Automatic measurement of the conductivity of an electrolyte solution by FFT electrochemical impedance spectroscopy

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It is now possible to measure automatically the conductivity of an electrolyte solution by FFT electrochemical impedance spectroscopy using the measurement and modelling possibilities of the Hewlett Packard 3562A dynamic signal analyser (DSA) with a rational fraction in the Laplace variable s. A new method has also been developed for synthesizing the equivalent electrical circuit of the conductivity cell. The electrolyte solution resistance can be readily measured by the DSA regardless of the form of the cell impedance graph. This measurement can be used to determine the electrolyte solution conductivity when the cell constant is known. It is thus possible to envisage automatic process control by conductivity measurements.

1. Introduction

Many physical or chemical phenomena result in conductivity variations. Conductivity measurements are therefore used widely in research and analysis laboratories as well as in industrial environments. One example is the identification, sorting and control of the circulation of fluids. Conductivity measurements can also be used to monitor the depletion of ion exchanging resins in water softening facilities, monitor ground water and detect oil in petroleum boreholes. It also permits threshold detection by conductivity variations (liquid level, foam detection, etc.).

Conductivity meters use various measurement methods (e.g. Kohlrausch bridge, ohmmeter, four-electrode and induction methods) and a number of conductivity cell geometries (e.g. planar/parallel, concentric annular or colinear electrode cells).

Conductivity measurements are often performed using a low-amplitude, fixed frequency a.c. electrical signal to reduce electrode polarization phenomena and prevent any reaction likely to modify the composition of the electrolyte. It is generally assumed that the conductivity cell behaves like a capacitor with a leakage resistance to be measured. The choice of the excitation signal frequency then results from making a compromise between the need to use a frequency which is sufficiently high to limit polarization phenomena and sufficiently low to limit the influence of extraneous capacitances.

It is shown in this article that it is possible to avoid this problem and to automatically measure the conductivity of an electrolyte solution by electrochemical

impedance spectroscopy (EIS) using the measurement and modelling possibilities of the Hewlett Packard 3562A dynamic signal analyzer with a rational fraction in the Laplace variable s.

2. Measuring the impedance of a conductivity cell using a dynamic signal analyser

It has previously been shown [1, 2] that the experimental plot of the impedance diagram of a conductivity cell over a wide range of frequencies determines the permissible measurement frequency range for a specified relative measurement accuracy. The equivalent electrical circuit of a conductivity cell comprises the resistance R_e of the portion of electrolyte between the two electrodes, the geometric capacitance, C_g, of the cell, the faradaic impedances of electrode reactions and their double layer capacitances. When the electrodes are identical and the cell operates near equilibrium, it is assumed that the impedances and double layer capacitances of the two electrodes are identical and the equivalent electrical circuit is simplified to that of Fig. 2. At high frequency, the faradaic impedances of the electrode reactions can be assimilated to the transfer resistances of electrode reactions.

The various types of experimentally measurable conductivity cell impedance diagrams are shown in Fig. 1. When the conductivity of the solution is fairly high, the complex plane shows a circular arc or a straight line at an angle of less than $\pi/2$ with respect to the real axis due to the faradaic impedances of the electrode reactions. The electrolyte resistance is then measured by the high frequency limit of the real part of the impedance (Fig. 1a). When the conductivity of

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(a)   **(b)**   **(c)**
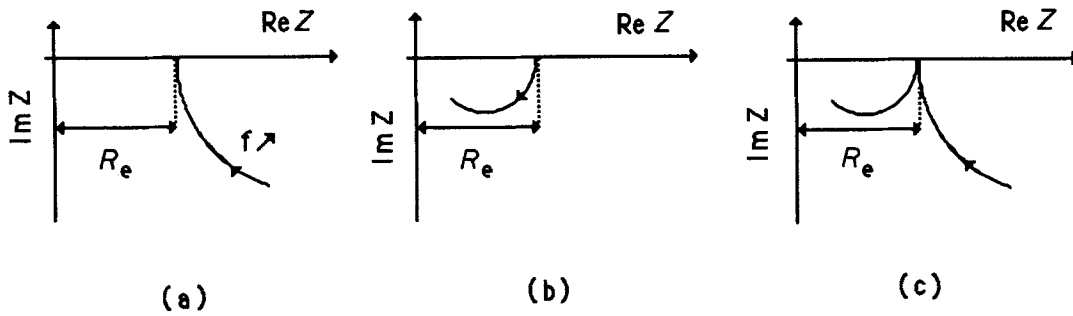
Fig. 1. Various types of conductivity cell impedance diagrams.

