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Introduction to electrochemical impedance

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Abstract

An overview of principles of impedance in electrochemistry, some pitfalls, practical information on experimentation and data evaluation and other pertinent observations are given.

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Electrical impedance, often measured in the study of electrochemical systems, is a more general form of electrical resistance, a force that opposes the flow of electric current through a system, when a potential difference is applied to the system. The system can be an electrical component, a piece of solid material, or, in electrochemistry, a cell containing solution, electrodes and possibly a film covering these electrodes.

Electrical resistance (denoted as R) is expressed as a ratio of the applied potential (U) given in volts and the current (I) given in amperes, that flows through the system:

$$R = \frac{U}{I}. \tag{1}$$

The units of electrical resistance are ohms (Ω). A diagram, illustrating the current flowing through a resistor (R), as a result of applied potential is shown in Fig. 1a. A rectangle with about 3 to 1 ratio is the standard symbol for a resistor encountered in publications strictly adhering to the SI (metric system). North American texts sometimes still use the symbol $-\wedge\wedge-$ for a normal resistor. SI uses this symbol for the special case of a wire wound resistor.
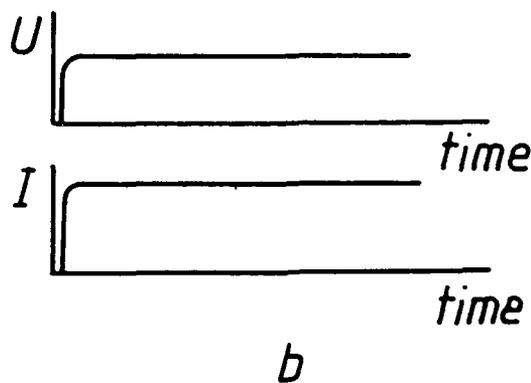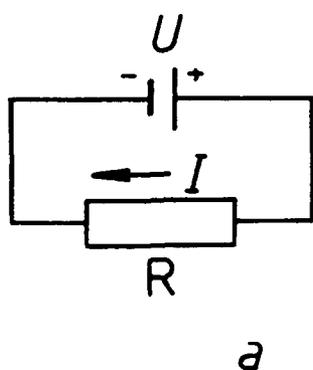

Fig. 1.

When a constant potential (usually called "direct current" (DC)) is applied to a resistor (U *vs.* I in upper part of Fig. 1b), the current will reach, almost immediately, a constant value and from then on the potential and the current will remain constant, as shown in Fig. 1b.

Alternating current (AC) is typically characterized by the fact that the magnitude of the current or the potential changes with time (t), usually as a periodic, sine, function. Thus, for instantaneous potential U,

$$U = U_{max} \sin(t) \tag{2}$$

and for current

$$I = I_{max} \sin(t) \tag{3}$$

The $_{max}$ values are the maximum values of the amplitude. It is customary and more straightforward to describe a periodic, repetitive function in the terms of its frequency (f), rather as a function of time, measured from some arbitrary point since the inception of the function, as would be the case with equations 2 and 3. The household current in North America, has frequency of 60 Hz (hertz, cycles per second). If the goniometric functions are expressed in degrees, equations (2) and (3) become

$$U = U_{max} \sin\left(\frac{2\pi \cdot f \cdot t}{360}\right) \tag{4}$$

and for current

$$I = I_{max} \sin\left(\frac{2\pi \cdot f \cdot t}{360}\right) \tag{5}$$

The current flow through a resistor, caused by alternating potential of any arbitrary frequency, is shown in Figure 2.
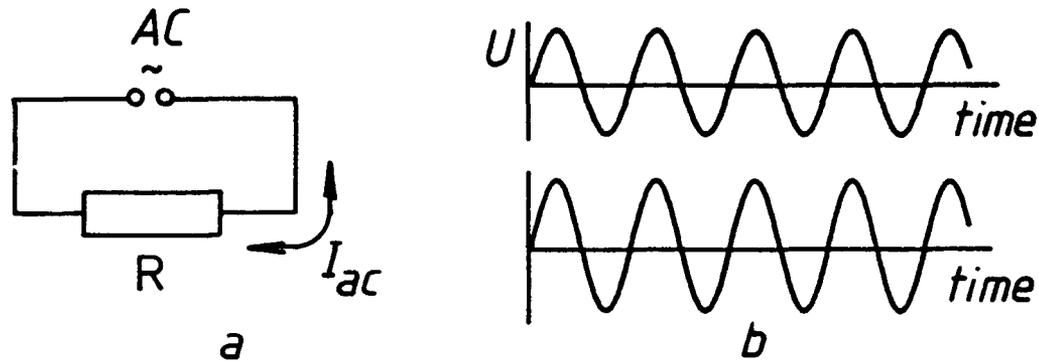
Figure 2

The resistance can be again calculated using equation (1), by taking current and potential at any given time along the time axis, except where $I = U = 0$. In practice, not the instantaneous values, but rather specially determined average values (root–mean–square) are used to calculate the resistance with the same result. Resistance of a resistor can be determined either with a DC or AC current and the result will be the same. A resistor has this special property because the potential applied across it and the current flowing through it are in–phase. That means that the current reaches its maximum at the same time as the potential does, and both cross the zero line at the same instant. This is, however, not the case in many electrical circuits containing capacitors and inductors. Such a case will for example happen in a circuit described in Fig. 3. The symbol for a capacitor are two parallel lines drawn in a way resembling two parallel plates of an air–gap capacitor. The current and the potential will be out–of–phase in this circuit. That means that the current and potential will peak at different times and there will be a lag between the two, called a phase shift (φ or θ) (Fig. 4).

$$AC$$
$$\sim$$

C   R

$10\mu F$ $1k\Omega$
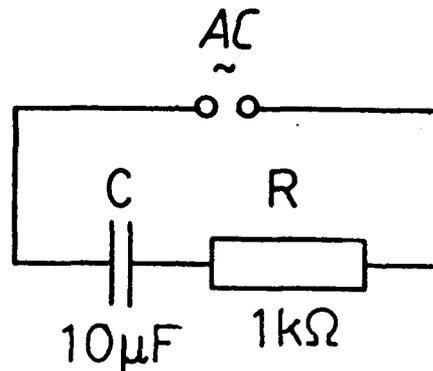
Figure 3

Figure 4

The phase shift can be expressed in units of time, but since the AC signal is periodic, it is more convenient to express the phase shift as an angle, usually in degrees.

For a circuit that displays a phase shift between current and potential, it is not possible to obtain resistance by dividing the potential by current, because the value obtained would depend on where, along the time axis the values I and U would be read. To remedy this problem, one can shift by a thought process the current along the time axis horizontally to the left or right such that its maximum is in registry with the maximum of the potential. Such a "transformed"

signal/time diagram will again yield a constant ratio of U/I, regardless of where along the time axis the ratio is obtained. However, the shift of the diagram, necessary to make the adjustment, has to be included in the description of the resistive property of the particular system. The resistance obtained for a system with a phase shift is called <u>impedance</u> and its value always consists of two components, the phase shift, denoted φ or θ, and the ratio of the U and I values, denoted $|Z|$ or sometimes just Z, and called the modulus of impedance, or often, not quite correctly, just the impedance.

