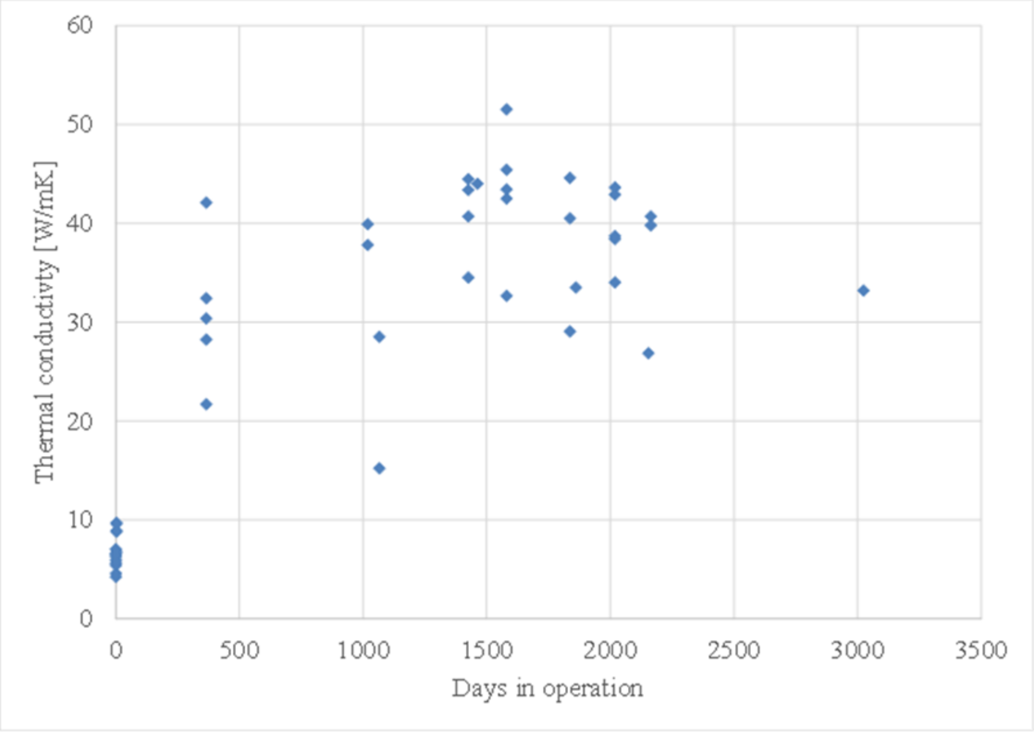

Figure 2. Thermal conductivity of all samples from narrow joints in Table 1. Data at 0 days are average virgin values.

2.3 Carbon Side Blocks

Data from four different side block grades were collected and are shown in Figure 3. The grades are from different commercial suppliers and vary in their graphite content. SB-A and SB-B contain 0 % graphite, SB-C contains 15 % graphite, and SB-D contains 30 % graphite. The thermal conductivity of the virgin materials ranges from 8 W/mK with 0 % graphite and up to 14 W/mK with 30 % graphite.

As with the ramming paste, the variation in values for different samples in the same cell is large. Values above 50 W/mK are seen in a cell of approximately 400 days in operation. The data set is somewhat limited, but it seems that grades with more graphite have a lower increase in thermal conductivity during operation. The large variation in values points to that the conditions in a cell probably influence the increase in thermal conductivity as well as the position where the samples are taken from.

