MEASUREMENT OF DISTRIBUTION OF ELECTRICAL RESISTIVITY USING MULTI-ELECTRODE CONDUCTIVITY CELL

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Abstract – In the paper application of multi-electrode conductivity cell is suggested to study the distribution of electrical resistivity of electrolyte solutions. Two- and four-electrode methods of measurement were analysed. Results of modelling of potential and current density distribution within conductivity cell are presented. Preliminary results of measurements verifying usability of the proposed method are given.

Keywords: electrical resistivity, multi-electrode cell.

1. INTRODUCTION

Electrical conductivity κ (which is reciprocal of resistivity ρ) of electrolyte solution is often a measure of its properties, for example solution's concentration. Usually this technique is used to measure bulk properties, being a measure of average conductivity of heterogeneous medium. An interesting question is possibility of determination of spatial distribution of electrical conductivity. This might be an attractive method of investigation of some processes like phase transition, e.g. solidification. The authors have studied the possibility of application of multi-electrode conductivity cell for that purpose. The method using metal electrodes being in galvanic contact with solution was considered. With this method an electrical resistance occurring between two pairs of electrode (two-electrode method) or between the potential electrodes, when another one pair is supplied (four-electrode method) is measured. Value of conductivity κ is then calculated on the basis of equation (1) on assumption that the value of constant k is known.

$$\kappa = k/R \qquad (1)$$

where R [Ω] is measured resistance and k [m^{-1}] is cell constant. The cell constant k is defined [1] by equation (2)

$$k = l / S \qquad (2)$$

where l [m] is the length of the lines of the electrical field existing between the electrodes and S [m^2] is cross-section of the current flow. In fact, this is a very rare case when k value is determined according the equation (2) – it is achievable only for special cell designs [2] or those, providing uniform electric field. Usually, in practice the value of cell constant k is determined experimentally: the cell chamber is filled with the solution of know

conductivity κ, resistance R between the pair of the electrodes is measured and the value of k is determined using equation (1). Another one possibility of estimation of k value is field modelling of the cell chamber [3]. Some attempts to find the cell constant k dependence on electrode/cell geometry, and the problem of determination of its value (including its variability) is discussed in the next chapters. The related problems are spatial resolution of the method and optimal measuring technique.

In the considered case, verified experimentally, metal electrodes where to be located in the opposite walls of the cell chamber of dimensions 50x50x40. The dimensions of the electrodes should be sufficiently small, to not disturb the optical transparency of the cell walls made of organic glass (plexi) (liquid crystal technique was used to determine spatial temperature distribution). Finally, 49 pairs of the platinum electrodes, each of diameter 1mm where located at opposite cell walls – Fig.1.
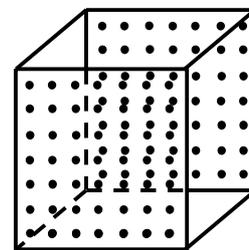

Fig.1 Sketch of the cell chamber with electrode's positions

2. MODELLING OF ELECTRICAL FIELD IN MULTI-ELECTRODE CONDUCTIVITY CELL

Field analysis was used to determine spatial resolution of the method, optimise measurement method and find optimum position of potential and supplied pairs of the electrodes. Finite Element Analysis (FEA) was carried out using COSMOSM 1.70 software package. An example of current density in the plane of the supplied electrodes (when one of the 49 electrode pairs is supplied), is shown in the Fig. 2a. The potential distribution at the planes of all electrodes (the cell chamber walls) is shown in the Fig.2b. Current of value 1 mA and solution conductivity 1 [S/m.] were assumed.

The results of the analysis show, that the current density distribution is not homogeneous in the cell space.

As expected, the maximum occurs in the vicinity of the electrodes. An interesting question is distribution of the current density along the axis connecting the centres of supplying electrodes (the depth of the cell) and dependence of this distribution on the cell dimensions.
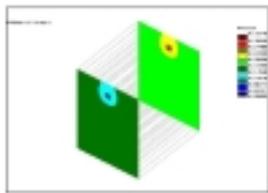
a)
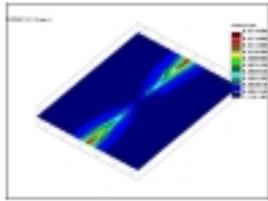
b)