A number that consists of two components can be expressed as a vector (Fig. 5).
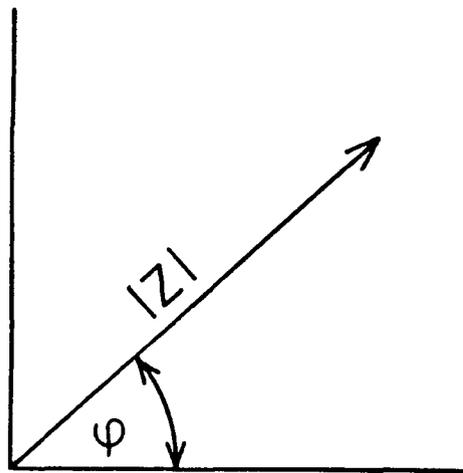
Figure 5

Therefore, impedance can be described by the means of a vector. The the phase angle of the impedance is conveniently the angle of the vector and $|Z|$ is then the length of the vector. A vector is a way of expressing a two—component number in polar coordinates. Other coordinates that are often employed and which are the most usual are the rectangular or Cartesian coordinates (Fig. 6).
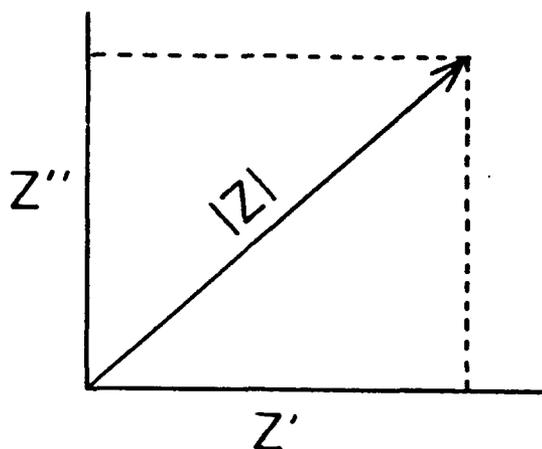
Figure 6

The $|Z|$ projection on the x and y axes are often labeled Z' and Z" (read "z prime" and "z double prime"). There is a simple conversion between the polar and rectangular coordinates, namely:

$$\frac{Z}{|Z|} = \cos\varphi \text{ and } \frac{Z''}{|Z|} = \sin\varphi \tag{6}$$

and

$$|Z| = \sqrt{Z'^2 + Z''^2} \tag{7}$$

A phase shift for a resistor is $\varphi = 0$ at all frequencies; U and I are always "in–phase." A capacitor behaves such that the current flowing through it precedes potential, and in an ideal capacitor, the phase shift is $-90°$. An inductor behaves such that current lags behind potential and for an ideal inductor the phase shift is $+90°$. Both capacitors and inductors are "out–of–phase," that is, their current and potential are out–of–phase.

Typical electrochemical systems consist of elements that can be described by various combinations of resistors and capacitors. An inductor is seldom manifested in an electrochemical system. Because of this, an electrochemical system has a behavior somewhere between a capacitor and a resistor. Moreover,

the contributions of the capacitive and resistive components change with frequency.

The resistive and capacitive components of an electrochemical system can be linked to structural and chemical features of the system. Study of impedance can thus, in connection with other supporting methods, elucidate electrochemical behavior. Because the contribution of capacitance and resistance is different at different frequencies, impedance measurements at a range of frequencies is performed and data thus obtained are used in judicious way to determine the components of the system. Such measurements are called impedance spectroscopy.

As shown, impedance can be described by two components, $|Z|$ and φ in polar coordinates and Z' and Z" in Cartesian coordinates. Algebra has a special way of expressing "two–component numbers" as complex numbers. This method has been also adopted for describing impedance. The x coordinate of the Cartesian projection is considered the real part of the complex number, called the "real" impedance, Z_r or Z', the y component is the imaginary component of the complex number, called the "imaginary" impedance, Z_{im} or Z", and the total impedance, Z, can be written as x+iy or Z_r+jZ_{im}. The symbols i and j are both imaginary units ($= \sqrt{-1}$); j is preferably used in electrical engineering. Note that there is nothing <u>imaginary</u> about Z_{im}. It is just a means of indicating that the two parts are out of phase. Perhaps more adequate is to call Z_r the in–phase and Z_{im} the out–of–phase impedance.

It is at first useful to consider impedance of pure, single component systems. The impedance of a resistor (R) (Fig. 7) is equal to its resistance

$$|Z| = R. \tag{8}$$
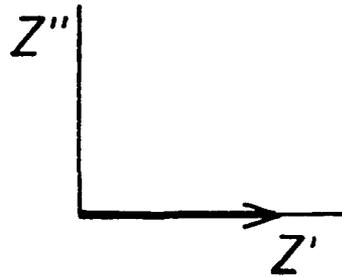
Figure 7

There is no phase shift and the impedance value is independent of frequency. Figure 7 shows a vector that corresponds to a pure resistor.

A capacitor (C) has an impedance which is -90° out–of–phase (Fig. 8). Its value can be expressed as

$$|Z| = \frac{-j}{\omega C}, \tag{9}$$

where $\omega = 2\pi f$.
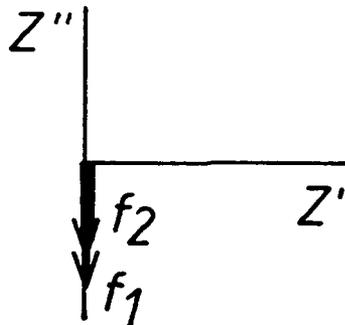
Figure 8

The negative sign is a convention that comes from electrical engineering, where the phase of the potential (lagging behind) is related to the current. Whereas the convention is somewhat arbitrary, it is important to use the signs consistently and correctly. The impedance of a capacitor is dependent on frequency, As shown in Figure 8, the impedance is larger for a lower frequency $(f_1 < f_2)$. It is infinite for f=0, i.e., a DC current.

An inductor (L) has a phase shift of $+90^O$ (Figure 9) and its impedance can be calculated as:

$$|Z| = j\omega L, \quad \text{where } \omega = 2\pi f. \tag{10}$$

The impedance of an inductance also depends on frequency, but inversely that capacitance. It increases with increasing frequency, as shown in the Figure 9 for for $f_1 < f_2$.
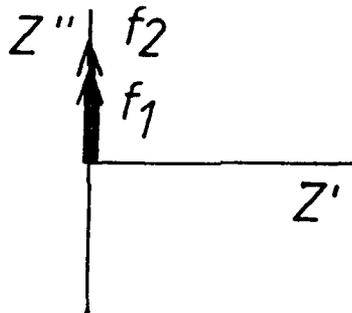
Figure 9

Electrochemical systems are most likely composed or modeled from resistors and capacitors and inductance appears only seldom. Such circuits are represented by a vector in the fourth quadrant in Cartesian projection. Therefore, for convenience, it is usual to plot the negative Z'' upwards, which then puts most impedance plots in the first quadrant.

Calculating the impedance of a circuit.

