

Electrical Resistivity Measurement of Carbon Anodes Using Van Der Pauw Method

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Abstract

Electrical resistivity of carbon anodes is an important parameter in the overall efficiency of aluminium smelting process. In order to characterize their electrical resistivity, a cylindrical core is extracted from the top of the anodes. The electrical resistivity of the core samples is measured according to ISO 11713 standard. This method consists of applying a 1A current along the revolution axis of the sample, and measuring the voltage drop on its side, along the same direction. Theoretically, this technique appears to be satisfying, but cracks in the sample, either generated during the anode production, or while coring the sample may induce high variations in the measured signal. Van der Pauw method, as presented in 1958 by L.J. van der Pauw, allows measuring the electrical resistivity of any plain sample with arbitrary shape and low thickness even in the presence of cracks. In this work, measurements were performed using both standard and van der Pauw method, on both flawless and cracked samples. Results provided by van der Pauw method appeared to be more reliable and repeatable.

Keywords: Carbon anodes; aluminum smelters; electrical resistivity; van der Pauw.

1. Introduction :

Carbon anodes, used in Hall-Héroult process to produce aluminium, are characterized to control the quality of produced anodes along the process. Usually, core samples are extracted from the top of the anodes, beside the stud holes. This location may lead core samples to have some structural flaws, especially at their bottom [1,3]. Core sampling itself may also induce flaws such as cracks in the samples [4]. The characterization of anode cores is achieved using ISO11713 standard method. This standard is merely an adaptation of ASTM B193-02, used as test method for resistivity of electrical conductors materials. Though, this latter method requires a sample with no cracks or visible defects. Cracks located in the radial axis may most probably induce overestimated values on the measured electrical resistivity, which would not necessarily be representative of the electrical resistivity of the anodic block.

Van der Pauw (VdP) method [5,6] for measuring electrical resistivity of samples of various shapes was presented 60 years ago. More recently, Kasl and Hoch [7] proposed a study using VdP method on circular and cylindrical samples. This study shows that samples with a thickness

smaller than their diameter gives an accurate value of electrical resistivity. In addition, contacts placed along the edge of the sample are preferred those placed on the top of the sample. Using VdP method allows working with samples much smaller than those used with ISO11713. By reducing the size of the sample, the risk of the presence of flaws reduces.

In this study, the reliability of the VdP method for electrical characterization of carbon anodes was investigated and compared with the standard method, currently used in aluminium industry. Finally, defects were intentionally introduced to the anode cores, and their electrical resistivity was measured using both methods in order to assess the sensitivity of these methods compared to the defects.

2. Materials and method:

For both methods performed at the university, the current is provided by a Laboratory DC Power Supply GW GPR-1810HD. Current and voltage are measured with an Agilent 34461A 6_{1/2} Digit Multimeter. In the case of the standard method, the sample was maintained between two steel plates, both placed on springs to apply the 3 MPa pressure required by the standard. Voltage drop was measured with two thin pins mounted on spring to apply the same pressure on each spots. These pins are located on a handle on which they keep the same distance apart. The description of the setting is presented schematically in figure 1. Measurement performed by our industrial partner were done using the R&D Carbon RDC 150 for Specific Electrical Resistance.

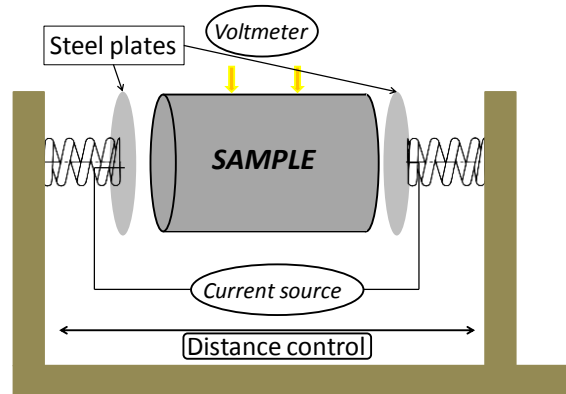


Figure 1. Schematic view of the setting used for the measurement of electrical resistivity of carbon anodes according to ISO11713 standard.