the solution is low, a single capacitive loop is observed (Fig. 1b) due to the resistance R_e of the portion of electrolyte between the two electrodes and the geometric capacitance, C_g, of the cell. The resistance of the electrolyte is measured by the low frequency limit of the real part of the impedance. In intermediate cases (Fig. 1c), the electrolyte resistance is measured at the maximum of the imaginary part.

The Hewlett-Packard HP 3562A (DSA) dynamic signal analyser is both a signal generator and analyser. The generator is adapted to various sorts of measurements: random noise, periodic pulses, sine waves. The DSA can record time-dependent signals, calculate the Fourier transform of these signals using a fast Fourier transform (FFT) algorithm, the frequency response of a system and the coherence function. The coherence function is a statistical characteristic of the causality relationship between two signals and is defined by:

$$\gamma^2 = \bar{G}_{xy}\bar{G}_{xy}^*/\bar{G}_{xx}\bar{G}_{yy} \qquad (1)$$

where

$\bar{G}_{xx}$ is the average channel 1 power spectrum;
$\bar{G}_{yy}$ is the average channel 2 power spectrum;
$\bar{G}_{xy}$ is the average cross spectrum; and
$\bar{G}_{xy}^*$ is the average cross spectrum complex conjugate.

The coherence function is an indication of the statistical validity of a frequency response measurement. We have shown that a plot of the coherence function against frequency provides a ready means of qualitative checking that the tested system behaves linearly and of locating the frequency of aberrant experimental points [3, 4].

The DSA has a modelling function which provides the transfer function expression of the system analysed by parametric identification. It has a curve fitting algorithm [5] which makes it possible to deter-

mine parameters a_i and b_j such that the weighted sum of the weighted least squares:

$$\varepsilon = W(H' - H) \qquad (2)$$

between the experimental frequency response H and the expression:

$$H'(p) = \frac{a_0 + a_1 s + a_2 s^2 + \ldots}{b_0 + b_1 s + b_2 s^2 + \ldots}, \qquad (3)$$

is a minimum, where W is a weighting function.

It is not necessary to use a potentiostat to adapt the DSA excitation signal used to measure the resistance R_e of the electrolyte portion separating the two similar metal electrodes of a conductivity cell. The impedance of the signal analyser generator used is sufficiently low to directly supply the circuit consisting of the conductivity cell connected in series with a resistance R_m used to measure the current through the cell (Fig. 3). The choice of the value of R_m is related to the value of R_e. As the analysis channels of the recorder are symmetrical, a resistance value of the order of magnitude of R_e is generally selected for R_m. The DSA signal source used to excite the conductivity cell is a noise signal with an amplitude selected so as to ensure good measurement accuracy while complying with the linear operating conditions of the system analysed. The input impedance of the DSA (1 MΩ) is sufficiently high to measure impedance up to 50 kΩ.
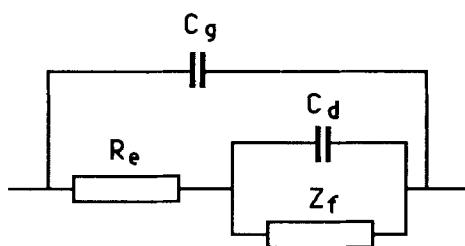