Two impedances in a series can be combined mathematically as a sum of the two impedances

$$Z_{total} = Z_1 + Z_2. \tag{11}$$

The rules for adding complex numbers (adding the real parts and the imaginary parts separately together) apply. Two impedances in parallel can be added as

reciprocal values:

$$\frac{1}{Z_{total}} = \frac{1}{Z_1} + \frac{1}{Z_2} \quad \Rightarrow \quad Z_{total} = \frac{Z_1 \cdot Z_2}{Z_1 + Z_2} \tag{12}$$

R 1000 Ω

C 10 μF
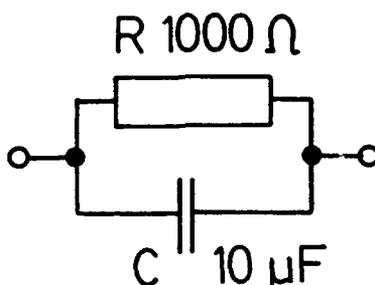
Figure 10

Let us solve the impedance of the circuit shown in Fig. 10. $Z_C = \frac{-j}{\omega C}$ and $Z_R = R$ (eq. 8 and 9). Therefore the impedance of the circuit, Z_{total}, can be expressed as:

$$\frac{1}{Z_{total}} = \frac{1}{Z_C} + \frac{1}{Z_R} = \frac{\omega C}{-j} + \frac{1}{R} = \frac{\omega RC - j}{-jR} \tag{13}$$

$$\Rightarrow \quad Z_{total} = \frac{-jR}{\omega RC - j} \tag{14}$$

In the next step, which may be rather tedious if the circuit is more complicated, we shall separate the real and imaginary components. First, a trick is employed to eliminate imaginary components from the denominator of the fraction. Recall that $(a+b)(a-b) = a^2 - b^2$ and therefore $(a+j)(a-j) = a^2 + 1$. Expression (14) can be simplified by multiplying first the numerator and the denominator by $\omega RC + j$. That will yield:

$$Z_{total} = \frac{1 - j\omega R^2 C}{\omega^2 R^2 C^2 + 1} \tag{15}$$

from which the real and imaginary components can be separated:

$$Z_r = \frac{R}{\omega^2 R^2 C^2 + 1} \tag{16}$$

$$Z_{im} = \frac{-\omega R^2 C}{\omega^2 R^2 C^2 + 1} \tag{17}$$

It is important to note that for $\omega \to 0$, $Z_r = R$; for $\omega \to \infty$, $Z_r = 0$, whereas both for $\omega \to 0$ and $\omega \to \infty$, $Z_{im} = 0$. The dependence of a real and imaginary component on the logarithm of frequency is shown in Fig. 11.
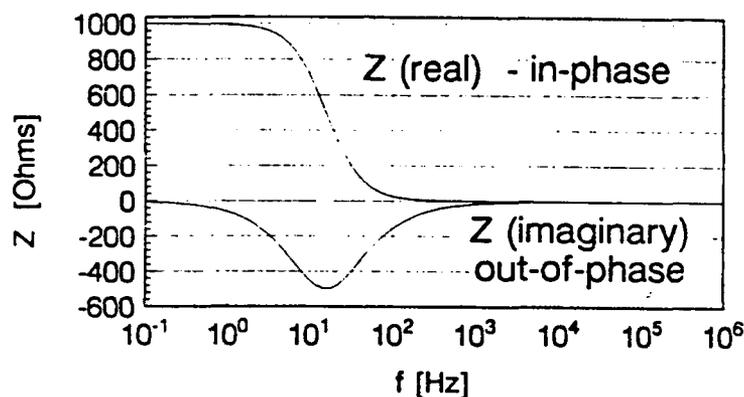
Figure 11

The maximum on the graph of the imaginary value can be calculated by taking a derivative of Z_{im}, $\frac{\partial(Z_{im})}{\partial \omega}$ and equating it to zero. The calculation will yield for the ω with the highest value of Z_{im} a simple relationship $\omega = \frac{1}{RC}$. The product of resistance and capacitance (RC), that has a dimension of time, is called the time constant of a parallel circuit.

There are several ways of plotting the impedance results in a graph. One possibility is to plot, in two associated graphs, the modulus of impedance and the phase angle as a function of logarithm of frequency. The logarithmic scale of frequency is convenient since it readily covers a broad frequency range. A result for

an RC circuit described above in Fig. 10, with R=1000 Ω and C=10 μF, is shown

in Figure 12. The analytical expression describing $|Z|$ is

$$|Z| = \sqrt{\frac{R^2 + \omega^2 R^4 C^2}{(\omega^2 R^2 C^2 + 1)^2}} \tag{18}$$

For low ω ($f \to 0$), $|Z| = R$, which explains the constant value to the left. For high

ω, $|Z| = \frac{1}{\omega C}$.
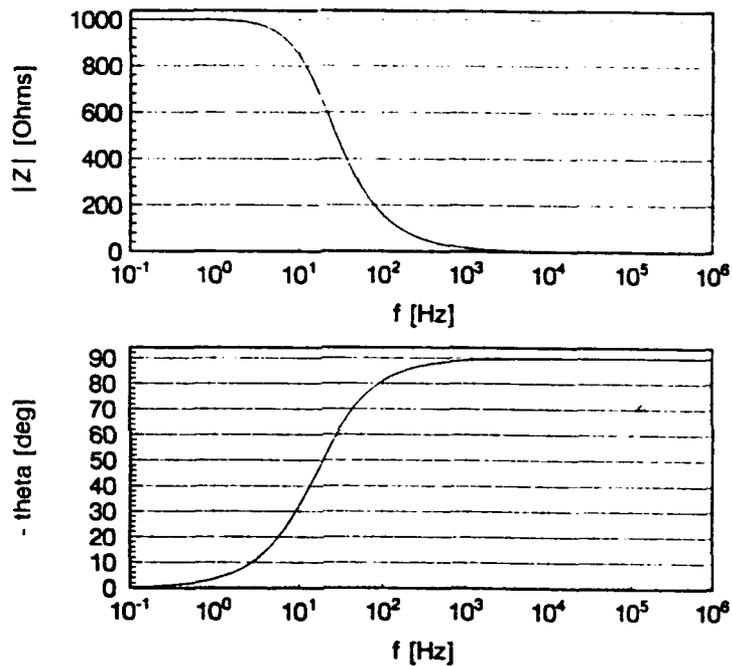
Figure 12

Often it is more convenient for the purpose of easy analysis of the data to

plot instead the logarithm of $|Z|$ versus log f, rather then just vs. $|Z|$. Such a

graph, accompanied by a phase angle diagram (Fig. 13) is called a Bode plot.
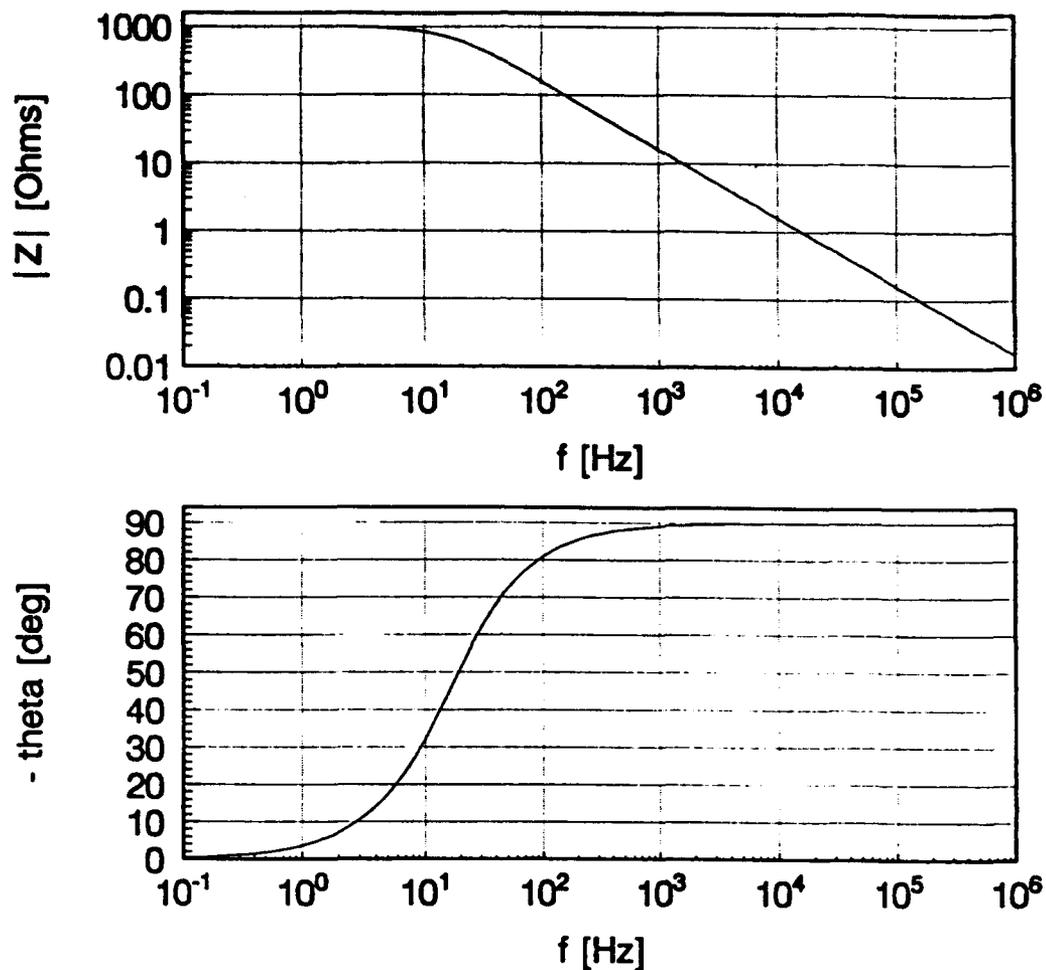
Figure 13 (Bode plot)