It has to be noted that a constant difference of $4.5 \mu\Omega\cdot\text{m}$ was measured between the standard method performed in the industry and at the university. The correction will be applied to each required situation, to clarify the graphs. For the Van der Pauw method, as it was decided to take advantage of the cylindrical symmetry, the sample holder was made of a self-centered chuck designed for turning machines. Current suppliers and voltage probes were made of copper bars, with a V shape facing the sample edge, to minimize the contact area, as can be seen in figure 2.a).

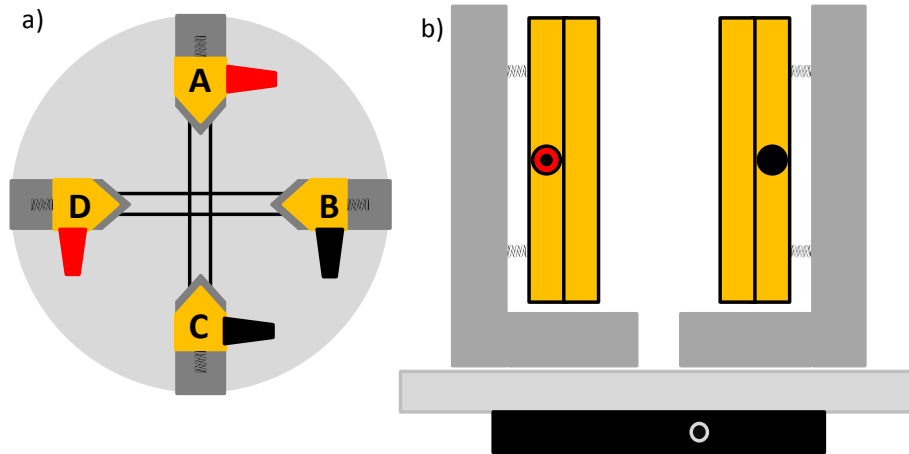


Figure 2. Top view a), and side view b) of Van der Pauw setting for laboratory measurement. A, B, C and D refers to the position of the connected probes.

Each copper bar is mounted with springs on plastic jaws, sliding on the chuck's body (figure 2.a), 2.b)). Plastic jaws are used to ensure a good electrical insulation between each copper bar and the chuck. The scroll ring (in black, at the bottom of figure 2.b)) turns to adjust the opening of the probes. All probes are related to move at the same time and with the same distance, to keep the sample centered. As presented by Van der Pauw [5,6], the electrical resistivity, resistance and thickness of the sample between two contiguous sets of points of measurement on its edge must be yielded by the following equation.

$$e^{-\pi \frac{d}{\rho} R_{AB,DC}} + e^{-\pi \frac{d}{\rho} R_{BC,AD}} = 1 \quad (1)$$

where: d thickness of the sample, m
 $R_{AB,DC}$ resistance measured when the current is injected between probes A and B, and the voltage drop is measured between D and C, $\mu\Omega$
 $R_{BC,AD}$ resistance measured when the current is injected between probes B and C, and the voltage drop is measured between A and D, $\mu\Omega$
 ρ electrical resistivity, $\mu\Omega \cdot m$

For the standard method, four measurements were performed around the sample. The average value and the standard deviation were calculated. While for the Van der Pauw method, eight measurements were performed; four in a first position and four more after rotating the sample by 45° . From the eight measurements, each two contiguous were combined together as a duet, following Equation 1 requirement, to lead to finally 4 pairs. The average and the standard deviation were calculated from the four obtained values. The sample remained all the time in the sample holder for each set of four measurements, and only the wires were changed from the copper bars.

