Measurement of Tortuosity of Anode Porosity by 3D Micro X-ray Computed Tomography

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Abstract

A series of samples taken from prebaked pilot anodes was analysed by micro X-ray computed tomography. The shortest path length through pores ascending from one side of the volume was calculated, giving a measurement of the tortuosity. Significant differences in the tortuosity were observed for the measured samples. In addition to the tortuosity calculations, the average pore diameter was calculated using a method from medical analysis of bone structure. The results are compared to the gas permeability, the coefficient of thermal expansion (CTE) and the electrical resistivity. The same model was applied to the solid carbon phase, providing tortuosity and inter-pore distances of the solid phase.

Keywords: Prebake Anode, Porosity, µCT, 3D, Image Analysis.

1. Background

In recent years, Micro X-ray Computed Tomography (µCT) has emerged as a strong supplement to microscopy based image analysis. SINTEF and Hydro Aluminium has collaborated in several projects, and has found µCT useful in studies of coke and carbon anodes, both structure, aggregate packing and for porosity distribution. Additionally, some work has been done on mapping of electrolyte bath at the anode working surface. A major advantage seen with µCT is that the technique can be used to image fairly large samples non-destructively at a good resolution within a reasonable time and cost. The data output is a recording of the whole 3D volume of the test piece, allowing for more complex investigation of the pore network and carbon structure. A variety of views can be generated post-measurement from the recorded raw data set. A previous paper presented on TMS Light Metals 2017 [1] provided details about our development of µCT as a characterization technique for carbon materials. The current paper goes further into the analysis of the pores as a 3D structure, rather than analysis of their 2D intersections in a plane.

Two main methods have been used for 3D analysis: Pore tortuosity and pore thickness. Since these terms are loosely defined, the chosen definitions and implementation will be described in detail in this paper.

2. Methods applied

The instrument used for the µCT analysis is an X-TEK XT H225 ST delivered by the UK company Nikon Metrology. It has a 225kV maximum acceleration voltage and employs a reflection source selectable between four different targets: Cu, Mo, Ag and W. The data used in the current paper was acquired using a W target at 135 kV acceleration voltage and 200µA current. The anode samples were drilled cores of 40mm diameter, and a sub-volume of each sample was exported as a 2024x2024x2024 volume at a voxel size of 10.8µm. The data was exported using the CT instrument software, and post-processed using ImageJ [3]. Further details can be found in [1].

2.1. Pore Tortuosity

Tortuosity is a concept that describes the difference between actual path-length (including twists and turns) and the shortest path-length (point-to-point distance). Tortuosity is commonly used to describe porous media in geo-science, such as soil and sandstones.

Figure 1 illustrates the concept of tortuosity in a pore network. The calculation was done from an X-ray tomography reconstruction of a porous sandstone; only the pores are shown [2]. The colour represents the shortest distance within the pore space from the left limit of the image to any point in the pores. Comparing this distance to the straight-line distance shows that the tortuosity is about 1.5 for this sample.

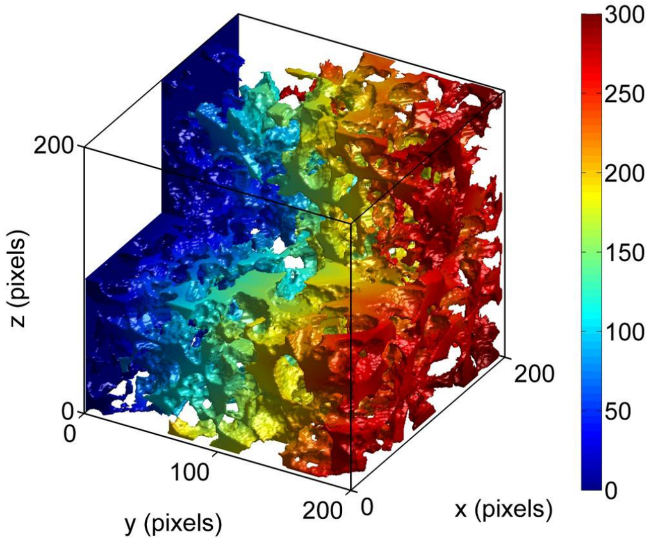

Figure 1. Illustration of the concept of tortuosity of a pore network. (Figure taken from the Wikipedia article on https://en.wikipedia.org/wiki/Tortuosity)

To simplify the calculations (since the datasets are large, up to 2048x2048x2048 voxels), the following algorithm for calculating a tortuous distance map was implemented.