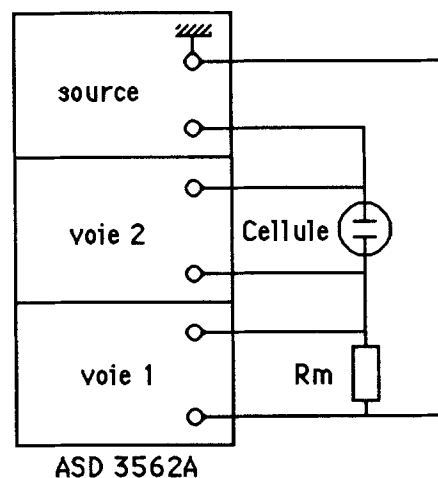Fig. 2. Equivalent electrical circuit of a conductivity cell.

Fig. 3. Device for measuring the transfer function Z/R_m of a conductivity cell. R_m: measurement resistance.

3. Experimental results

3.1. Impedance diagram type a

The Tacussel type XE140 conductivity cell consists of a glass body carrying two platinum plates measuring 2 mm by 2 mm perpendicular to the axis of the cell and 40 mm apart. The cell geometrical constant calculated using its geometrical dimensions equals 0.1 cm. The use of this type of cell is recommended for the measurement of the conductivity of concentrated ionic solutions (with a high conductivity and low resistance). Figure 4 shows the graph in the Nyquist plane of the transfer function Z/R_m of this conductivity cell in a 1 M HCl solution. This graph is of the a type. The coherence function (Fig. 4) calculated provides a means of checking the validity of measurements and the choice of the amplitude of the excitation signal. Figure 5 shows the experimental and theoretical graphs of the impedance of the XE140 conductivity cell after modelling. After identification and synthesis in polynomial form, the following expression for the impedance was obtained:

$$Z = \frac{21.39s + 5119}{s + 13.87} \qquad (4)$$

The Cauer method was used for the synthesis of an equivalent electrical circuit of the conductivity cell [6]. This method results in a ladder circuit adapted to the case of a conductivity cell. The following values are obtained for the components of the equivalent electrical circuit shown in Fig. 6: $R_1 = 21.4\,\Omega$; $R_2 = 348\,\Omega_2$; $C_2 = 33\,\mu\mathrm{F}$.
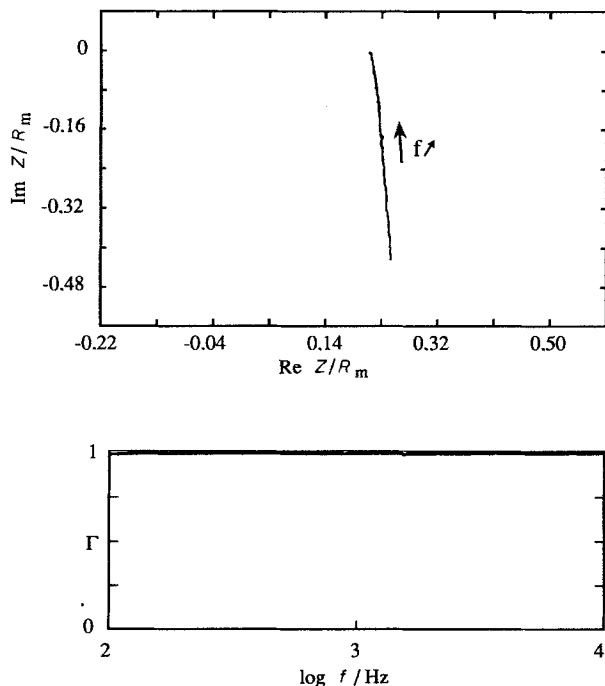