First, eight samples, cored from the bottom of a single anode, were tested using both methods. The anode cores have a diameter of 5 cm, and a length of 10 cm. This part was done to compare the reproducibility of the measurement, assuming that the samples would have very close resistivity, as they were taken from the same anode. Then, six samples, provided by the industry, were tested; some flawless, others with noticeable defects.

The three flawless samples were tested using the standard method from both the industrial and the university laboratories in order to compare the results obtained. Three slices were cut out between the locations of the voltage probes to measure the electrical resistivity using VdP method, on each slices. The position of the slices in an anode core is presented in figure 3.



Figure 3. Anode core shapes for measurement of electrical resistivity using standard method (A), and Van der Pauw method (B)

In a second time, the three other samples containing defects were directly cut in three slices, as their condition would not allow to measure their resistivity using standard method. The figure 4 shows the condition of broken anode core after sampling for measurement using VdP method.



Figure 4. Broken sample prepared for measurement using Van der Pauw method.

Finally, to identify the effect of noticeable defects in the material on the measurement of electrical resistivity, samples were machined to obtain cracks placed in radial, then in transversal positions, as shown in the figure 5 (A-2, B-2). The samples used in this experiment were taken from the same anode as those from the first set of measurement.

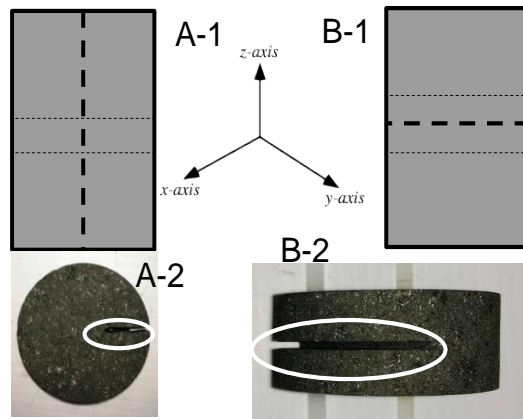


Figure 5. Schematical view of the cut performed along revolution axis (Radial crack) (A-1), cut on the sliced sample, top view (A-2), schematical view of the cut performed normal to revolution axis (Transversal crack) (B-1), cut on the sliced sample, side view (B-2).

The measurement were performed on samples containing the defect, before cut, using standard method, then after cut, slices were characterized using VdP method. Finally, numerical simulation were ran using Abaqus to compare results with those obtained on flawed samples.

2.1 Results:

In the first part, eight samples, cored from the same anode block, were tested using both standard and Van der Pauw methods. The graph presented in figure 6 shows the values of relative electrical resistivity of the eight samples, based on the average electrical resistivity measured by the standard method. The results presented in this graph shows that the standard deviation using Van der Pauw tends to be much smaller than using the standard method. In the graphs presented at figures 6, 7 and 8, as well as table 1 and 2, the origin is set as the average value of the electrical resistivity of the eight anode cores, measured using standard method. Though, the standard deviation depends on the raw results. All the values were compared to this average value, which explains the negative values presented in the graphs. It can be seen after figure 6 that the average value obtained after the eight measurements, using both methods is really close (less than $1 \mu\Omega\cdot m$ difference). Though, the standard deviation using the standard method is twice as big as using Van der Pauw method.

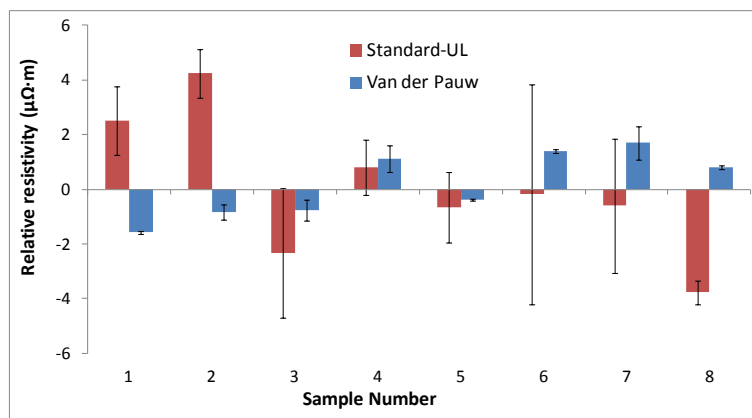


Figure 6. Comparison of electrical resistivity using standard method and Van der Pauw method for carbon anode cores.