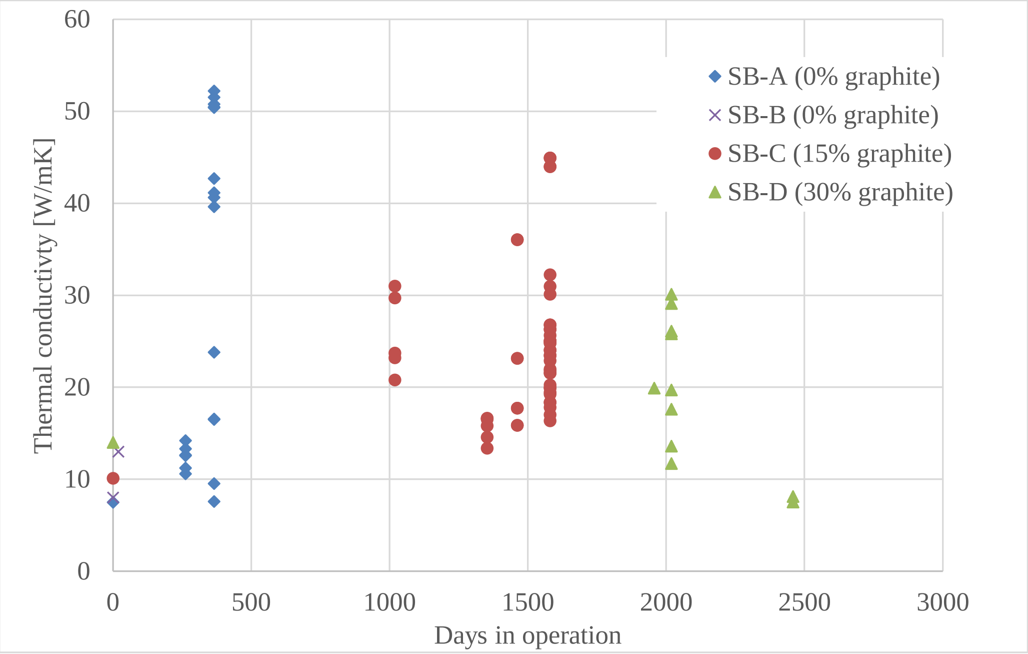

Figure 3. Thermal conductivity of side block samples from cells at different ages. Data at 0 days are average virgin values.

2.4 Cathode Blocks

Measured thermal conductivity values for two different cathode block types are shown in Table 2, one graphitic block (100 % graphite) and one graphitized block. As expected [1], the graphitized grade has the highest thermal conductivity, but the graphitic block has the highest increase in thermal conductivity in use. The thermal conductivity of the graphitized grade did show a small increase after operation, however more data is needed to say if the increase is significant.

Table 2. Thermal conductivity of new and used cathode block types. Data at 0 days are virgin values.

Grade	Block type	Cell life [days]	Thermal Conductivity [W/mK]
CB-A	Graphitic	0	44
CB-A	Graphitic	460	75
CB-B	Graphitized	0	110
CB-B	Graphitized	856	130

3. Lab Test for Ageing of Carbon Materials

3.1 Experimental Set-up

The experimental set-up for the ageing test was based on the standard method for Na-swelling of carbon materials [ISO 15379:2004]. A sketch of the set-up is shown in Figure 4. A graphite crucible contains the bath and serves as the electrochemical anode during the test. The test-sample is the cathode, and the bath composition is basic (CR 4) to ensure a high Na activity during the test even though the current density is lower than for an ordinary Hall-Héroult cell. The experiments were carried out at different durations, see test parameters summarized in Table 3.

Table 3. Test parameters in the ageing test.

Parameter	Value
Current [A]	64.4*
Current density [A/cm^2]	0.4
Cryolite ratio	4
Temperature [˚C]	980
Time [h]	1, 6, 24

* Only for the specimen dimensions shown in Figure 3.

3.2 Materials

The materials used in the lab tests were basically the same as in the industrial tests, however materials with low thermal conductivity were prioritized in early phase. Samples from side blocks were core drilled from regular blocks. In addition to the grades mentioned in Table 1 and Figure 3, a new grade side block material, SB-E with 15 % graphite, was used in the tests. However, for the SB-E grade, there was large variation in measured thermal conductivity among the samples. The results for SB-E were therefore omitted in the results from the industrial test, as there was too high uncertainty of the initial value. Two different samples of the SB-E grade were used in the lab tests, SB-E H and SB-E L with respectively high and low virgin thermal conductivity. Samples from ramming paste were compacted with 50 strokes and baked according to ISO 20202:2004.

3.3 Analysis Methods

Thermal conductivity and electrical resistivity of the samples were measured similarly as for the industrial samples. Some samples were analysed by X-ray tomography before and after the test to investigate eventual microstructural changes.

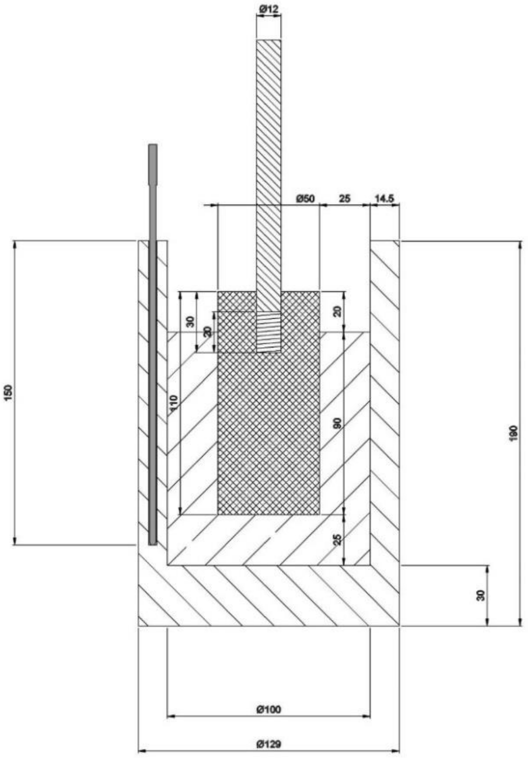

Figure 4. Schematic drawing of the test set-up. Dimensions are in mm.