For low ω, log $|Z|$ will again be a constant, because log $|Z|$ = log $|R|$. At higher frequencies, log $|Z|$ = $-$log(ω) $-$ log(C). Therefore, the slope of the line will be -1. In Bode plots, a straight line with a slope of -1 is used as an indication that the impedance data are originating from a parallel RC circuit. By extrapolating the line to $\omega=1$, the value of capacitance can be determined.

Another extremely popular display of impedance data is to plot the out–of–phase versus the in–phase impedance (Figure 14).
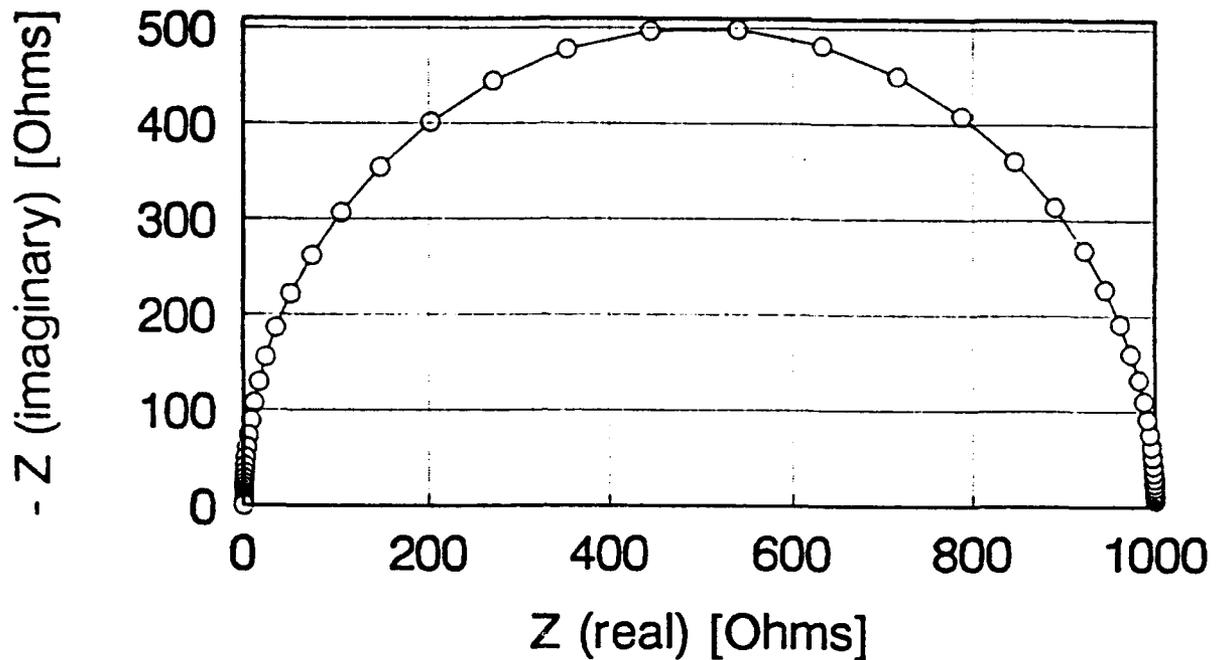
Figure 14 (Nyquist diagram)

It is quite useful for the purpose of quick visual evaluation that both the axes have the same scale. Such a plot is called a Nyquist plot, an Argand diagram, a complex plane impedance plot, or simply a Z–Z plot. By rearranging the impedance results for the RC parallel circuit, it can be shown that

$$(Z_r - \tfrac{R}{2})^2 + Z_{im}^2 = \frac{R^2}{4} \tag{19}$$

which is an equation of a circle, with the center at (0,R/2) and the radius equal to R/2.

Therefore, as long as the axes are of equal scale, the appearance of the semicircle in the Argand diagram signifies the existence of a parallel RC circuit. Again, ω which corresponds to the frequency at the apex of the semicircle is inversely proportional to RC ($\omega = \frac{1}{RC}$), where RC is the time constant of the

network. The value of the resistance R can be easily determined directly from the diameter of the semicircle (1000 Ω in the illustrated case).

It is rare that a simple circuit is all what is needed for data analysis. A few more details will be given later in this chapter, when the nonlinear fitting process is outlined. Here we illustrate just one example of a more complicated circuit. It consists of two parallel RC circuits, connected is series, with yet another resistor in series (Fig. 15). It is not particularly rare to encounter electrochemical cell, whose response would correspond to such circuit.
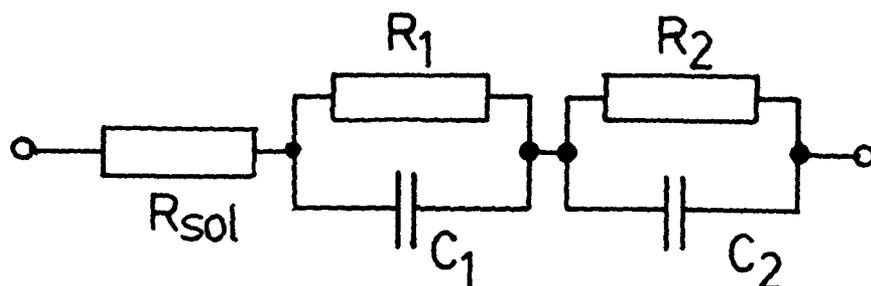
Figure 15