1. A cubic volume is cropped from the inside of the original dataset (40mm core)
2. The calculations are done on a matrix of fractional numbers (32-bit)
3. All pore voxels in the volume are set to a value of -1.0, and background voxels to 0.0
4. The pores at the bottom slice are set to a value of 1.0
5. The slices are traversed from the bottom and up, and all adjacent pore voxels in each slice get added a value according to the smallest geometrical distance to a pore voxel in the previous slice:
    - Directly adjacent voxels (horizontally or vertically) get added a value of 1
    - Voxels adjacent diagonally in one direction (a connected edge) get added a value of $\sqrt{2}$
    - Voxels adjacent diagonally in two directions (a connected corner) get added a value of $\sqrt{3}$
6. Voxels that are not connected to voxels in the previous slice, retain their value of -1.0
7. When the top is reached, the dataset is traversed in the other direction using the same algorithm
8. The process is repeated from step 5 through 7 several times, until no more pixel values get changed, or a maximum number of iterations has been reached.

The algorithm was implemented as a plugin in ImageJ [3], written in the Java programming language. The original cropped CT data volume used as examples in this paper is shown in Figure 2. The volume size is 1024x1024x1024 voxels, with a voxel size of 10.8 µm, corresponding to a physical sample size of 11x11x11mm. An example output distance map is shown in Figure 3. This is analogue to the example in Figure 1. Blue means a short path length from the bottom plane, and red means a long path length. Non-connected pores are not shown.

Since the tortuosity value is defined as the ratio between the path length and the geometrical distance, the distance map is simply divided by the slice number (distance from the bottom). An example of this is shown in Figure 4. The colours are now relative; dark blue corresponds to a value of 1.0 and red corresponds to a value of 2.0. This implies that the colour scale shows how hard it is to access a pore from the outside of the sample. Non-connected pores are not shown.

Figure 5 shows a horizontal slice through such a relative tortuosity map. The cracks between coke grains are relatively low in value, while the pores inside coke grains have a relatively high value. This also illustrates why coke pores are usually not filled with the binder phase; the coke pores reside inside the coke grains with only a few narrow paths to the outside.

Figure 6 shows a horizontal slice (same data as Figure 5) showing the non-connected pores in white colour. They are more or less evenly distributed through both the coke grains and binder matrix.

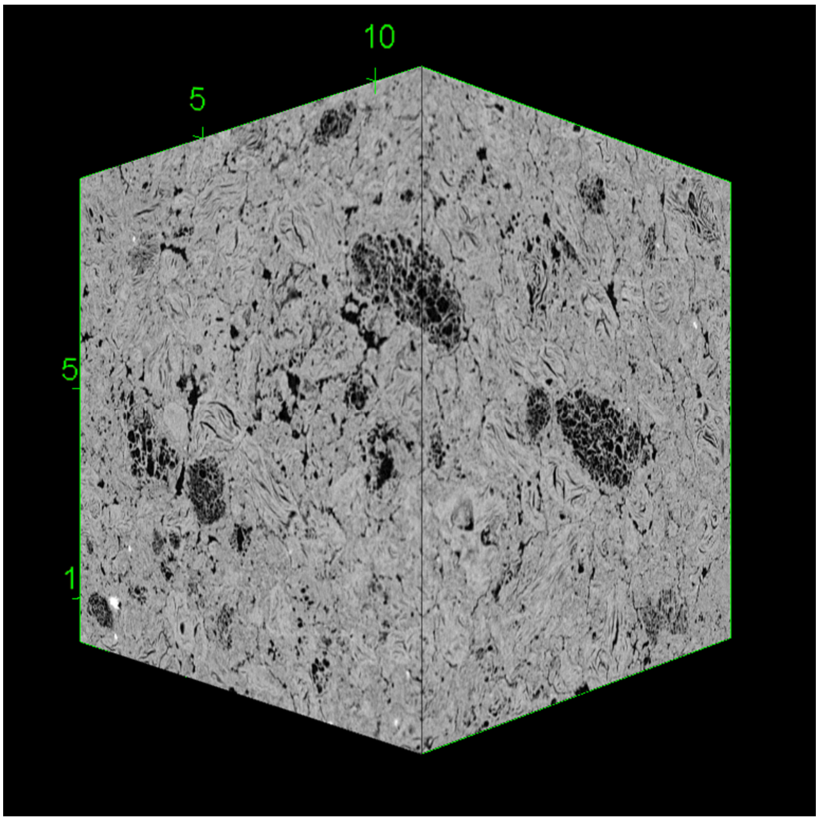

Figure 2. Sample volume (11x11x11 mm cube) shown in greyscale. Dark is pores (air). The bright white spots are heavier metal impurities in the carbon. Coordinates are in mm.