Fig. 4. Nyquist diagram of the transfer function Z/R_m for a Tacussel XE140 conductivity cell in a 1 M HCl solution ($T = 14\,°\mathrm{C}$) and coherence of the frequency response. Frequency range measurement: 100 Hz, 10 kHz.
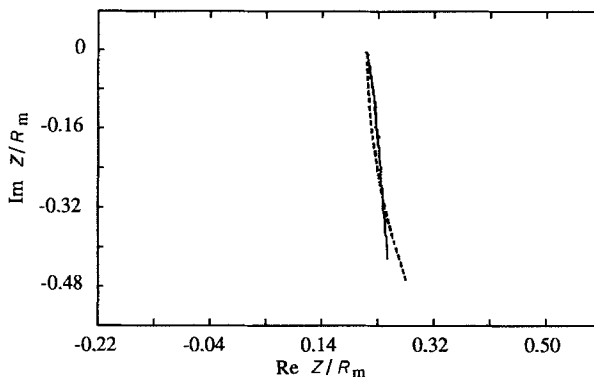

Fig. 5. Comparison between the experimental Nyquist graph and the theoretical graph obtained by modelling for the Tacussel XE140 cell in a 1 M HCl solution.

The value of the resistance of electrolyte between the two electrodes of the conductivity cell is given by that of R_1: $R_e = 21.4\,\Omega$.

As the 1 M HCl solution is a standard solution with a conductivity $\gamma(T)$ determined at various temperatures, we carried out a polynomial regression of the literature values to determine the equation giving the conductivity at intermediate temperatures [7].

$$\gamma(T) = 0.21094 + 0.00509047T - 7.1428787 \times 10^{-6}T^2 \qquad (5)$$

The value of the conductivity of the solution, calculated using Equation 5 is:

$$\gamma_{HCl\,M}(14\,°\mathrm{C}) = 0.2808\,\mathrm{S\,cm^{-1}} \qquad (6)$$

This value is used to calculate the cell constant k' in cm:

$$k' = 1/(R_e\gamma_{HCl\,M}(14\,°\mathrm{C})) = 0.166\,\mathrm{cm} \qquad (7)$$

The electrodes of the Tacussel XE140 conductivity cell are covered with platinum black and the active areas of the electrodes are larger than their geometrical areas. The value of the cell constant is greater than the value (0.1 cm) which can be calculated from the geometrical dimensions. The value of the conductivity cell constant thus determined is close to that measured by the manufacturer (0.15 cm).

3.2. Impedance diagram type b

The impedance diagram of an Electrofact 52030 annular 52030 annular type colinear conductivity cell in tap water is of the b type. Figure 7 shows the Nyquist graph of the transfer function Z/R_m and the
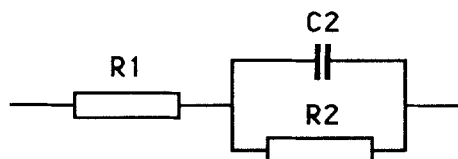

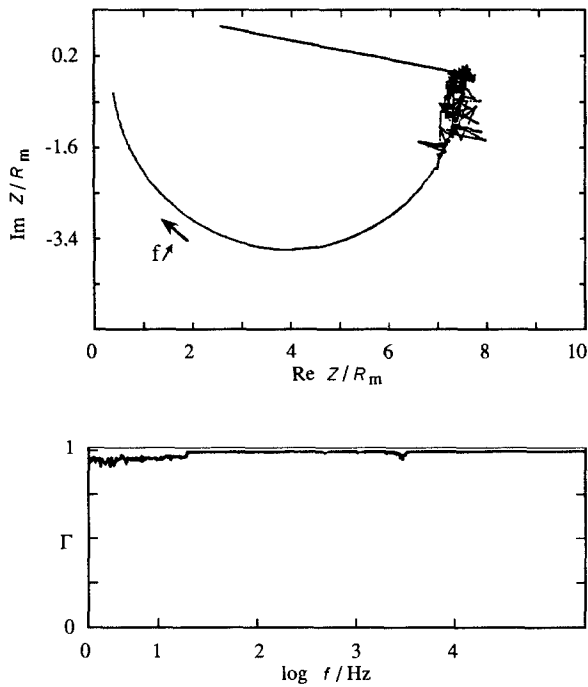Fig. 6. Equivalent electrical circuit for the Tacussel XE140 conductivity cell in a 1 M HCl solution.