First resistor (R_{sol}) will in electrochemistry almost invariably represent the solution resistance. One of the RC circuits then can represent the double–layer and the second RC might be, for example, a contribution of a film on the electrode surface. The common wisdom teaches, that if the time constants ($\tau=RC$) of the two RC circuits differ by two orders of magnitude or more, than two distinct semicircles will be formed on the Nyquist plot (Fig. 16). It cannot be predicted which of the semicircles is the one stemming from the double–layer response. The ordering of the semicircles depends on their time constants. The circle with the shorter time constant will be the one on the left.
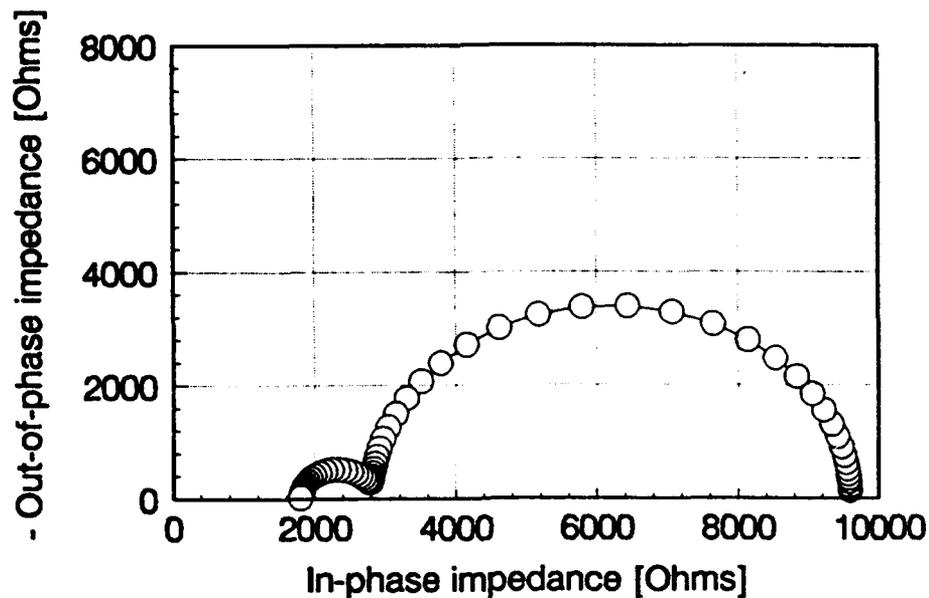
Figure 16

The distance form the coordinate origin to the beginning of the first circle corresponds to the solution resistance R_{sol}. The diameters of the semicircles corresponds to the resistors in the parallel RC circuits and the apexes of the semicircles follow the relationship $(\omega = \frac{1}{RC})$. If the time constants are close to each other, the two semicircles will merge into each other. More of such examples are illustrated in the catalog of the impedance responses, attached to this report.

Admittance, modulus and complex permittivity representations

The Bode and Nyquist plots are the most usual, but there is a number of other possibilities for displaying results. In many cases where capacitance is the predominant term, the Nyquist plot (real *vs.* imaginary impedance) shows essentially a straight line, with emphasis on the low frequencies. Any graphical detail stemming from the high frequencies is therefore lost. One way how to closely examine the contribution from the high frequencies is to plot data in a manner similar to the Nyquist plot, but to use, instead of real and imaginary impedance, the corresponding real and imaginary admittance. Since an impedance analyzer usually provides real and imaginary impedance, a conversion must be made first. Whereas it holds that $Y=1/Z$ a mistake would be to assume that Y_r is equal to $1/Z_r$. The correct relationship is for the real components:

$$Y_r = \frac{Z_r}{Z_r^2 + Z_{im}^2} \tag{20}$$

and for the imaginary

$$Y_{im} = \frac{-Z_{im}}{Z_r^2 + Z_{im}^2} \tag{21}$$

An example is shown in Figures 17 and 18. Actual data obtained for impedance study of iridium oxide (IR4–48.z) are given in both representations. In this case it can be seen that the data points in the Y–Y representation (Fig. 17) are displayed more evenly and almost all (72 in this experiment) can be accounted for, whereas in the Z–Z representation (Fig. 18), the high frequency data are clustered together and only about 20 points at the low frequency end can be distinguished.
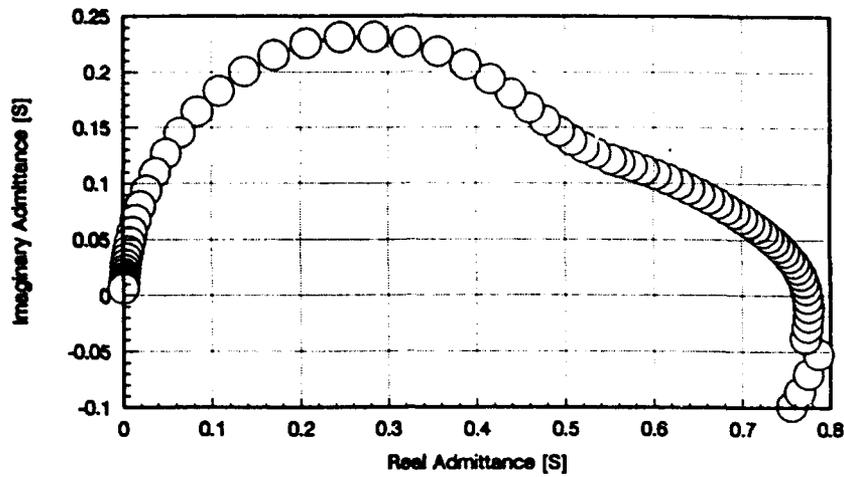
Figure 17
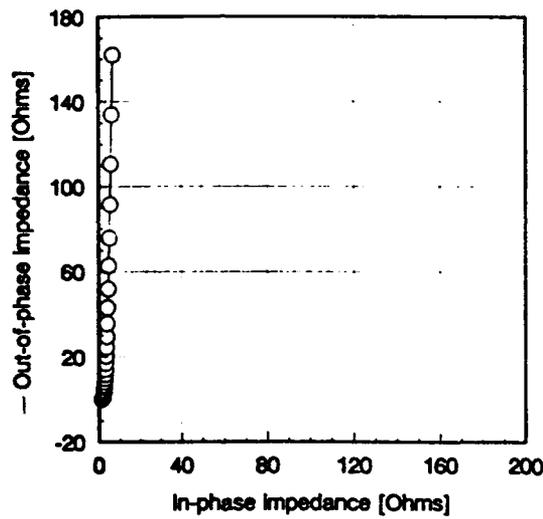
Figure 18

A popularly used representation is that called the "Modulus" or pseudo complex modulus $M(\omega)$ which is the complex inverse of the dielectric response ϵ (vide infra). It is defined as

$$M(\omega) = 1/\epsilon = 1/(\epsilon' + j\epsilon'') =$$

$$= \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_{im}^2} - \frac{j\epsilon_{im}}{\epsilon_r^2 + \epsilon_{im}^2} \tag{22}$$

Example of its graphical representation is shown in Fig. 19.
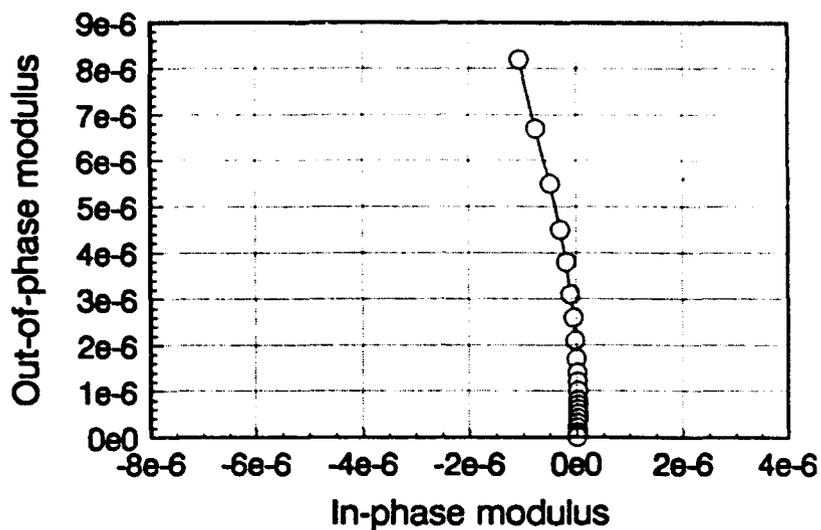
Figure 19

