XVI IMEKO World Congress
Measurement - Supports Science - Improves Technology - Protects Environment ... and Provides Employment - Now and in the Future
Vienna, AUSTRIA, 2000, September 25-28

CONDUCTANCE CELLS BASED ON VAN DER PAUW THEOREM

Z. Moron
Division of Measurement and Measuring Systems, Faculty of Electronics
Wroclaw University of Technology, 50-317 Wroclaw, Poland

Abstract: Conductance cells designed and used according to the van der Pauw method are suitable for the absolute determination of the electrolytic conductivity of solutions and they are more advantageous for this purpose than other calculable cells. Three designs of such cells have been constructed and tested by the author. Results of experimental investigations confirm theoretical expectations and indicate that such a cell can be employed to substitute for standards of electrolytic conductivity. An absolute determination of electrolytic conductivity of 0.01 and 0.1 kmol/m^3 NaCl solutions, with an uncertainty lower than 0.1%, has been obtained by the author using the cell of a new design.

Keywords: electrolytic conductivity, absolute measurement, four-electrode method

1 INTRODUCTION

The practical method of measuring the electrolytic conductivity of solutions, proposed in the 19th century by Kohlrausch and applied up until now [1], is based on the assumption that the resistance R_A of a solution of conductivity k, filling the cell A of length L and cross-section S is equal to:

$$R_A = \left(\frac{L}{S}\right)_A \frac{1}{k} = \frac{K}{k} \tag{1}$$

where the ratio $(L/S)_A$, denoted by K, is called the cell constant (the term *cell constant* was introduced by Kohlrausch considering two-electrode cells but later it has been extended also for other ones). If the effective cross-section of the cell is variable, an integral formula is more suitable:

$$R_A = \int_0^L \frac{l}{S(l)} \frac{1}{k} dl \tag{1a}$$

It is assumed that a cell constant defined in this way has, for a given cell, at a given temperature, a certain and non-variable value. Most real cells do not fulfil these postulates. They do not have theoretically calculable geometry and their constants show a variability both in relation to the conductivity measured and the measuring frequency (this variability results from the electrode polarisation and parasitic electrical effects) [2]. Therefore the cells require calibration at conditions close to those of the expected application. It is usually performed using material standards of electrolytic conductivity - solutions of chemically pure substances, of known concentration. An alternative means of calibration is in comparison with a cell of exactly known constant.

In some cases, however, there is a lack of material standards having properties close to those of the substances measured and (or) the absolute conductivity value at the actual conditions of application which are required. Measurements of: melted salts, non-aqueous solutions, paints and lacquers and all measurements of the conductivity of liquids carried out at high temperatures may be shown as examples of such situations. The application of an absolute method of measurement, with use of a *calculable cell* (i.e. a cell designed and applied in such a way that calculation of its cell constant from its geometrical dimensions is possible) can be a good solution in such circumstances. However the basic purpose of calculable cells is the determination of the primary standards of electrolytic conductivity, though they can be also applied as common usable cells.

2 CONDUCTANCE CELLS FOR ABSOLUTE DETERMINING OF ELECTROLYTIC CONDUCTIVITY

Calculable conductance cells should posses the following features [2, 3]:

- well defined, calculable geometry,
- invariable cell constant value, independent of the medium measured and the conditions of measurement (that consists in ensuring a constant pattern of current paths and potential distribution),
- good averaging of the conductivity of the medium measured [4],
- weak temperature influence on the cell constant value.

Calculable conductance cells can be realised in at least three ways:
i) with uniform electric field [5, 6] (Fig. 1a),
ii) according to the van der Pauw theorem [7, 8, 9, 3] (Fig. 1b),
iii) according to the Thompson-Lampard theorem [10] (Fig. 1c).