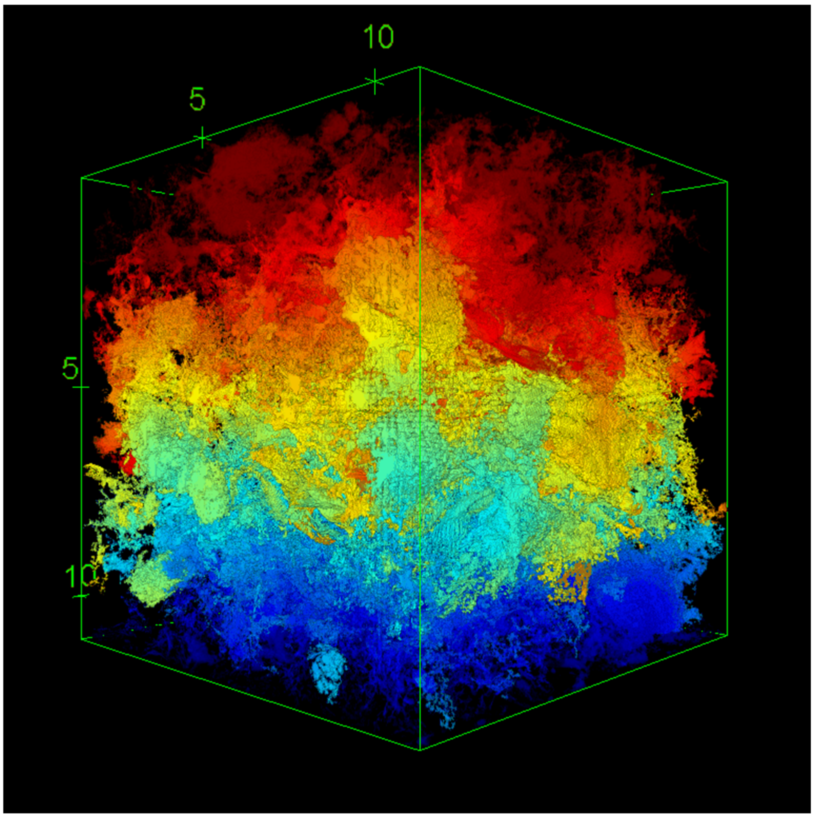

Figure 3. Tortuous distance map of pore path distance for one sample. Coordinates are in mm.

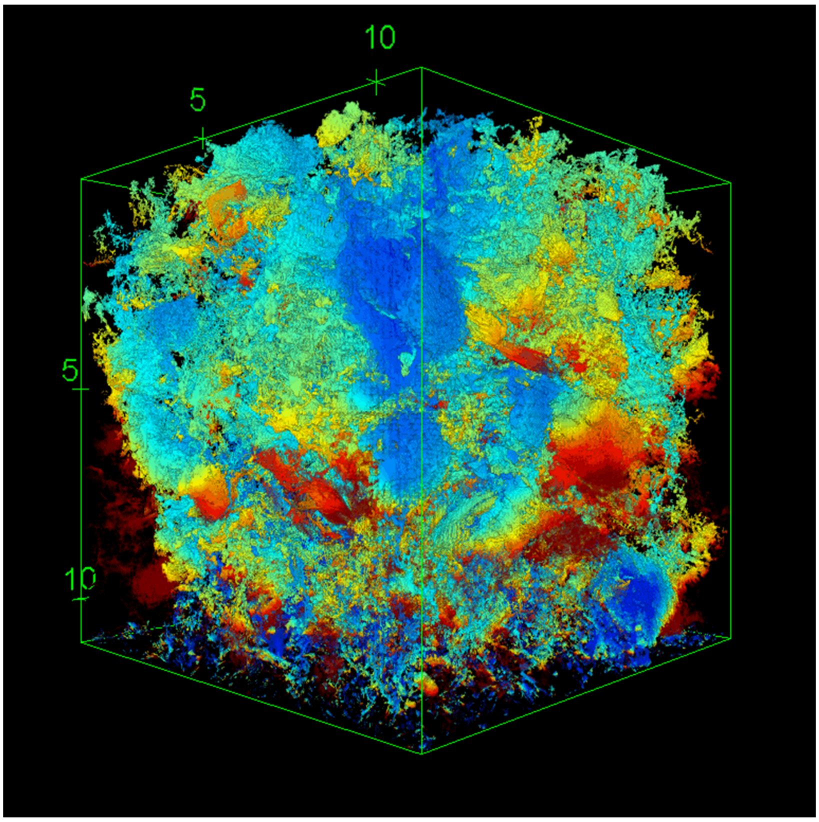

Figure 4. Relative tortuosity map for the same volume as in Figure 3. Coordinates are in mm.