Another useful representation is that of the pseudo complex permittivity
(dielectric response) ϵ used in the modulus definition (Fig. 20).
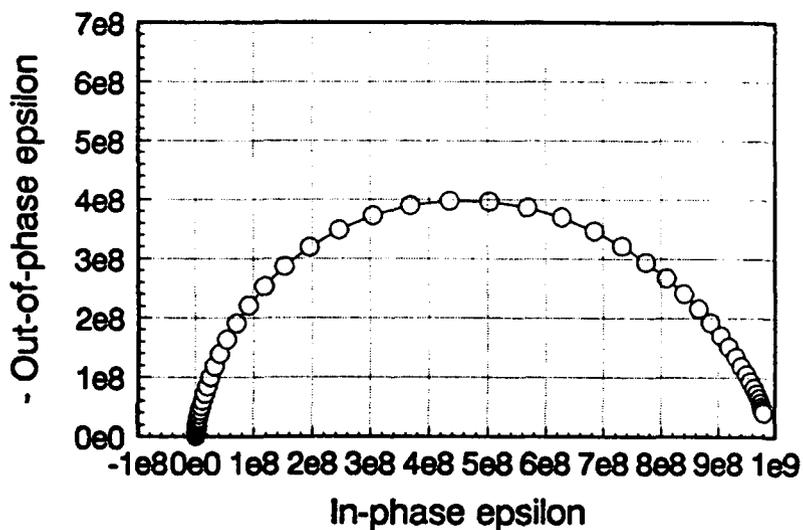
Figure 20

It is assumed, when this representation is used, that the measured response
is due to a capacitor with a dielectrics with complex permittivity. Thus, from the
impedance data it is solved what the permittivity would be. Since this calculation
can be done even if the response has nothing to do with permittivity of a capacitor,

it is aptly called pseudo permittivity. It is obtained from the admittance by:

$$\epsilon = \frac{Y}{j\omega C_c} = \frac{Y_{im}}{j\omega C_c} - \frac{jY_r}{j\omega C_c} \tag{23}$$

With

$$\epsilon = \epsilon_r + j\epsilon_{im} \tag{24}$$

where ϵ is the permittivity of the system, ω is the circular frequency and C_c is a capacitance of an empty cell. For the examples in Fig. 19 and 20 $C = 10^{-11}$ F was used. (Note, the definitions of M and ϵ are from personal communication by B. Boukamp and follow his EQUIVCRT program. There could be another, different , definition in the literature.) A very good book on the subject of impedance spectroscopy is J. Ross Macdonald, "Impedance Spectroscopy, Emphasizing solid materials and systems", Wiley, New York 1987.

It should be noted that a number of representation, only limited by the imagination of the person willing to do the transformations, can be used to observe data and some of them may be more helpful than others for understanding the impedance data. But the ultimate step of impedance measurement rests in the data evaluation and interpretation of the results.

Data fitting:

Unlike other electrochemical techniques, interpretation of impedance data in electrochemistry is still in its infancy, although the method is well in its adolescent years. Impedance spectra are extremely rich in information, interpretation is not always straightforward and often, experimental artefacts creep in the results and make interpretations often impossible or incorrect. With the advent of digital impedance instruments, the volume of data obtained per experiment has increased tremendously. It is essential to treat the numbers with

respect and caution. The change in fifth significant figure, easily readable on many modern instruments, is not always significant.

There is a lot of literature that describes the use impedance spectroscopy in monitoring changes in certain property, such as degradation of paints, etc. In many cases interpretation is not given. As long as a standard is used for comparison, impedance is a valuable tool. A physical chemist in heart will want to derive more from the data than just parametric changes.

Some of the ways of interpreting will be described later.

A useful software for the evaluation is the EQUIVCRT.PAS written by Bernard Boukamp. The manual, accompanying the program contains a lot of important suggestions. As of February 1994 we have available an updated version of this software. It allows screen dumps on a laser printer and it also has a subprogram, that allows to calculate the Kramers–Kronig transformation, a test that is deemed important for ascertaining that the evaluated fits are correct.

A special volume of Electrochimica Acta (No. 14, Vol. 38, 1993) edited by Digby D. Macdonald is devoted to impedance spectroscopy and provides lot of useful material for understanding of the method.

IMPEDANCE OF THE ELECTROCHEMICAL INTERFACE

The purpose of the electrochemical impedance spectroscopy is to, ultimately, unearth the secrets of the electrochemical interface, therefore, the electrochemical phenomena that give a rise to impedance response have to be well understood.

Let us at first consider a general reversible reduction reaction

$$Ox + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Red \tag{25}$$

where k_f and k_b are the forward and backward reaction rates. Here we consider the simple "electroanalytical" process, where oxidized form of the species, Ox, diffuses to the electrode and the reduced form, Red, diffuses away from the electrode, unhindered by preceding or subsequent reactions. Also, mass transport is due only by diffusion, thus migration and convection are considered to be negligible. For a planar electrode, the concentration c_r and c_o of species Ox and Red are described by the Fick's law

$$\frac{\partial c_o}{\partial t} = D_o \frac{\partial^2 c_o}{\partial x^2} \tag{26}$$

$$\frac{\partial c_r}{\partial t} = D_r \frac{\partial^2 c_r}{\partial x^2} \tag{27}$$

The species diffuses perpendicularly to the planar electrode in the direction x.

The initial conditions are:

$$t = 0 \ x \geq 0 \quad c_o(x,0) = c_o^* \text{ (bulk conc.)} \quad c_r(x,0) = c_r^* \text{ (bulk conc.)}$$

and the boundary conditions

$$t \geq 0, x \to \infty \quad c_0(x,t) \to c_0^* \quad c_r(x,t) \to c_r^* \tag{29}$$

$$x = 0, \quad D_0 \frac{\partial c_0}{\partial x}(0,t) = -D_0 \frac{\partial c_r}{\partial x}(0,t) = \frac{I_F(t)}{nFA}. \tag{30}$$

The faradaic current I_F is also given by the heterogeneous kinetics law

$$I_F(t) = nFA(k_f c_0(0,t) - k_b c_r(0,t)) \tag{31}$$

where

$$k_f = k_f^* \exp(-anFE/RT) \tag{32}$$

and

$$k_b = k_b^* \exp((1-a)nFE/RT) \tag{33}$$

At the standard potential E^O the forward and the reverse reaction rates are constant and equal

$$k_f^* \exp(-anFE/RT) = k_b^* \exp((1-a)nFE/RT) = k_s \tag{34}$$

and for the faradaic current the Butler–Volmer relationship is obtained:

$$I_F = nFAk_s[c_0(0,t)\exp(\frac{-anF(E-E^O)}{RT}) - c_r(0,t)\exp(\frac{(1-a)nF(E-E^O)}{RT})]$$

and

$$E^O = \frac{RT}{nF} \ln \frac{k_f^O}{k_b^O} \tag{36}$$

at the equilibrium potential E_{eq} the overall faradaic current is zero. The exchange current is given as

$$\frac{I_0}{nFA} = k_f(E_{eq})c_0(0,t) = k_b(E_{eq})c_r(0,t) \tag{37}$$

Without a net current flowing, there is no concentration gradient at the electrode surface, thus the expression for exchange current can be written as:

$$I_o = nFAk_f^o c_o^* \exp(-anFE_{eq}/RT) = nFAk_b^o c_r^* \exp((1-a)nFE_{eq}/RT)$$

In impedance studies a perturbing potential is applied and response of the current is measured. A small perturbation $\Delta E \exp(j\omega t)$ leads to changes in $\Delta I_F \exp(j\omega t)$, that can be obtained by differentiating equations (31), (26) and (27).

$$\frac{\Delta I_F}{nFA} = \frac{-anF}{RT}k_f\overline{c_o(0)}\Delta E + k_f\Delta c_o(0) - \frac{(1-a)nF}{RT}k_b\overline{c_r(0)}\Delta E - k_b\Delta c_r(0) \tag{39}$$

and

$$j\omega\Delta c_i(z) = D_i\frac{\partial^2\Delta c_i(x)}{dx^2} \tag{40}$$

where Δc_i is a small variation in c_i, where i represents suffix o or r. The concentrations denoted by a bar are the concentrations of the species for dc polarization, such that

$$c_i(x,t) = \overline{c_i(x)} = \Delta c_i(z)\exp(j\omega t) . \tag{41}$$

Equations (39) and (40) lead to two important concepts in electrochemical impedance — the charge transfer resistance and the Warburg impedance.