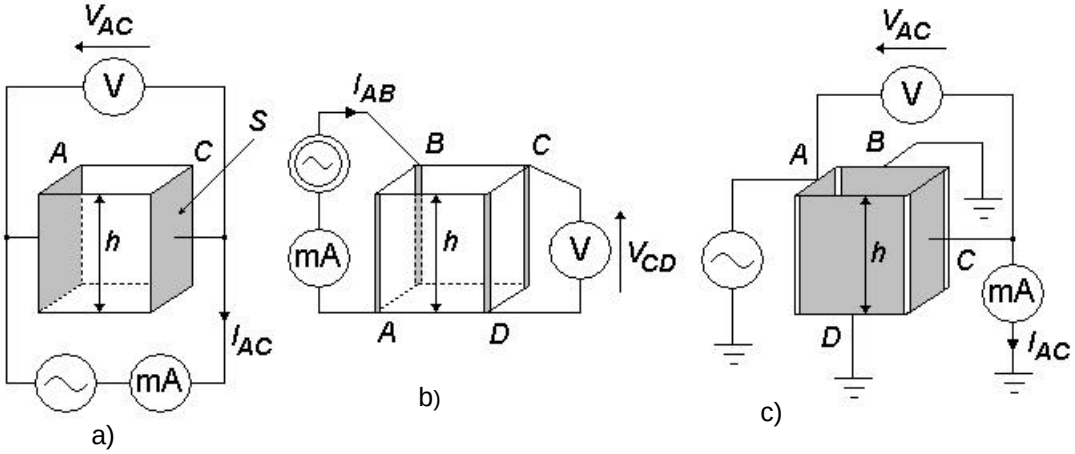

Figure 1. Conductance cells for absolute determination of the electrolytic conductivity: (a) cell with uniform field, (b) van der Pauw type cell, (d) Thompson-Lampard type cell.

The first, classic approach has two versions: with two- [1] and four-electrode [6] method of measurement. The two-electrode cell with a uniform field, measured by a differential method, has been until now the best known realisation of the calculable cell [5]. It has been proposed by NIST for determination of the primary standards for electrolytic conductivity.

The cells realised according to two dual methods: van der Pauw and Thompson-Lampard ones, have such a unique feature that their cell constant depends on a single geometrical dimension only - their height *h* (for symmetrical electrode arrangement only one measurement suffices). It results from their geometric structure, which, when ensuring homogenous height *h*, gives plane-parallel potential distribution in the measuring space filled by the solution. Therefore the problem of determining the cell constant resolves itself to electric field analysis in the cross-section plane of the cell and it can be solved using conformal representation and complex potential theory [7, 8]. In the van der Pauw type cell the electrodes have their widths negligibly small in comparison with the cell circumference, while in the Thompson-Lampard type cell they cover almost the whole circumference, and the spaces between them are negligible. Furthermore, the van der Pauw method is, in principle, a four-electrode one, while the Thompson-Lampard one is two-electrode.

Definition formulae for the three above mentioned calculable cells are given in Table 1. Assuming that all the cells have a form of a regular cube of height h = 1 cm, their cell constant values are respectively equal to: 1 cm^{-1}, 0.220636 cm^{-1} and 4.53236 cm^{-1}.

Table 1. Calculable conductance cells.

cell type	Kohlrausch	van der Pauw	Thompson-Lampard
basic definition formula	$R_A = \left(\frac{L}{S}\right)_A \frac{1}{k}$	$\exp(-phR_{AB,CD}k) + \exp(-phR_{BC,DA}k) = 1$ (2)	$\exp\left(\frac{-phG_{AC}}{k}\right) + \exp\left(\frac{-phG_{BD}}{k}\right) = 1$ (3)
cell constant	$K = h/S = 1/h$	for $R_{AB,CD} = R_{BC,DA} = R$ $K = \ln 2 / (\pi h)$ (2a)	for $G_{AC} = G_{BD} = G$ $K = \pi / (\ln 2\, h)$ (3a)
for h = 1 cm	1 cm^{-1}	0.220636 cm^{-1}	4.53236 cm^{-1}

Legend to Table 1:
k - conductivity, $R_{AB,CD} = V_{CD} / I_{AB}$ - resistance of the solution measured when C, D are the potential electrodes and A, B are the current-carrying ones (Fig. 1b), $R_{BC,DA} = V_{DA} / I_{BC}$ - analogous resistance when D, A are the potential electrodes and B, C are the current ones, $G_{AC} = I_{AC}/V_{AC}$ - conductance of the solution measured between A and C electrodes (Fig. 1c), $G_{BD} = I_{BD}/V_{BD}$ - conductance of the solution measured between B and D electrodes.