Fig. 2 Example of distribution of a) current density,
b) potential

Especially for that question current flow in the two cubicoid cells of dimensions 25x25x75 and 75x75x75 respectively (the ratio of cell volumes and surfaces containing the electrodes is thus 1:9), was modelled. In both cells, electrodes were of dimensions 5x5x3. Thus, surface of the electrodes was 1/25 and 1/225 of the side surface of each cell. Fig.3 shows current density distribution along the axis connecting the electrode centres – a) for smaller and b) for bigger cell chamber, respectively. Current density at the edges of both cells is also shown in the Fig. 3 c) and d).
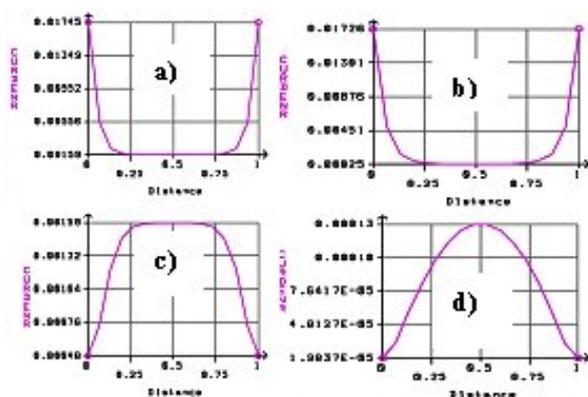

Fig.3 Current density distribution along a), b) axis of the
cells, c), d) edges of the cells

As is shown in the Fig.3a,b current density is constant in the middle part of the cell's depth (the distance between cell's walls). The region of uniform current density extends from 0.25 to 0.75 of cell's depth. The similar distribution occurs along the edge of lower cell chamber –

Fig. 3c. The exception is current density distribution along the bigger cell edge (Fig. 3d).

Very useful average measure of current distribution within the cell chamber is the value of the cell constant k. This value was estimated using equation (1), on the basis of assumed conductivity κ and resistance R, obtained by FEA modelling. The calculated values were 19.8 [1/m] and 12.4[1/m] for smaller and bigger cell chambers, respectively. This means that in spite of the fact that the side surface of the small cell has increased 9 times, the effective surface (cross-section enclosing current flow determining the value of cell constant), has increased 1.6 times. This, in turn, means that in the case of bigger cell, 40% of the current still flows across the surface of the smaller cell, and 60 % across the rest of the surface. However, this 60% of the current, flows across higher cross-section and thus the current density at some distances from the axis, connecting the electrodes, is rather low. For example, value of current density along the edge of bigger cell is $(2 \div 13) \cdot 10^{-5}$ A/m^{-2}. That is several times less than current density along the cell axis - $(16 \div 175) \cdot 10^{-5}$ A/m^{-2} – Fig.3. This indicates that when point or small electrodes (placed at opposite walls of the cell) are used, then the resistance measured between these electrodes is mostly determined by a limited space, neighbouring the axis connecting the electrodes. In the other words, in the case of multi-electrode cell, the values of resistance (resistivity) measured between any individual pairs of the electrodes are representative for the space "seen" by that pair. Thus some spatial selectivity and capability of determination of the resistivity distribution is obtained.

2.1. Comparison of two- and four-electrode method of resistance measurement
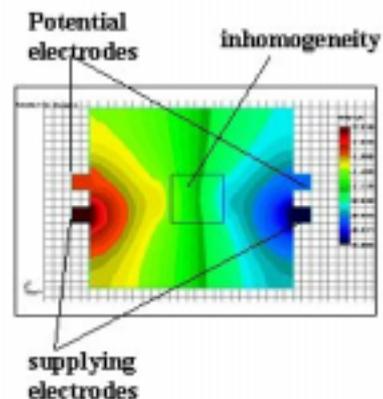

Fig. 4 Field model illustrating distribution of the potentials in the
four-electrode cell

The estimation of the applicability of the two- and four-electrode method of the measurement of the resistance has been carried out using field model, shown in the Fig.4.

The model contains four electrodes: two of them are supplied from current source and another two are used as potential (measuring) ones. The conductivity of the metal electrodes was assumed to be 10000 [S/m]. The value of conductivity of the bulk was 1 [S/m], and in the middle of the bulk, inhomogeneous region was modelled. The cross-

section of this region was 1/25 of the total cell cross-section. Two cases were modelled: without and with electrochemical layer at the metal electrodes - bulk interface. In the second case thin electrochemical layer of conductivity 0.1 [S/m] was considered. The variation of the resistance measured between supplying electrodes (two-electrode method) and between potential electrodes (four-electrode method) was estimated. This variation was caused by change of conductivity of inhomogeneous region, from the value 1 [S/m] to 0.5 [S/m]. Registered relative variation of the resistance is shown in the Table I.