This first set of measurements showed the good accuracy of the Van der Pauw method to characterize electrical resistivity of anode core. This first test confirm that VdP method is suitable to characterize this kind of materials.

In the second set of measurements, three samples, A, B, and C, apparently flawless, provided by our industrial partner, were tested. The measurement performed in the industrial characterization laboratory were achieved using the R&D Carbon RDC 150 for Specific Electrical Resistance, those results are labeled as Indus. Then, a four-point measurement, using the standard method was performed at Université Laval, using our own device for this measurement, labeled as STD-UL. Finally, three slices are cut out of each anode core, between the location of the voltage sensor. The resistivity of these slices was measured using Van der Pauw method. In each case, the obtained electrical resistivity is labeled as VDP-1, VDP-2 and VDP-3, then, an average of each set of measurement is included as VDP AVG.

The results of the measurement are presented in the graph at figure 7. Considering a correction of $4.5 \mu\Omega\cdot m$, as mentioned in the Material and Method section, it can be seen that the electrical resistivity measure at the industrial laboratory and at the university are very close.

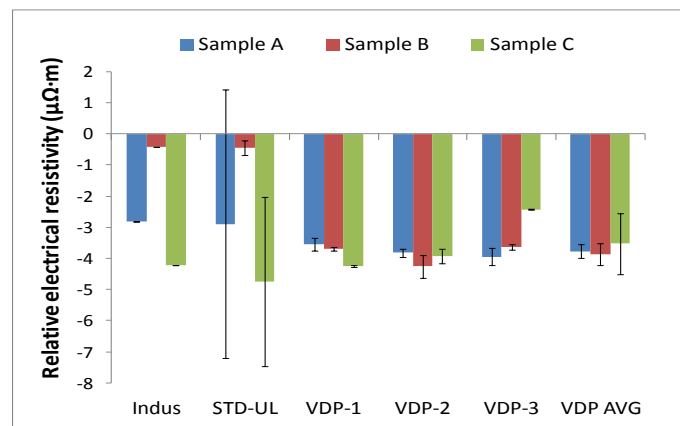


Figure 7. Comparison of Standard method and Van der Pauw method, for flawless sample from the industrial laboratory, Indus. are measurement provided by the laboratory, Std are measurement achieved using standard method, VDP (1-3) are measurement performed on slices 1, 2 and 3 of each samples, using Van der Pauw method, VDP AVG UL is the average of the three combined measurement.

Even though the samples A, B and C, show a strong difference in electrical resistivity, using the standard method either at university or at the Indus laboratory, their resistivity tend to be roughly the same using VdP method. The average value of electrical resistivity obtained after 3 slices of each samples, A, B, and C confirm a similar electrical resistivity, with a standard deviation much smaller than using the standard method.

Then, another set of tests was performed on three samples, also provided by our partner, but containing noticeable flaws. The samples D and E were originating from the same anode plant, Plant 2, while the sample F came from another different one, Plant 3. Those samples were received already broken. This condition prevented from performing any measurement using the standard method, as shown in figure 4.

The comparison was only be done using provided values of electrical resistivity obtained at the Indus. laboratory, and values measured using VdP method. As specified in the previous section, the provided electrical resistivity had to be corrected. Though, enough material remained to cut

again three slices out of those samples. On figure 8 are presented the results provided by the Indus, corrected by removing the $4.5 \mu\Omega\cdot\text{m}$, and obtained using the VdP method.