By virtue of the four-electrode method of measurement and very small surface area of the electrodes, the van der Pauw type conductance cell is only slightly susceptible to the influence of electrode impedance and non-homogeneity of the electrode surfaces - when the current-carrying electrodes are supplied from a constant-current source [11, 3]. Therefore this type of calculable cell in particular seems to be the best suitable for determining electrolytic conductivity standards or to substitute for them. This problem has not yet been completely solved, however it has been raised many times [8, 9, 12, 3]. Although the cells can be applied in practical situations, this publication is devoted mainly to the realisation of accurate calibration cells.

3 PRINCIPLES OF VAN DER PAUW METHOD APPLIED FOR MEASURING ELECTROLYTE SOLUTIONS

The method of the four-point probe elaborated by van der Pauw [7], originally applied for determining the resistivity of semiconductor materials, can be applied also in measurements of electrical conductivity of ion conductors, especially of electrolyte solutions [9]. Knowledge of the pattern of current paths in a sample of arbitrary shape is unnecessary if the sample is homogenous in thickness, the electrodes have negligible dimensions and they are at the circumference of the sample, and the surface of the sample is singly connected.

Transfer of the method from measurements of semiconductor wafers to measurements of ionic conductors requires consideration some additional factors, such as the influence of electrodes, electrode impedances and the relatively large thickness of the sample [3]. The potential of a voltage electrode immersed in an electrolyte solution in general is not equal to the potential of the solution before its immersion. Two identical electrodes, made up of the same material, generate identical distortions of the potential distribution and hence they can compensate each other. However, in practice, it is difficult (if possible) to ensure identity of the electrodes. Therefore it is advantageous to minimise their surface. Some deviations from the assumptions of the method, i.e. finite dimensions of the electrodes and non-ideal electrode location at the circumference, can be calculated theoretically [7, 8, 9]. Effects of the other ones can be modelled or have to be determined experimentally.

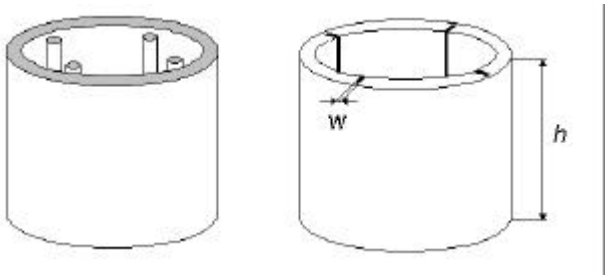

Figure 2. Four-electrode cylindrical cells: (a) with rod electrodes, (b) with stripe electrodes.

In practical realisations of the cells, the electrodes have a form of thin rods placed near the wall of the cell body (Fig. 2a) [8,9] or thin strips entered into grooves cut in the wall (Fig. 2b) [8,3]. The second solution is more advantageous - it better fulfils the assumptions of the method and the electrodes are fixed in their locations. Also a third solution is possible. It consists in placing the electrodes in individual chambers, separated from the measuring vessel of the cell by gaps of small width s (Fig. 3) - virtual electrodes [13]. If the $R_{AB,CD}$ and $R_{BC,DA}$ resistances are not equal, as assumed in formula (2a) - Table 1, an equivalent mean value R_m, calculated from (4) should be used in (2a) instead of R:

$$R_m = f \cdot (R_{AB,CD} + R_{BC,DA})/2 \qquad (4)$$

where f is a coefficient depending on the ratio $R_{AB,CD} / R_{BC,DA}$ (when this ratio approximates 1, also the coefficient f approximates to 1) [7]. If the solution measured is not closed et both ends by two parallel planes (e.g. the system of electrodes is dipped in a vessel and does not reach its bottom), it is possible

perform two measurements, at two different depths, and calculate the conductivity measured [9]. It is also unnecessary to switch the measuring circuit to particular electrode configurations - the measurements can be done simultaneously with two different configurations, applying two different measuring frequencies [14]. It has significant practical implications because switching of electrodes may be in some cases difficult (e.g. when measured resistances have very low values).