Charge transfer resistance

The charge transfer resistance R_{ct} is defined by:

$$1/R_{ct} = (\partial I_F/\partial E)_{c_i} \qquad (42)$$

It is important to realize that the concept of R_{ct} is valid even for a system at equilibrium potential, where there is no current flow. An infinitesimal change in potential will cause current flow which will lead to a (noninfinite) value of R_{ct}. Equation (42) can be rewritten with the help of equation (31) to the form

$$1/R_{ct} = \frac{nF}{RT}(-ak_f\overline{c_o} - (1-a)k_b\overline{c_r})nFA \qquad (43)$$

where $\overline{c_o}$ and $\overline{c_r}$ are c_o and c_r at the surface of the electrode at $t \to \infty$.

This equation allows to obtain kinetic parameters for an electrochemical process. When the system at equilibrium (no net current flow), a simple relationship useful for measurement of exchange current is found:

$$R_{ct} = (RT/nF)(1/I_o) \qquad (44)$$

For an ideally reversible process, where $I_o \to \infty$ the R_{ct} will tend to zero.

The Warburg impedance

Differential equation (40) allows to calculate the resulting concentration perturbation $\Delta c_i(0,t)$ that results from the potential perturbation during impedance measurement. The perturbation has to do not only with the applied

perturbing signal, but also with the electrode surroundings. Diffusion will replenish the ions lost to electrochemical change, but the replenishment will not be infinitely fast. The case of an electrode with processes limited by charge transfer and by diffusion to and from infinity (actually, several cm from the electrode constitutes the case) gives the following relationships

$$\frac{\Delta c_o(0)}{\Delta I_F} = -\frac{1}{nFA\sqrt{j\omega D_o}} \tag{45}$$

$$\frac{\Delta c_r(0)}{\Delta I_F} = \frac{1}{nFA\sqrt{j\omega D_r}} \tag{46}$$

Combining these two equations (45) and (46), plus equation (39) one obtains

$$\Delta I_f = \frac{1}{R_{ct}}\Delta E - (\frac{k_f}{\sqrt{D_o}} + \frac{k_b}{\sqrt{D_r}})\frac{\Delta I_F}{\sqrt{j\omega}} \tag{47}$$

For impedance one obtains

$$Z(\omega) = \frac{\Delta E}{\Delta I_F} = R_{ct}(1 + \frac{\lambda}{\sqrt{j\omega}}) \text{ where } \lambda = \frac{k_f}{\sqrt{D_o}} + \frac{k_b}{\sqrt{D_r}} \tag{48}$$

In this equation $R_{ct}\lambda/\sqrt{j\omega}$ is usually called the Warburg impedance.

When this complex number is split in its real and imaginary components, one gets:

$$Z_r = Z_{im} = \frac{R_{ct}\lambda}{\sqrt{2\omega}} \tag{49}$$

The charge transfer resistance and the Warburg impedance are forces impeding current flow that are often encountered together. Taking into account also solution resistance and the double layer capacitance, a circuit that often satisfactorily describes and electrochemical system is found in the form of the so called Randles circuit (J. E. B. Randles, Trans. Faraday Soc., 44, 327–228 (1948)) (Figure 19).
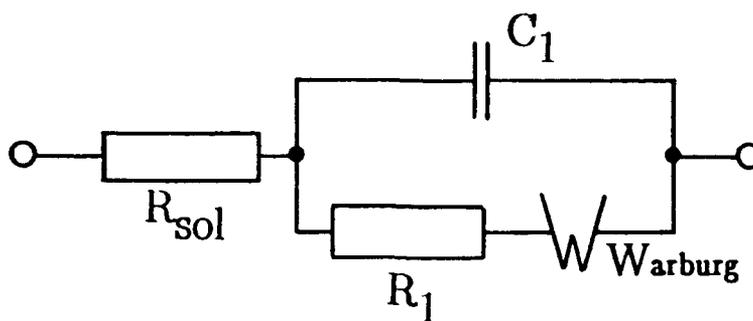
Figure 19

This circuit is often mentioned in various data fits. It is a circuit that would be denoted in the notation of the Boukamp's data fitting program as R(C(RW). R_{sol} is the solution resistance, R_1 is the charge transfer reaction resistance, C is the double–layer capacitance and W is the infinite–length Warburg impedance. The pertinent references are: original Randles paper: J. E. B. Randles: Kinetics of rapid electrode reactions, Disc. Faraday Soc. 1, 11–19 (1947). Appreciable discussion on relevance of this circuit is touted to be in J. R. Macdonald: Electrical response of materials containing space charge with discharge at the electrodes. J. Chem. Phys., 54, 2026–2050 (1971).

The Nyquist diagram for a Randles circuit with $R_{sol}=100$ Ω, $R_1=1000$ Ω, $C_1=1$ μF and $W=10^{-4}$ s$^{-1/2}$ shown in Fig. 20.
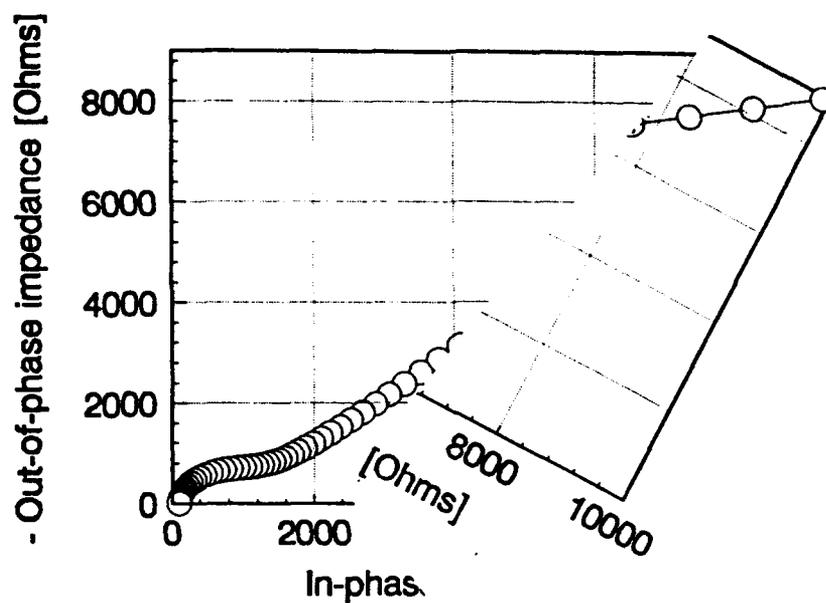
Figure 20

Catalog of simulated responses.