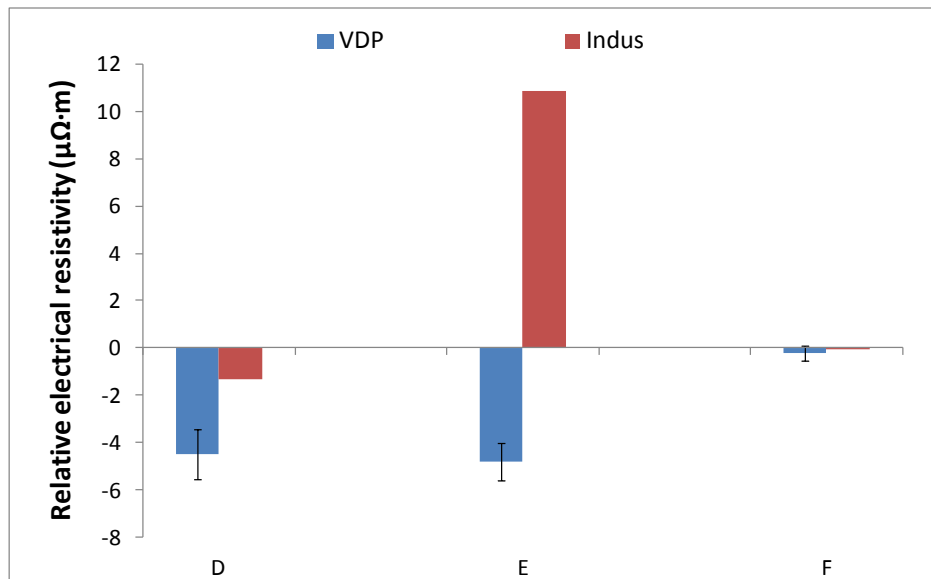


Figure 8. Comparison of Standard method and Van der Pauw method, for flawed sample from the industrial laboratory,

It can be seen that there are strong differences between samples D and E, using standard method, performed by the industrial partner (Indus). Both those samples were produced by the same provider, also, the measurement performed using Van der Pauw method show that they exhibit the same relative electrical resistivity ($-4.57 \mu\Omega\cdot\text{m}$ for D and $-4.91 \mu\Omega\cdot\text{m}$ for E). Then, after the correction brought to the results provided from Indus. laboratory, it appears that the sample F shows the same electrical resistivity using either the standard method or Van der Pauw's.

Finally, measurement were conducted on samples containing noticeable cracks. The samples used for this set of experiment were taken from the same anode block as from the first experiment conducted. To simplify the problem, cracks were made either along the revolution axis (radial crack) and normal to it (transverse Crack). In the first case the crack was performed on a sample before slicing, allowing to make electrical measurement using the standard method, before and after performing the cut. Then, 3 slices were cut out of the sample to measure the electrical resistivity using VdP method. While measuring the electrical resistivity following VdP method, two positions were used for the crack toward the probes. First, the crack was placed between two probes, at equal distance, then, the second option had the crack close to one of the probes. Those options were chosen to measure the effect of position of the crack on the obtained results.

The figure 5 A-2 shows the way the cut was performed on the sample. The second test was performed with a transverse crack, normal to the revolution axis, again, this was performed on an anode before slicing, to enable measurement using both standard and Van der Pauw method. A side view of the sliced cracked sample is shown on figure 5 B-2. The following tables shows the results obtained after measuring the electrical resistivity of the samples on each configuration.

As the surface and length of the sample are taken account in the calculation of the electrical resistivity of the material using the standard method, the void created had to be removed from the electrical resistivity calculated. The results obtained are presented in the table 1.