4 EXPERIMENTAL INVESTIGATIONS OF THE CONDUCTANCE CELLS

The author has carried out investigations of the van der Pauw type cells realised in three variants: (i) with stripe electrodes entered into the wall - an open vessel, (ii) as before but with the vessel closed at both ends [3], (iii) with electrodes located in chambers separated from the measuring space of the cell by narrow gaps - Fig. 3 [13]. All the cells are made up of polymethacrylate, all electrodes of stainless steel. In all cases the electrodes (or gaps) have negligible width in comparison with the cell circumference. A detailed description of the experiments can be found in [3,13]. Consistency between the cell constant value calculated and that determined experimentally has been considered as a main criterion for evaluation of the cells. In case (i) the available consistency is not better than 0.5-1%, because of evaporation and the influence of the meniscus. Cases (ii) and (iii) give consistency in the range 0.5% to <0.1%. The last solution has a number of advantageous features: electrodes are easily removable, they can have large surface areas, and the influence of electrode location and non-uniform electrode impedances can be very weak in terms of its impact on the results obtained.

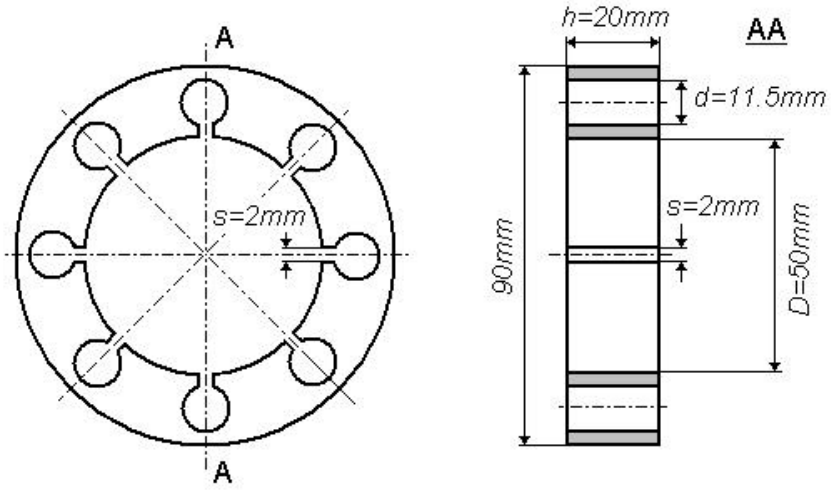

Figure 3. The body of the cell of new design: (a) top view, (b) a cross-section ($\Delta h = \pm 0.03$ *mm*).

The following investigations of the cell of a new design (iii) have been performed using NaCl solutions of concentrations 0.01 and 0.1 kmol/m^3: determining of the cell constant, the cell asymmetry influence on its cell constant value, frequency dependence of the measured cell resistances, and influence of electrode location in the chambers. Furthermore, in comparison with previously reported works, the conditions of measurements have been better determined - e.g. temperature measurement uncertainty has been lowered to below $\pm 0.05^0$C. The results obtained are presented in Figs. 4 - 6.

The resistances measured show a variablilty $<\pm 0.1\%$ in the frequency band 70-600 Hz for the 0.01 kmol/m^3 solution and 30-1000 Hz - for the 0.1 kmol/m^3 one ($<\pm 0.05\%$, respectively, in the band 150-400 Hz and 80-1000 Hz). Thus in the band 150-400 Hz the variability of resistances of both solutions is minimum. Theoretical values of the resistances have been determined from the theoretically calculated cell constant (0.110318 ± 0.000017 cm^{-1}) and from the tabular values of the electrolytic conductivity of the solutions. Even though the resistance values obtained in single measurements, for particular electrode configurations, differ from the theoretical values by 1 - 2% (it may be attributed to asymmetric location of the gaps in the cell body - Fig. 3), the mean values of these resistances differ from the theoretical ones by no more than $\pm$ 0.1%. Changes of any electrode position in a chamber, from the co-axial to maximum deflection, results in R_m resistance variation of less than 0.05%.