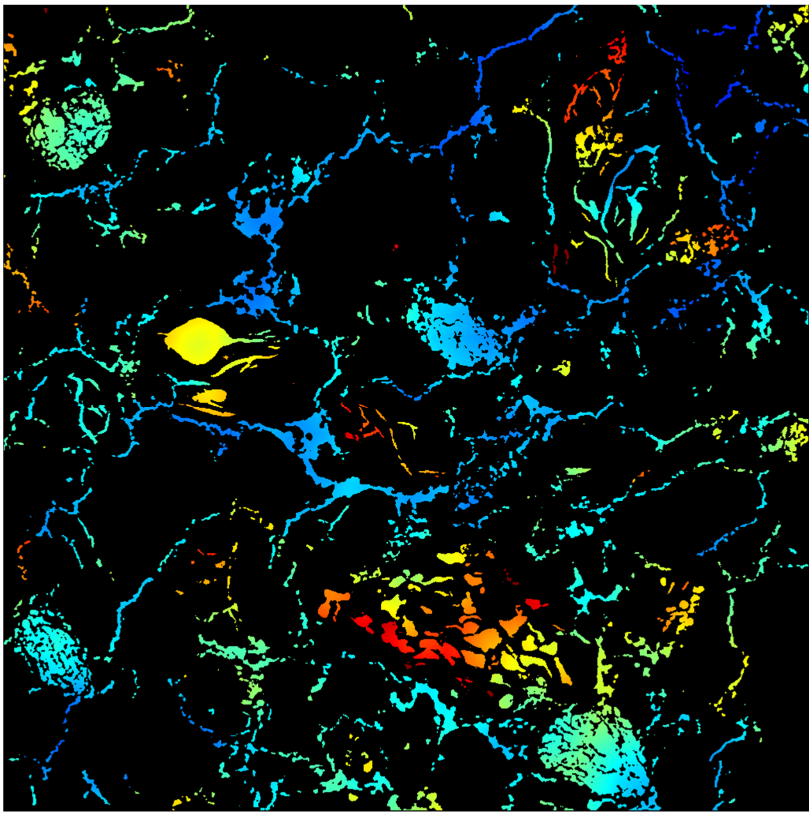

Figure 5. A horizontal slice through a relative tortuosity map. Size 11x11mm.