3.4 Results

The thermal conductivity and the electrical resistivity of samples exposed for different durations, are shown in Figure 5 and Figure 6, respectively. The value in the figures is an average of 2 repetitions. The thermal conductivity is generally increasing with increasing exposure time. Two samples have a dip in value after one-hour of exposure, and two samples have a dip in the range of 6 to 24 h of exposure. The ramming paste, starting out with the lowest virgin values, has an increase of 80 % to 200 % in thermal conductivity after only 6 hours of exposure. The side blocks have a smaller relative increase in thermal conductivity from 0 to 6 h of exposure than that of the ramming paste, and small increase from 6 to 24 hours exposure. One exception is the SB-E H sample with a high virgin value and more linear increase with exposure time.

The trends in the electrical resistivity results are not that evident. Generally, the resistivity increases after the test, and a peak is seen after one-hour exposure except in one sample. Electrical resistivity and thermal conductivity are normally inversely related in electrical conductors, but it seems that there is not a direct relationship here. The discrepancy might arise from different transport mechanisms of heat and electrical current. To further explore the effect of microstructure, X-ray tomography were carried out on the SB-B samples after 1- and 24-hours exposure in the test. Slice of the tomography images taken from the middle of the samples are shown in Figure 6. The images show that bath penetration is approx. 10 mm into the samples after one hour, and that bath has reached, but not filled the pores in the centre of the sample after 24 hours exposure. There are no other observable microstructural changes such as crack formation images with the magnification used.

The change in lattice parameters for all samples (including industrial samples in Table 1 and Figure 3, where data were available), are shown in Figure 8 as a function of change in thermal conductivity. It seems that the d002 interplanar spacing between the graphite layers increases after the test, however there is no correlation with the change in thermal conductivity. The crystallite size, Lc, seems to decrease with increasing change in thermal conductivity, but there are two outliers that do not follow this trend. The La parameter vs. thermal conductivity is very scattered and no trend is seen.

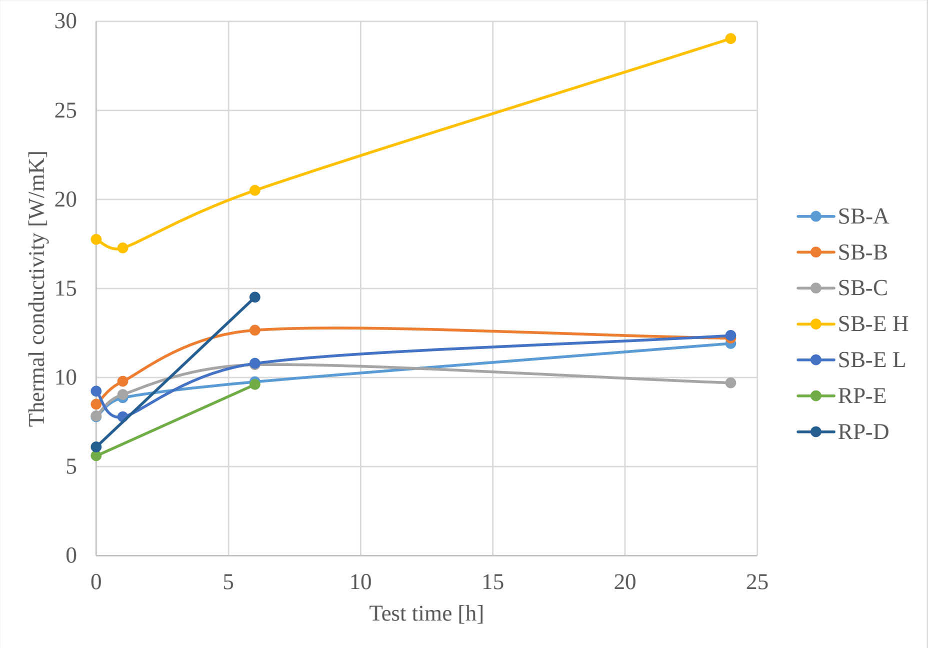

Figure 5. Thermal conductivity of different side block and ramming paste samples after aging tests. Data at 0 days are average virgin values.