TABLE I. Relative variation of measured resistance [%] caused by changes of conductivity of inhomogeneous region

Method of measurement	Electrochemical layer	
	exists	does not exists
Two-electrode	0.1	3.7
Four-electrode	7.1	7.1

The results shown in the Table I show higher sensitivity of four-electrode method of measurement. Moreover, this sensitivity does not depend on the existence of the electrochemical layer – two-electrode method fail completely in this case.

2.1.1. Optimal position of the potential electrodes

Assuming four-electrode method of measurement (i.e. separation of supplying electrodes from those where potential difference is measured) relative position of these two pairs were studied. In both opposite walls of the cell chamber, ring-shape supplying electrode were considered (to decrease current density at the surfaces of this electrodes).
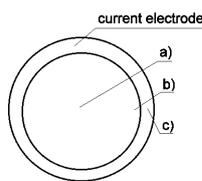

Fig. 5 Shape of the current electrodes

In the space between supplying electrodes, non-homogeneous region being 25% of the total cross-section was placed. The conductivity of non-homogeneous region varied from the value 1 [S/m] (the same as for rest of the bulk) to value 1.1 [S/m] (10% higher than the conductivity of the bulk). The electrochemical layers at the surface of the electrodes were assumed of conductivity 0.01 [S/m]. Two different positions of the point potential electrodes labelled as a) and b) in the Fig.5 were considered. The sensitivity of potential differences measured by potential electrodes at location a) and b), on the variation of the conductivity of non-homogeneous region was studied. For comparison, potential difference

between points c) (i.e. difference at supplying electrodes – two-electrode method) was measured as well.

The electrodes were supplied from 1 [mA] current source. In the Fig. 6 potential distribution along the axis connecting the points c) at both supplying electrodes is shown. Dominant voltage drop at electrochemical layers is seen, confirming once again that two-electrode method is not suitable in this case – sensitivity is 0.04% at 10% variation of non-homogeneous region conductivity. Fig. 7 presents potential distribution along axis connecting the points a) (in the centre of the ring electrodes) and points b) (adjacent to the ring electrodes). Continuous curves show potential distribution in homogeneous medium and dotted ones distribution when non-homogeneous region exists. When the inhomogeneity occurs, potential differences decrease and the variation is higher (2.7%) for the curves b) than for the curves a) (2.05%), for 10% increase of non-homogeneous region conductivity. This means that from the point of view of the sensitivity, potential electrodes should be placed just near the supplying ones.
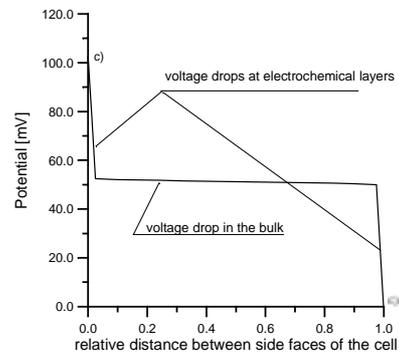

Fig. 6 Distribution of the potentials between a pair of the supplying electrodes – intersection along axis
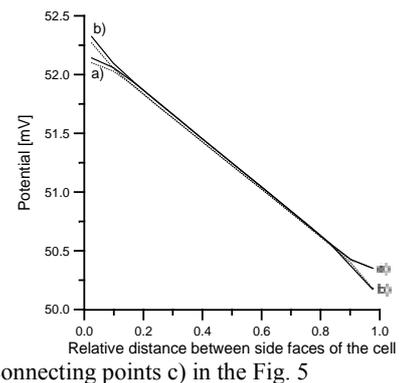

connecting points c) in the Fig. 5

Fig. 7 Distribution of the potentials between a pair of the supplying electrodes – intersection along axis connecting points a) and b) electrodes shown in the Fig. 5

The potential drop in the Fig. 7 is linear, with the exception of the neighbourhood of the surface of supplying electrodes. Current density in this region is non-homogeneous and some non-linear effects in curves a) and b) might be observed.