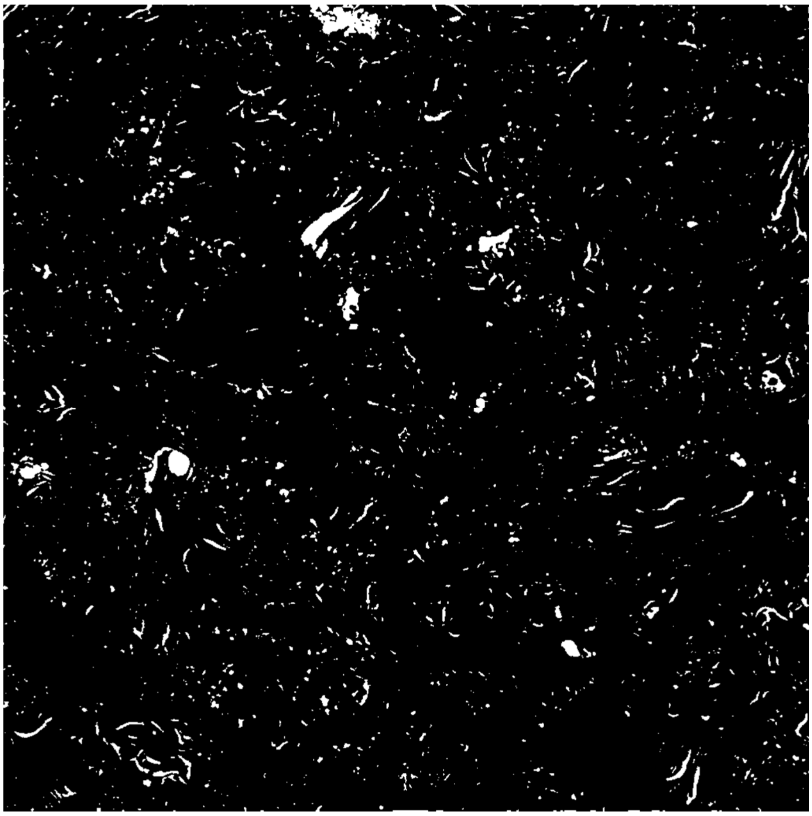

Figure 6. A horizontal slice (same data as Figure 5) showing the non-connected pores.

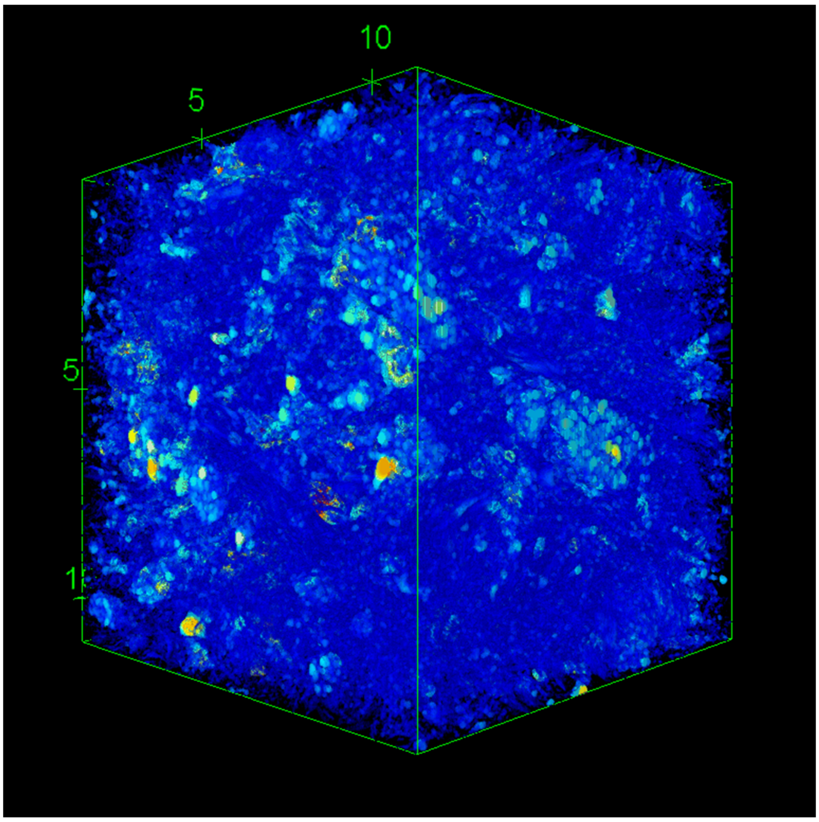

Figure 7. Pore thickness distribution for the same volume as in Figure 3.