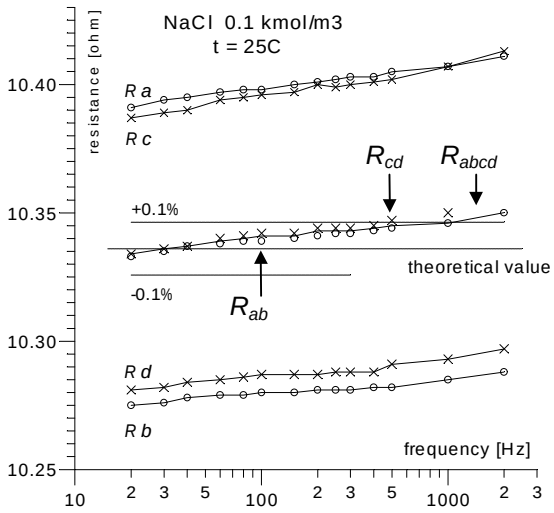

Figure 4. Resistances of 0.1 kmol/m^3 NaCl solution measured using the conductance cell of new design (R_a, R_b, R_c, R_d denote particular electrode configurations).

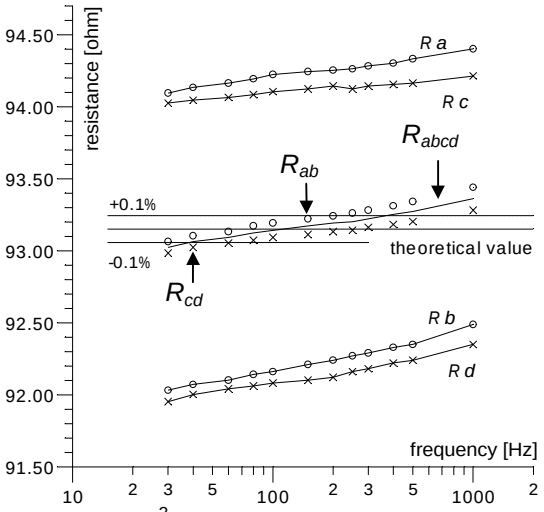

Figure 5. Resistances of 0.01 kmol/m^3 NaCl solution measured using the conductance cell of new design (R_a, R_b, R_c, R_d denote particular electrode configurations).

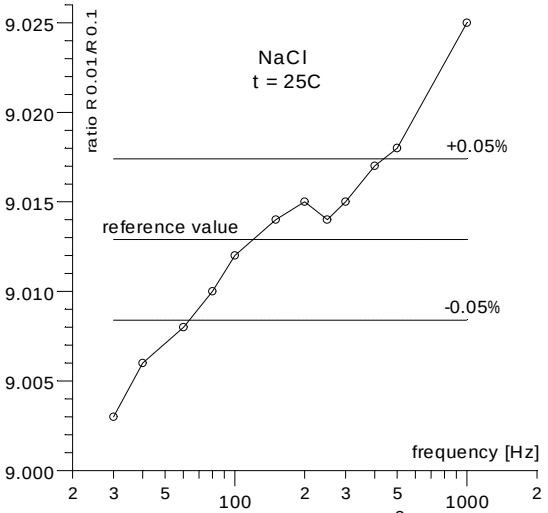

Figure 6. Ratio of the resistances of 0.01 and 0.1 kmol/m^3 NaCl solutions measured at 25^{0}C as a function of frequency.

The ratio of the cell resistances measured for two solutions applied, $R_{0.01}/R_{0.1}$, (often considered as a test of quality of conductance cells) is presented in Fig. 6 as a function of measuring frequency. It

should be the reciprocal of the solution conductivities and independent of frequency. The results obtained differ from the correct value 9.132 by less than ±0.05% in the frequency range 70-400 Hz (the best agreement is in the range 100-200 Hz). The results obtained may be considered as very good and promising. Consistency of the experimental and theoretical results is evidently better than the uncertainty of measurements evaluated as ±0.28% (a root-mean-value of partial uncertainties).