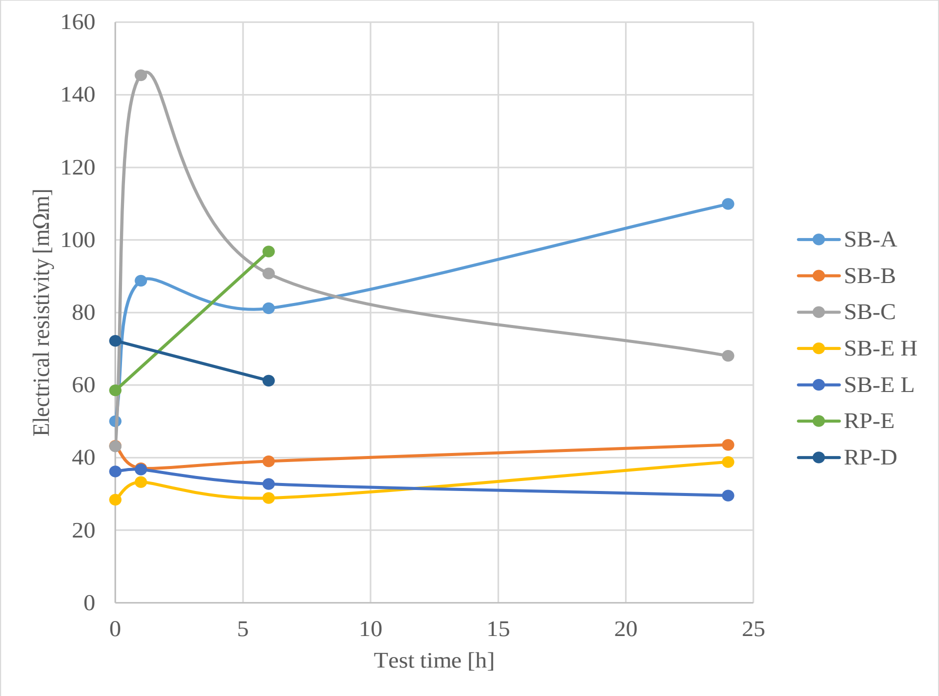

Figure 6. Electrical resistivity of different side block and ramming paste samples after aging tests. Data at 0 days are average virgin values.

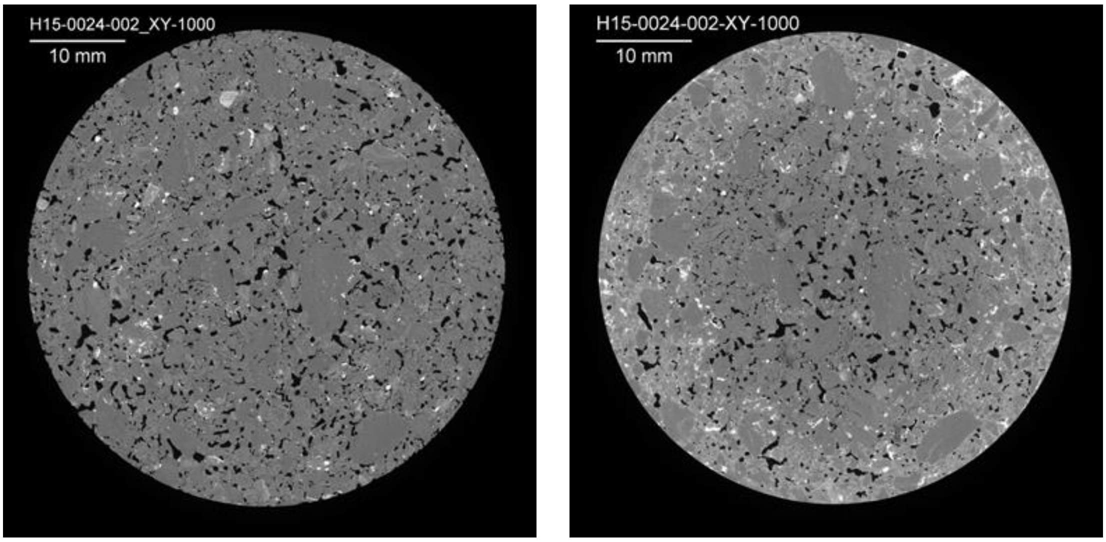

Figure 7a. Xray tomography of SB-B samples before and after ageing test. Left image is virgin samples. Right image is after 1-hour test, lower right image is after 24 hours test.