Fig. 7. Nyquist diagram of the transfer function Z/R_m for an Electrofact 52030 conductivity cell and coherence of the frequency response. Frequency range measurement: 1 Hz, 100 kHz.

Fig. 9. Nyquist diagram of the transfer function Z/R_m for a Tacussel XE140 conductivity cell ($T = 14\,°C$) and coherence of the frequency response. Frequency range measurement: 100 mHz, 10 kHz.

coherence function of the measurement. The theoretical graph obtained by modelling and the experimental graph coincide (Fig. 8). After parametric identification and synthesis in polynomial form, the following expression was obtained for the cell impedance:

$$Z = \frac{4007s + 48.38 \times 10^7}{s + 6.49 \times 10^3} \qquad (8)$$

If the same Cauer representation as for type a impedance is used, the ladder equivalent electrical circuit of Fig. 6 is obtained with the following values for components:

$$R_1 = 4.01\,k\Omega; \quad R_2 = 70.5\,k\Omega; \quad C_1 = 34.8\,nF.$$

The resistance of the electrolyte solution between the two electrodes of the conductivity cell is given by the low frequency value of the impedance, that is, by
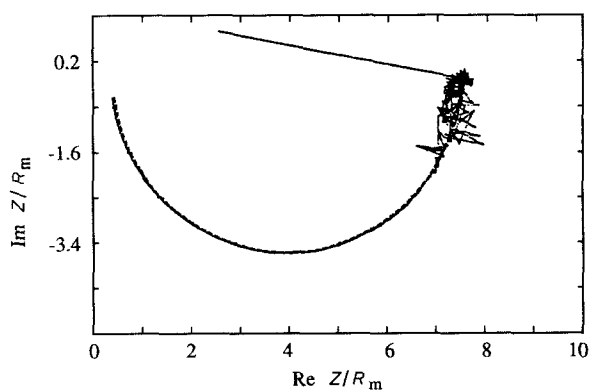

Fig. 8. Comparison between the experimental Nyquist graph and the theoretical graph obtained by modelling for the Electrofact 52030 cell in tap water.
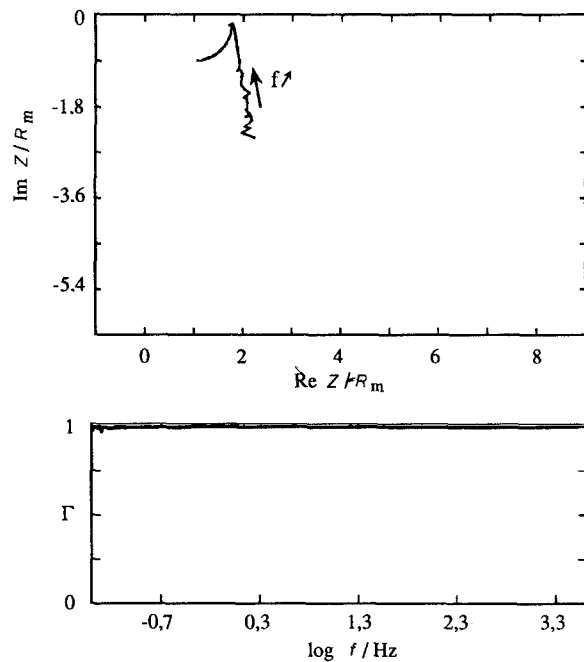
the value of the resistance R_2. The resistance R_1 is, in this case, a resistance obtained from the sum of the various extraneous resistances (contact, connecting, etc.).