3. MEASURING EXPERIMENT

Calibration procedure of the cell (shown in Fig. 1 and described in the Chapter I), containing 49 pairs of the electrodes has been carried out. An objective of the calibration was to determine the cell constant k of each pair of the electrodes and then, some preliminary determination of distribution of resistivity in the investigated medium. Water solutions of NaCl of concentration 0.58% and 1.75% by weight and accurately known conductivity were used to fill the cell chamber. Measuring system shown in the Fig. 8 consisted of the cell, standard resistor and Solartron 1253 instrument. Solartron 1253 contains sinusoidal generator, and is capable to measure the ratio of two voltages, enabling direct determination of the unknown impedance (resistance). The resistance occurring between every pair of the electrodes has been measured at signal frequency 2000 Hz. Four-electrode method was used - one pair was used as supplying and another one as potential electrodes. The potential difference at potential electrodes was measured as voltage U_x and current was measured indirectly as voltage drop U_{RN} at standard resistor R_N. All measurements were taken at temperature 22 [^{0}C]. On the basis of measurements, cell constant k of each pair of the electrodes was calculated according to equation (1).
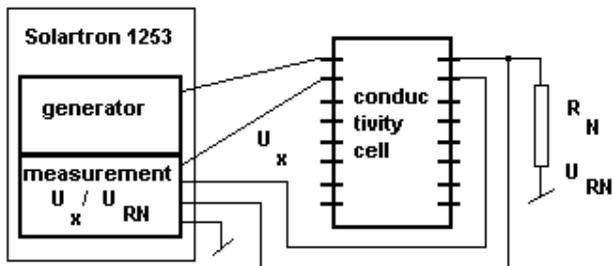

Fig. 8 System for calibration of the multi-electrode cell

The results obtained – Fig. 9 - show that these results range from 50 to 90 [1/m]. Higher values of k characterize the electrodes at the cell corners and those that are located near the walls of the cell. This results from deviation of current density in these locations from that in the middle of the cell – the walls of the cell form spatial distribution of the current density.

An experiment has been made to estimate the usefulness of the method used, for investigations of the resistivity distribution. The cell chamber was filled up with 0.1 M NaCl solution. The ceramic rod of 8 [mm] diameter was vertically immersed in the cell. Measured values of the resistances were converted, interpolated and displayed as resistivity, using own software package. An example of the image reconstruction is shown in the Fig.10. It should be notice that in spite of the fact, that the diameter of the rode (8 [mm]) is lower than the distance between the walls containing the electrodes (50 [mm]), the image of the rode is sharply outlined in the left part of the image.
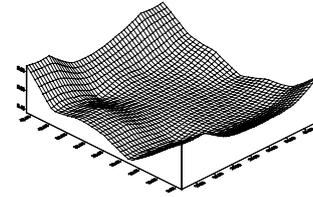

Fig. 9 An example of the distribution of measured the cell constant

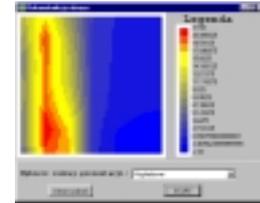

Fig. 10 An example of image reconstruction – image of ceramic rod placed in the cell chamber (red – higher values of resistivity)

4. CONCLUSIONS

It was found that multi-electrode conductivity cell is capable to measure resistivity distribution in the space of the cell chamber – some spatial resolution has been obtained. The cell constant k of each pair of the electrodes must be known to determine the values of the resistivity. The values of the k are individual property of each pair and should be taken into consideration during image reconstruction. Results of modelling show that sensitivity of the measured potential depends on the electrode's design and this problem should be a subject of further investigations.

REFERENCES

[1] Jones G., Bollinger G. M., *The Measurement of the conductance of electrolytes. III. The Design of cells,* J. Am. Chem. Soc., Vol. 53, Feb. 1931, pp. 411-451.
[2] Moron Z., Rucki Z., Szczepanik Z. *The possibility of employing a calculable four-electrode conductance cell to substitute for the secondary standards of electrolytic conductivity*, IEEE Transactions on Instrumentation and Measurement, December 1997,Vol.46, pp.1268-1273
[3] Z.Szczepanik, Z. Rucki, Z. Moroń, *Application of finite element analysis for modeling of electric field didstribution in conductance cells,* Proc. IEEE Intrumentation Measurement Technol., Conf. IMEKO TC-7, Brussels, Belgium, 1996, vol. 2, pp 123-126

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