5 SUMMARY

The new design of calculable cell has a number of virtues: the cell constant depends on the cell body height only, electrodes are easily exchangeable, influence of electrode positions is negligible. However the gaps increase both the resistance of the current circuit and also the heat dissipated. This influence may be minimised by reducing the depth of the gaps and decreasing the measuring current.

The possibility of employing the van der Pauw type cell for determining the primary standards of ionic conductors has been confirmed. It seems that it is also possible to design simple and inexpensive calculable conductance cells which may be applied as common usable cells not requiring calibration with the use of material standards.

Until now the consistency obtained for the cell constant determined experimentally and calculated theoretically seems to be limited rather by non-ideal properties of applied measuring instrumentation than by the principle of the method. It can be improved further by the following means:

- good quality amplifiers for measuring the voltages an the currents,
- decrease of measuring current, to eliminate residual thermal drift,
- use of more suitable material for the cell body - of lower temperature coefficient and harder,
- use of purer material for testing solutions and increased accuracy of temperature measurement.

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, 1931, p. 411-451
[2] Moroñ Z.: Conductance cells for absolute measurement of electrolytic conductivity (in Polish), *Elektronizacja* 1/98, p. 25-28
[3] Moroñ 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 Trans. IM*, vol. 46, No 6, Dec. 1997, p. 1268-73
[4] Koon D.W., Knickerbocker C.J.: What do you measure when you measure resistivity?, *Rev. Sci. Instrum*., vol. 63, No 1, 1992, p. 207-210
[5] Wu Y.C., Koch W.F., Pratt K.W.: Proposed new electrolytic conductivity primary standards for KCl solutions, *J. Research NIST*, vol. 96, No 2, 1991, p. 191-201
[6] Tamamushi R., Takahashi K.: Instrumental study of electrolytic conductance measurements using four-electrode cells, *J. Electroanal. Chem*., vol. 52, 1974, p. 277-284
[7] Van der Pauw L.J.: A method of measuring specific resistivity and Hall effect of discs of arbitrary shape, *Philips Research Reports*., vol. 13, 1958, p. 1-9
[8] Nowak J.A.: A four-electrode conductance cell of calculable cell-constant (in Polish), *Proceedings of the IX Miêdzyuczelniana Narada Metrologów*, Gliwice 1974, p. 127-136
[9] Ohta Y., Miyanaga A., Morinaga K.: Study on the measuring method of the electrical conductivity of ionic solutions and melts, *J. Japan Inst. Metals*, vol. 45, No 10, 1981, p. 1036-1043
[10] Rehman M., Murti V.G.K., Gupta M.R.: A novel precision type liquid conductivity measuring system, *J. Phys. E: Sci. Instrum*. vol. 18, 1985, p. 902-903
[11] Szczepanik Z., Rucki Z., Moroñ Z.: Application of finite element analysis method for modelling of electric field distribution in conductance cells, *Proceedings of IEEE Instrumentation and Measurement Technology Conference & IMEKO TC-7*, Vol. 1, Brussels, Belgium, June 4-6,1996, p. 123-126
[12] Neapolitansky J.A., Hazuyev B.N., Suvorov W.I.: Application of Lampard-Thompson theorem to measurement of electrical conductivity of liquids (in Russian), *Metrologia* 1988, No 5, p. 49-53
[13] Moroñ Z.: A conductance cell realised according to van der Pauw idea (in Polish), *Proceedings of the XXXI Miêdzyuczelniana Konferecja Metrologów*, Bia³ystok, Poland, 1999, p. 353-358
[14] Kim G.T. *et al*, Muller-Schwanneka C. *et al*: Nonswitching van der Pauw method technique using two different modulating frequencies, *Rev. Sci. Instrum.*, vol 70, No 4, 1999, p. 2177-2178

AUTHOR: Dr. Zbigniew MOROÑ, Division of Measurement and Measuring Systems, Faculty of Electronics, Wroclaw University of Technology, B. Prusa 53/55, 50-317 Wroclaw, Poland, Phone +48 71 3206388, E-mail: moron@zwmsp.pwr.wroc.pl