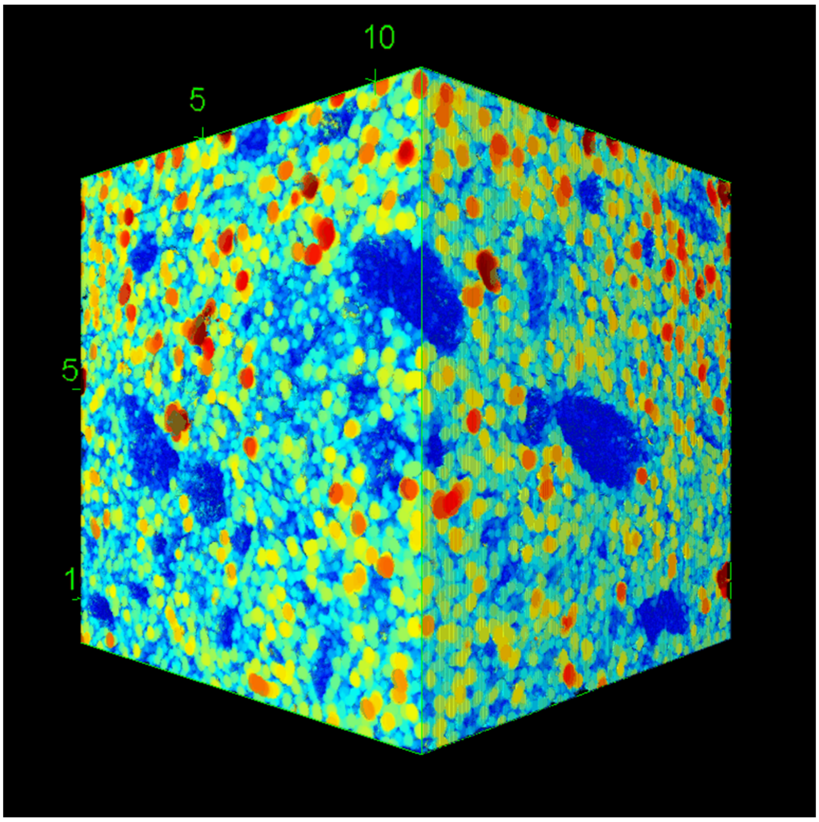

Figure 8. Carbon thickness distribution for the same volume as in Figure 3.

2.2. Pore thickness

Pore thickness is defined as follows: The thickness at a point in 3D space is equal to the diameter of the greatest sphere that fits within the structure and which contains the point. This measure is commonly used in medical science for the characterization of trabecular bone [4]. The method is implemented as a plugin for ImageJ, named BoneJ [5] available on http://bonej.org/. The plugin was used as-is, there was not any need for modifications.

Figure 7 shows the thickness distribution for the same volume as in Figure 2. The circular shapes represent pores that are big enough to fit a sphere of this size. In this figure, deep red corresponds to a pore size of 432 µm. The main advantage of this method is that it does not rely on any definition of a pore entity as a separate object, and is thus very suitable for connected pore networks. Keep in mind that the examples in both Figure 3 and Figure 4 represents *one* connected pore network and consists therefore in a strict sense just *one* pore.

Since the thickness method is not object dependent, it also applies to the carbon (the inverse of the pore volume). Figure 8 shows an example on this. The scale is the same as in Figure 7. Carbon thickness is a plot of the maximum sphere size that can fit between pores; or the same as the minimum pore to pore distance.

3. Results and discussion

The µCT method has been tested in several studies on pilot scale and full scale anodes. An example of results is given here from a series of 5 pilot anodes that were manufactured at the Hydro Aluminium research laboratory in Årdal, Norway.

The pilot scale anodes were produced for an electrochemical study. The anodes were made with cokes from 5 different refineries, i.e. given five unique single source cokes of different quality. Further details of that study have no part in this work. The granulometry and pitch level was adjusted to give good quality anodes with density close to full scale anodes. Table 1 summarizes the physical properties of interest in this structural study. Abbreviations: *CTE* is the Coefficient of Thermal Expansion, while *SER* is Specific Electrical Resistance.

The *Pore Thickness Factor* is defined as the average pore thickness multiplied by the porosity fraction. The latter is calculated as the ratio between pore volume (ρ) divided by sample volume (ν). A *Carbon Thickness Factor* (distance between pores) is calculated in the same way. The *Mean Tortuosity* is defined as the average tortuous path length (λ) divided by the Euclidean distance (ε); both measured from the bottom plane of the volume.

Table 1. Measured and calculated properties.

The air permeability of anode W15 was omitted, because the measured core sample had cracks.

Anode Sample ID	Baked Density g/cm³	Specific Electrical Resistance µΩm	Air Permeability nPm	Coeff. of Thermal Expansion µm/mK	Pore Thickness Factor µm * ρ/ν	Carbon Thickness Factor µm * ρ/ν	Mean Tortuosity λ / ε
W11	1.654	48.6	0.44	4.63	12.6	161.6	1.4928
W15	1.620	51.0	#N/A	5.59	11.3	200.1	1.4934
W18	1.632	50.6	0.44	5.10	12.6	173.0	1.5513
W21	1.644	42.8	0.58	6.61	14.5	232.4	1.4231
W26	1.649	50.0	0.33	4.93	11.7	206.7	1.6178