$$R_e = 70.5\,k\Omega$$

The Electrofact 52030 conductivity cell constant determined in a 1 M HCl solution, is $k = 30\,cm^{-1}$. It is thus possible to determine R_e and calculate the conductivity of tap water at 14 °C:

$$\gamma_{H_2O} = k/R_e = 425\,\mu S\,cm^{-1}$$

3.3. Diagram type c

The impedance diagram of a Tacussel XE140 conductivity cell in tap water is of the c type. Figure 9 shows the Nyquist graph of the transfer function Z/R_m and the coherence function. After modelling, we compared the theoretical Nyquist graph against the experimental graph (Fig. 10). Modelling of the low frequency part is more difficult and of less interest and we used the possibility, offered by the DSA, of limiting the number of poles and zeros used for modelling. As assimilating the low frequency part to a half-circle was well suited to subsequent synthesis, we chose two poles and two zeros. After parametric identification and synthesis in polynomial form, the following expression was obtained for the cell impedance:

$$Z = \frac{3109s^2 + 42.63 \times 10^7s + 92.71 \times 10^7}{s^2 + 24.42 \times 10^3s + 10.39 \times 10^3} \qquad (9)$$

Using the Cauer method, the equivalent electrical circuit of Fig. 11 is obtained, the components of which

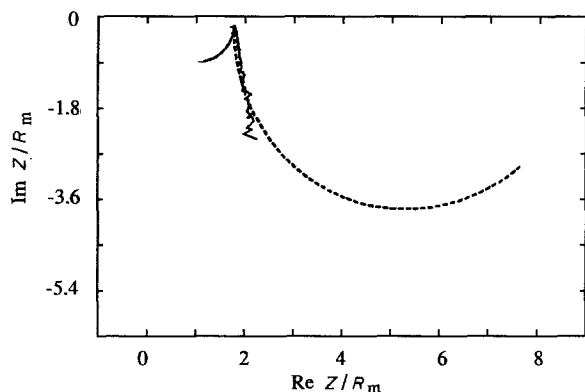Fig. 10. Comparison between the experimental Nyquist graph and the theoretical graph obtained by modelling for the Tacussel XE140 cell in tap water.

Fig. 11. Equivalent electrical circuit for the Tacussel XE140 conductivity cell in tap water.

have the following values:

$$R_1 = 3.11 \, k\Omega; \quad R_2 = 14.3 \, k\Omega; \quad R_3 = 71.8 \, k\Omega;$$

$$C_1 = 454 \, pF; \quad C_3 = 5.21 \, \mu F$$

The value of the tap water resistance measured at the maximum of the imaginary part of the impedance is that of resistance R_2.

$$R_e = 14.3 \, k\Omega.$$

The value of the Tacussel XE140 conductivity cell determined previously is 0.166 cm. Knowing the resistance and the cell constant, it is possible to determine the conductivity of tap water at 14 °C:

$$\gamma_{H_2O} = 1/(k' R_e) = 419 \, \mu S \, cm^{-1}$$

The value found was very close to the one measured with the Electrofact 52030 conductivity cell.

4. Conclusion

The resistance of an electrolyte solution can be readily measured by the DSA regardless of the form of the cell impedance graph. The main advantage of the technique is to avoid the difficult choice of the excitation signal frequency. This measurement, which may be automated, is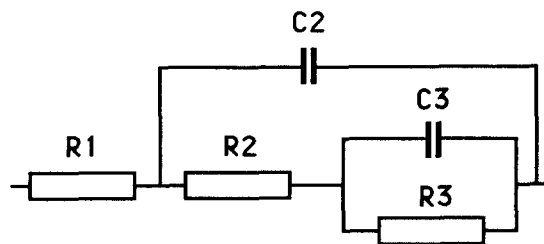 used to determine the solution when the cell constant is known. It is then possible to envisage automatic control of processes by conductivity measurement.

The use of the method described in this article makes it possible to envisage the use of conductivity cell impedance measurements continuously in industrial facilities. Indeed, a cell impedance diagram plotted over a wide frequency range provides comprehensive information regarding the dynamic behaviour of the system consisting of the conductivity cell and the electrolytic solution. It is therefore possible, by performing this measurement at regular intervals, to detect any operating discrepancy by comparison against a reference curve obtained under normal operating conditions, and to deduce whether the reason lies in electrode degradation or in a change in the measurement environment. This would be of particular interest in cases where it is difficult to measure conductivity because of problems associated with electrode contamination or rapid wear.

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