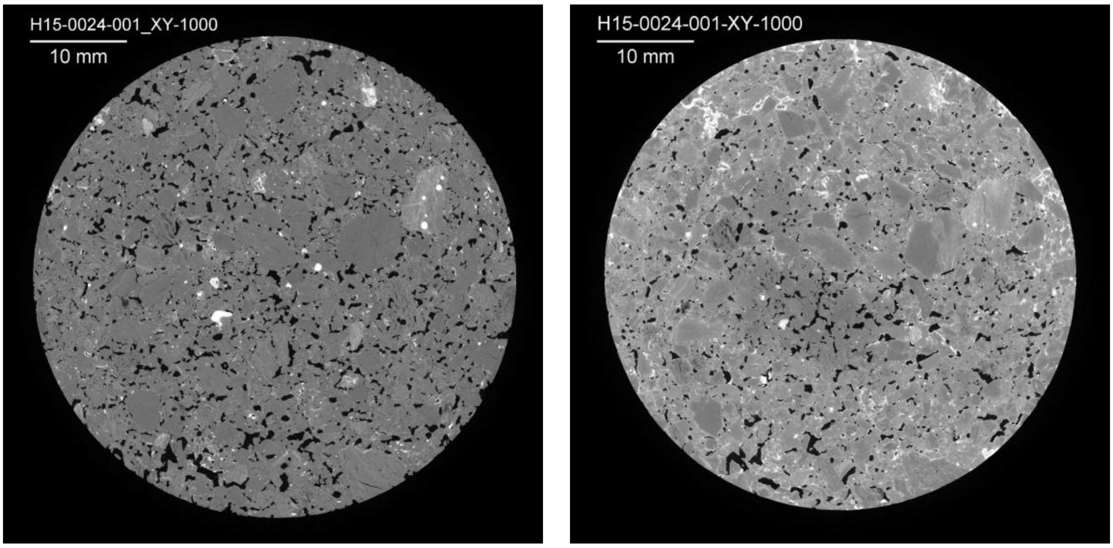

Figure 7b. Xray tomography of SB-B samples before and after ageing test. Left image is virgin sample. Right image is after 24 hours test.