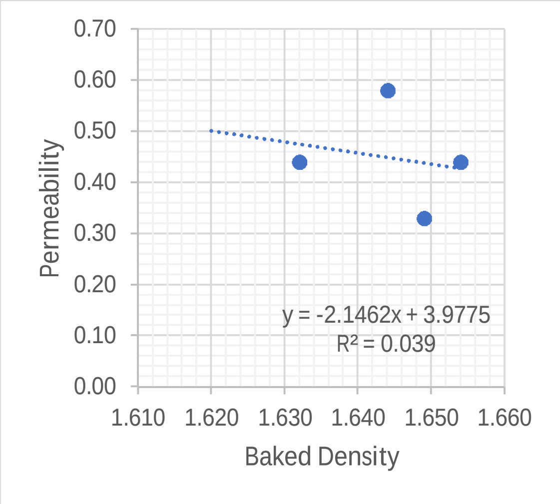

Figure 9. Permeability vs. baked density

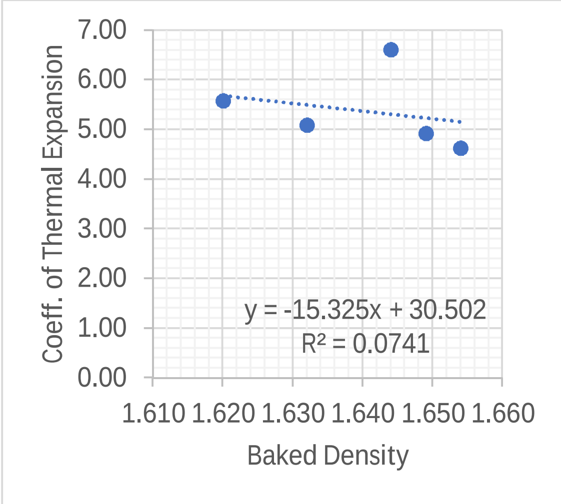

Figure 10. CTE vs. baked density

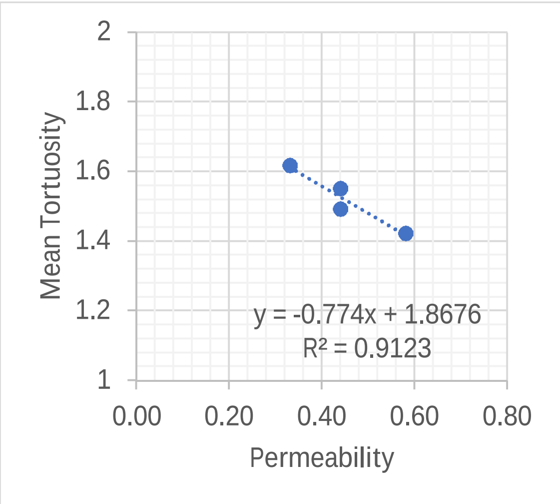

Figure 11. Tortuosity vs. air permeability

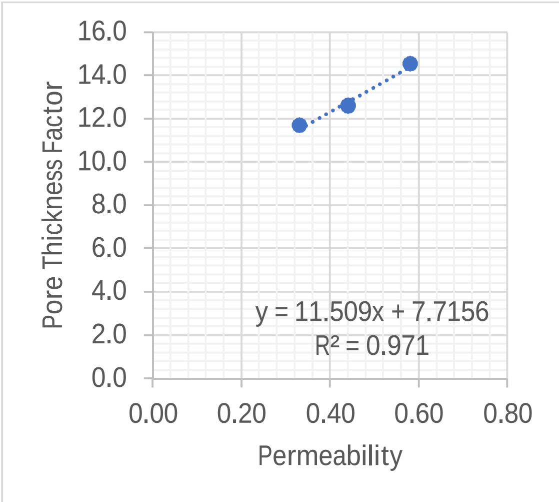

Figure 12. Pore thickness vs. permeability

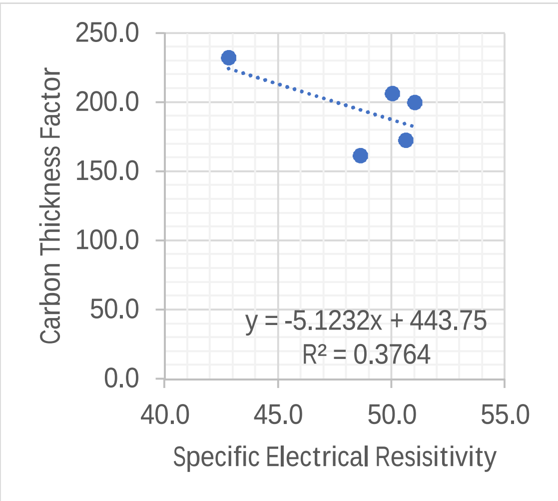

Figure 13. Carbon thickness vs. SER

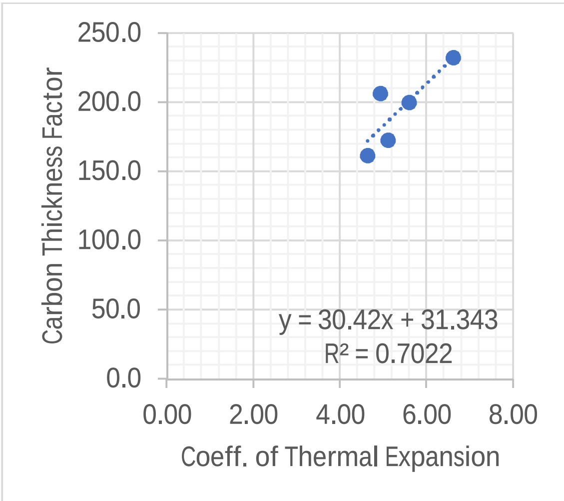

Figure 14. Carbon thickness vs. CTE

Table 2. Correlation coefficients, R^2

	Baked Dens.	SER	Air Perm.	CTE
Pore Thickness Factor	0.137	0.861	0.971	0.423
Carbon Thickness Factor	0.008	0.376	0.162	0.702
Mean Tortuosity	0.009	0.504	0.912	0.484

Table 2 shows the correlation coefficients for the properties measured by the µCT analysis against the four bulk anode properties. The R^2 values above 0.35 are indicated in yellow, and those above 0.70 are indicated in green.

Figure 9 compares air permeability to the baked density, while Figure 10 compares CTE to the baked density. The lack of correlation here is typical when comparing structurally different anodes; and is an important motivation for examining the relevance of the structural factors as measured by image analysis of the µCT volumes presented in this paper.

Figure 11 compares the pore tortuosity to the air permeability, indicating a strong negative correlation. It is often assumed that the permeability is dominated by the hydraulic diameter of the largest pores; while the correlation indicated here suggests the permeability also is dependent on how much the open paths winds through the anode.

Figure 12 compares the pore thickness to the air permeability. The correlation is good showing a strong positive correlation. In Figure 12 there appears to be only three points but there are four; the two anodes with permeability 0.44 nPm also have the same pore thickness factor. A correlation here is expected; the pore thickness is directly related to the hydraulic diameter of the pore network; while the tortuosity is directly related to the path length within the pore network.