Sample and Configuration	Relative electrical resistivity ($\mu\Omega\cdot m$)
Sample without defect	-2.4 ± 6.3
Radial Crack Void : 1.7 %	$+6.2 \pm 6.5$ $+5 \pm 6.5$
Transverse crack Void : 0.18 %	$+12.9 \pm 10.9$ $+12.87 \pm 10.9$

Table 1. Electrical resistivity of sample containing defects, measured in laboratory using standard method, depending the orientation of the defect.

It appears clearly that a strong difference is measured between sample without crack and sample containing a crack, the effect of crack depend on its orientation toward the current flow.

Sample and Configuration	Relative electrical resistivity ($\mu\Omega\cdot m$)
Sample without defect	$+2.46 \pm 0.23$
Radial Crack Crack placed between two probes	$+3.17 \pm 1.29$
Radial Crack Crack placed between two probes	$+3.25 \pm 1.06$
Transverse crack	$+4.54 \pm 4.07$

Table 2. Electrical resistivity of sample containing defects, measured in laboratory using Van der Pauw method, depending the orientation of the defect and its position toward the sensors.

The results presented in table 2 shows there is a very small gap between the electrical resistivity measured using Van der Pauw method on sample containing defects. The differences presented here are consistent with the differences between the samples presented in the figure 1. The bigger standard deviation for the transverse crack is due to the difference of the size of the sample toward the crack induced. Using van der pauw allows to retrieve the electrical resistivity when the crack is radial, thought, depending its size, a transversal crack may induce a bigger error in the calculation, due to its impact on actual height of the sample.

To confirm the work previously presented, simulations were run using finite element method (FEM), to reproduce the experiment performed, then to simulate specific cases not easily achievable in laboratory. In those cases, the cracks were performed in the same directions (radial and transverse), but had a negligible thickness. Those simulation were run to confirm the impact of the size of the defect on the measurement of electrical resistivity.

Those experiment were done both in the lab and reproduced using Finite Element Method. The aim of those comparison was to simulate the effect of an infinitesimally thin crack that would not be reproduced easily or well controlled in the laboratory. This final simulation would show the electrical resistivity of the material can be retrieved even with a flawed sample.

3. Finite element modelling:

To reproduce the conditions obtained in the laboratory, a 1 cm thick, 5 cm diameter cylindrical sample was modelled. The connectors bar were also reproduced using electrical properties of copper. The current density was applied on a 1 mm diameter circle on each supply connector bars, to reach a current of 1 Ampere. In those conditions, the current flows the same way as it does in the laboratory. As the electrical resistivity of an anode is usually obtained around $50 \mu\Omega\cdot\text{m}$ [8], the simulations were ran using different values surrounding the latter one. Thought, numerical software such as Abaqus require an electrical conductivity as the input. The authors decided to use values of 18000, 20000 and 22000 S/m, as those values of electrical conductivity equals electrical resistivity of, $55.5 \mu\Omega\cdot\text{m}$, $50 \mu\Omega\cdot\text{m}$ and $45.5 \mu\Omega\cdot\text{m}$. Then, the contact resistance between the connectors and the sample was set at a value of $10000 \text{ ohm}\cdot\text{m}^2$, as several preliminary test were ran an this rang of value for electrical resistance gave the best correlation between laboratory test and simulation. The first simulation ran was performed to validate the numerical model.

Using the parameters above mentioned, tests were run with each models presented previously. The potential at the voltage probes was measured and ad to the VdP equation to measure the electrical resistivity in each case. In the case of radial defect, the crack was designed as 2 mm thick and 1,7 cm deep. In the case of transverse crack, the thickness and depth were also 2 mm and 1.7 cm, respectively. In the case of radial crack, simulations were performed with the crack placed between the probes, and close to one of the probes, like in experimental measurement.

3.1 Results:

A first simulation, was ran on a simple circular sample, with an electrical conductivity of 20000 S/m, or $50 \mu\Omega\cdot\text{m}$. This simulation allowed us to retrieve an electrical resistivity of $49.8 \mu\Omega\cdot\text{m}$. The error in calculation using this method is very small. After the validity of the model was confirmed, tests were ran on other configuration. The obtained results are stored in the following tables. First, simulation were done on sample containing a crack parallel to the axis of rotation (Fig 10, A-2). The crack was placed in the same way as experimentally, between two sensors, then close to one.