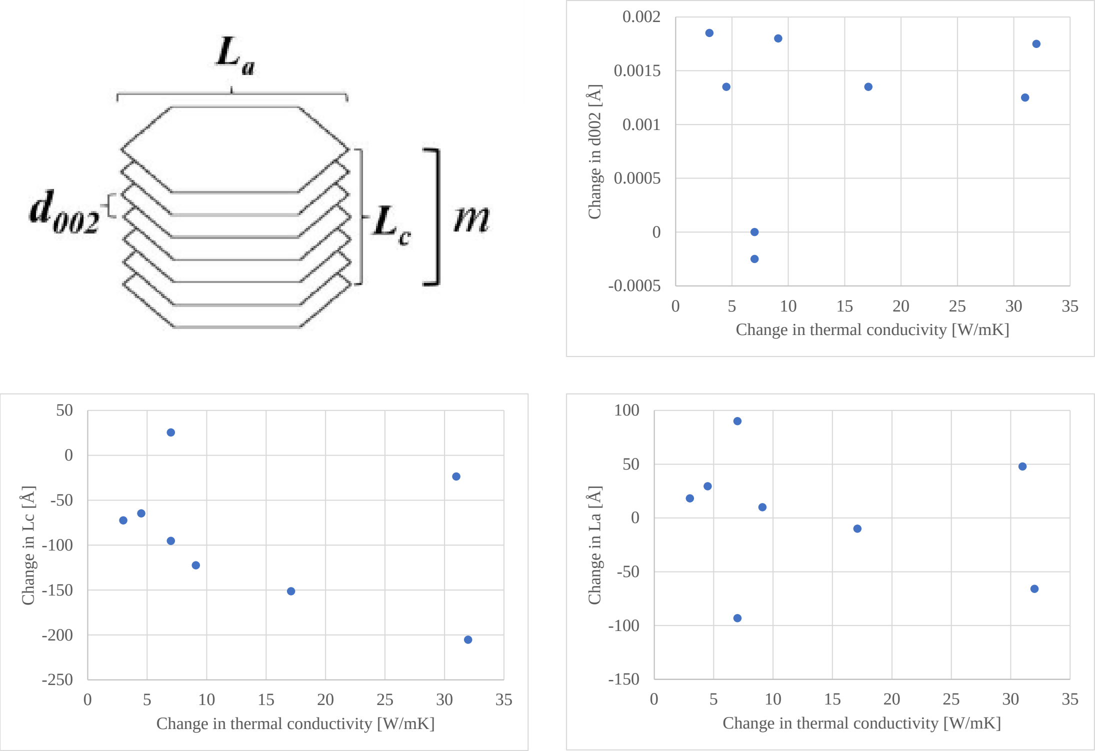

Figure 8. Change in lattice parameter d002, Lc and La as a function of change in thermal conductivity after electrolysis in lab test or in operation. Schematics of graphite crystal for reference.

4. Discussion

It is evident that the anthracite-based carbon materials undergo a significant increase in thermal conductivity during operation. The increase in thermal conductivity from approx. 5 W/mK to 50 W/mK makes the anthracitic based materials approach the properties of fully graphitized graphite materials. The operational temperature is less than 1000 °C and the anthracite has been calcined at significantly higher temperatures than the operational temperature. It is known that Na intercalates into C-materials, but Na is not stable in the C-structure [3]. During electrolysis the C-material swells due to Na-intercalation, and this might cause cracks, either on micro- or macro-scale. No significant macro-cracks were observed. It is expected that cracks would reduce the overall thermal conductivity of a material if they exist. Bath penetrates the samples during operation, and the presence of a solid phase during measurement at room temperature would probably increase the overall thermal conductivity by increasing the solid-solid heat transfer. However, solid bath has a relatively low thermal conductivity at room temperature (~ 2.5 W/mK), and it is not expected that the presence of bath in the porosity would significantly influence thermal conductivity when the overall value is 50 W/mK. The electrical resistivity values do not follow the expected trend with respect to thermal conductivity. One explanation could be that the presence of microcracks hinders the transport of current, but not the transport of heat to the same extent.

It is plausible that increase in thermal conductivity observed in this work must be due to the change in lattice structure of the carbon crystals, as shown in Figure 8. During the graphitization process of carbon materials, the interplanar spacing (d002) decrease and the crystallite width (Lc) normally increase [4] at the same time as the thermal conductivity increases. The results in Figure 8 shows the opposite trend, higher interplanar spacing and lower crystallite width correlate with a higher thermal conductivity change. A reasonable explanation for this observation is not identified, however remaining intercalated Na in the lattice might increase the electronic component of the thermal conductivity.

Further, the results show that operational conditions are important for the ageing of carbon materials in the cell. Exposure to Na at high chemical activity, either dissolved in molten metal/bath or gas will rapidly increase the thermal conductivity of the anthracitic C-materials. This behaviour can be reproduced in a lab test in a relativity short time scale. The results show the differences between the materials; however, more data is needed to be able to screen materials with respect to ageing behaviour. One complicating factor is inhomogeneities in the virgin material from commercial sources, and care should be taken in selecting materials for testing.

5. Conclusions

The present study on primarily anthracitic carbon materials has shown that these materials undergo significant ageing during operation, where up to 10 times increase in thermal conductivity is observed. A laboratory test has been developed to study this behaviour, and ageing effect can be studied in the timescale of a few days. Although the tests results show a quite different behaviour for different materials, more data is needed to use the test for a material screening purpose. The results also show that the increase in thermal conductivity during operation/exposure is accompanied by a higher interplanar spacing and lower crystallite width of the carbon crystallites. This is the opposite response compared to increasing thermal conductivity of carbon materials during a normal graphitization process.

Acknowledgments

Authors would like to thank Lorentz Petter Lossius, Hydro Aluminium, Norway, for performing the XRD analysis and Stein Rørvik, SINTEF, Trondheim, Norway, for performing the Xray tomography analysis.

6. References

1. Morten Sørlie, Harald A. Øye, *Cathodes in aluminium electrolysis*, 3rd Edition, Dusseldorf, Aluminium-Verlag, 2010, 662 pages
2. Https://www.hotdiskinstruments.com/ (Accessed on 20 August 2022).
3. Zhaohui Wang et al, Interaction of Sodium Vapor and Graphite Studied by Thermogravimetric Analysis, *Light Metals* 2014, 1239-1244.
4. David González et al., Structural Characterization of Graphite Materials Prepared from Anthracites of Different Characteristics: A Comparative Analysis, *Energy & Fuels* 2004, 18, 365-370.