It was expected that the carbon thickness would correlate strongly and negatively with the electrical resistivity, see Figure 13, but though the correlation is negative, it is only moderate. The correlation between carbon thickness and CTE (Figure 14) is stronger. This can be interpreted to indicate that large pore-to-pore distances give a more stiff and unyielding structure, and thus a stronger thermal expansion.

Since only a limited number of samples was analysed in this work, these observations only indicate some possible trends. Also, the anode series for this study was chosen because of its lack of correlation between SER, CTE and air permeability, against the baked density. Further comparisons in similar work is planned, focusing on parameters for improving the anode quality.

4. Conclusion

The purpose of this work was to examine microstructural properties in a series of prebaked carbon anodes that can help explain differences in gas permeability and electrical resistance, which cannot be explained by baked density. The microstructural properties were measured by image analysis of µCT data. The pore tortuosity has a good correlation to air permeability, and the pore thickness has a correlation to air permeability as well as electrical resistance. Carbon thickness (inter-pore distance) correlates with the coefficient of thermal expansion.

5. Acknowledgement

Thanks to Hydro Aluminium for releasing data on the anode and coke test material and to Hydro Aluminium and the Norwegian Research Council for funding through the SHIFT Program. Thanks to Rain Carbon for supplying specified coke materials.

6. References

1. Stein Rørvik, Lorentz Petter Lossius: Characterization of Prebake Anodes by Micro X-ray Computed Tomography, *Light Metals* 2017, 1237-1246.
2. C.J. Gommes, et.al.: Practical Methods for Measuring the Tortuosity of Porous Materials from Binary or Gray-Tone Tomographic Reconstructions. *Published online June 23, 2009 in Wiley InterScience* (www.interscience.wiley.com).
3. Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, www: http://imagej.nih.gov/ij/, 1997-2017
4. Hildebrand T, Rüegsegger P (1997) A new method for the model-independent assessment of thickness in three-dimensional images. *Journal of Microscopy*. 185: 67-75
5. Doube M, Kłosowski MM, Arganda-Carreras I, Cordeliéres F, Dougherty RP, Jackson J, Schmid B, Hutchinson JR, Shefelbine SJ.: BoneJ: free and extensible bone image analysis in ImageJ. *Bone* (2010) 47:1076-9