Method of calculation Original conductivity (S/m) ↓	⇒	Equation 1
18000		18308 Error: 1.71 %
20000		19363 Error: 3.18 %
22000		21945 Error: 0.25 %

Table 3. Electrical resistivity of a sample containing a crack, parallel to axis of rotation, calculated using FEM method. Crack placed between two sensors.

Then, the crack is placed close to one of the sensors:

Method of calculation Original conductivity (S/m)	Equation 1
18000	18339 Error: 1.87 %
20000	20260 Error: 1.30 %
22000	22144 Error: 0.65 %

Table 4. Electrical resistivity of a sample containing a crack, parallel to axis of rotation, calculated using FEM method. Crack placed close to one sensor.

Finally, to prove the volume of a defect parallel to the axis of rotation, which is actually normal to the electric current line, does not interfere with the results, a very thinner defect was modelled on the sample.

Method of calculation Original conductivity (S/m)	Equation 1
18000	18296 Error: 1.64 %
20000	20253 Error: 1.27 %
22000	22197 Error: 0.98 %

Table 5. Electrical resistivity of a sample containing a thin crack, of negligible volume, parallel to axis of rotation, calculated using FEM method. Crack placed close to one sensor.

In a second approach, the crack was placed in a plan normal to the axis of rotation (Fig 10 B-2). In this case, the void interfere with the real height of the sample and most probably affect the results obtained. In the Table 5, the results presented do not contain correction by removing the void in the sample.

Method of calculation Original conductivity (S/m)	Equation 1
18000	17379 Error: 3.45 %
20000	19362 Error: 3.19 %
22000	21122 Error: 3.99 %

Table 6. Electrical resistivity of a sample containing a crack, normal to axis of rotation, calculated using FEM method.

The void is calculated to be 6.3 % of the volume of the modelled sample. We decided to remove the contribution of void on the obtained results. The final electrical resistivity in this case is presented in table 6.

Method of calculation Original conductivity (S/m)	Equation 1
18000	18587 Error: 3.26 %
20000	20665 Error: 3.33 %
22000	22542 Error: 2.46 %

Table 7. Electrical resistivity of a sample containing a crack, normal to axis of rotation, calculated using FEM method. Void volume removed from the calculation.

To ensure the validity of the statement that the void contribution has to be taken account in the case of a defect place in the plan, the same simulation was performed with a thinner crack, of negligible volume, as presented in table 7.

Method of calculation Original conductivity (S/m)	Equation 1
18000	18189 Error: 1.05%
20000	20215 Error: 1.07%
22000	22229 Error: 1.04%

Table 8. Electrical resistivity of a sample containing thin crack of negligible volume, normal to axis of rotation, calculated using FEM method.

The results presented in the tables 3 to 8 show that, using FEM, the Van der Pauw method is adapted to the measurement of electrical resistivity of material containing structural defects.

4. Conclusion:

The results obtained experimentally shows that on industrially produced anode cores, the Van der Pauw method appears to be more accurate and less sensitive to macro and micro structural defects in the material. As the cracks in anode cores are not necessarily representative of the microstructure of the whole anode, the knowledge of electrical resistivity of the material without the effect of crack gives a better information on the electrical properties of the anode block. This method shows a good repeatability in the measurement of electrical resistivity of samples. Numerical simulation using Finite Element Method showed that this method is perfectly suitable for the measurement of electrical resistivity of samples containing defects or flaws such as macroscopic cracks, in different orientation, as presented in the last section. It has to be noted that depending the size and orientation of the defect toward the sensors, the defect may induce an error in the calculation of electrical resistivity.

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