(This work was done by Giselle Sandí as part of her thesis work under advisement of Petr Vanýsek).

For a novice in the field of impedance studies, the assignment of an appropriate equivalent circuit can be a bewildering experience. Whereas no perfect fit seems to be ever found for data stemming from actual measurements, a number of fairly good fits can be found. These fits can have quite different equivalent circuits and may not well represent any perceived real behavior. Practitioners in the field of impedance have the same experience. For them, it is not as much a bewildering encounter as a matter of life. The most appropriate approach to resolve the ambiguity of available circuits is to match particular models to a microscopic model of the interface and see how well each element in the model can be understood as a physical or chemical process occurring in the system. With availability of data fitting programs it is useful to explore how inclusion of a particular element, or its change, in a circuit, will affect the appearance of the Nyquist plot. With enough plots encountered in daily practice, it may be possible by visual screening to decide which circuits are likely to be studied and which should be excluded from further consideration.

The following catalog is a collection of 12 plates showing effect of two parameters of a given fit changing, while the rest is kept constant. The representation is that used by the Boukamp's program; the simulations were also obtained from the program.

The elements in the simulations are resistors (R), capacitors (C), constant phase elements (Q) and hyperbolic tangent element (T), appearing in finite length diffusion considerations.

Table 1

Description of the circuits and parameters used, obtained using Boukamp program.

Circuit Configuration	Constant Parameters	Variable Parameters
(RQ)	$R = 1\ k\Omega$	$Q = [0.01, 100]\ \mu Ss^a$ $n = [0.1,\ 0.9]$
(RQ)	$Q = 1\ \mu Ss^a$	$R = [10,\ 10^5]\ \Omega$ $n = [0.1,\ 0.9]$
$(R_1C_1)(R_2C_2)$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$	$C_2 = [0.01,\ 100]\ \mu F$ $R_2 = [10,\ 10^5]\ \Omega$
(RT)	$B = 10^{-5}\ s^{1/2}$	$R = [10,\ 10^5]\ \Omega$ $T = [0.01, 100]\mu Ss^{1/2}$
$R_1(C_1(R_2C_2))$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$	$C_2 = [0.01,\ 100]\ \mu F$ $R_2 = [10,\ 10^5]\ \Omega$
$R_1(R_2C)$	$R_1 = 1\ k\Omega$	$C = [0.01,\ 100]\ \mu F$ $R_2 = [10,\ 10^5]\ \Omega$
$(R_1C_1)(R_2Q)$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$ $n = 0.4$	$Q = [0.01, 100]\ \mu Ss^a$ $R_2 = [10,\ 10^5]\ \Omega$
$(R_1C_1)(R_2Q)$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$ $n = 0.5$	$Q\ [0.01, 100]\mu Ss^a$ $R_2 = [10,\ 10^5]\ \Omega$
$(R_1C_1)(R_2Q)$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$ $n = 0.6$	$Q = [0.01, 100]\ \mu Ss^a$ $R_2 = [10,\ 10^5]\ \Omega$
$(R_1C_1)(R_2Q)$	$R_1 = 1\ k\Omega$ $C_1 = 1\ \mu F$ $n = 0.7$	$Q = [0.01, 100]\ \mu Ss^a$ $R_2 = [10,\ 10^5]\ \Omega$
RQ	$n = 0.9$	$Q = [0.01, 100]\ \mu Ss^a$ $R = [10,\ 10^5]\ \Omega$
$R_1Q_1(R_2Q_2)$	$R_1 = 110\ \Omega$ $Q_1 = 1\ \mu Ss^a$ $n_1 = 0.9$ $n_2 = 0.6$	$R_2 = [10,\ 10^5]\ \Omega$ $Q_2 = [0.01, 100]\mu Ss^a$

KEY TABLE

Orientation of the axes,
impedance in ohms.

Circuit diagram

Common parameters
of the plate

$R = 1\ k\Omega$

$f = 1\text{-}100000\ Hz$

8 points per decade

-Z Im [Ω]

Z real [Ω]

R

Q

Variable parameters

$Q\ [\mu S s^{n}]$

n

500.0

100 Hz

10 Hz

1 Hz

100000 Hz

0.0

0.0

1000.0

$R = 1\ k\Omega$

$f = 1\text{-}100000\ Hz$

8 points per decade of frequency

R

Q

$-Z_{img}\ [\Omega]$

$z_{real}\ [\Omega]$

$n \rightarrow$

0.1 0.3 0.5 0.7 0.9

$Q\ [\mu Ss^n]$

0.01

0.1

1

10

100
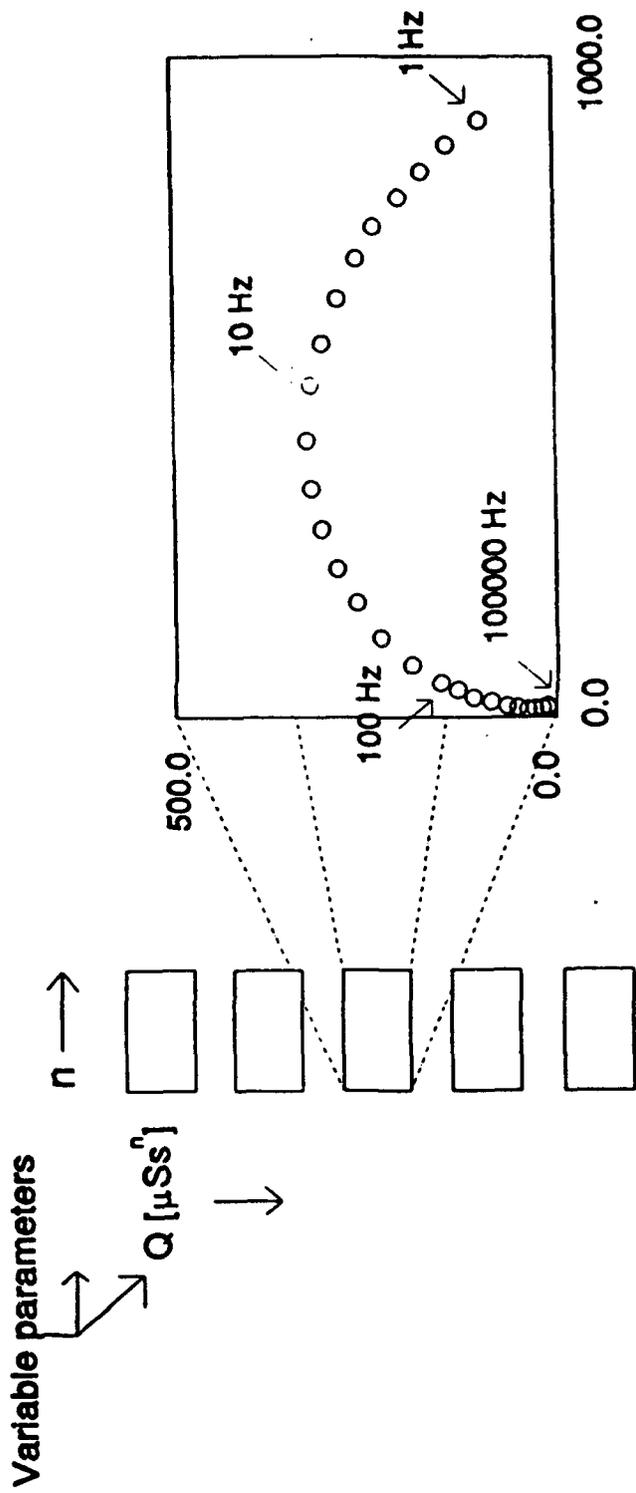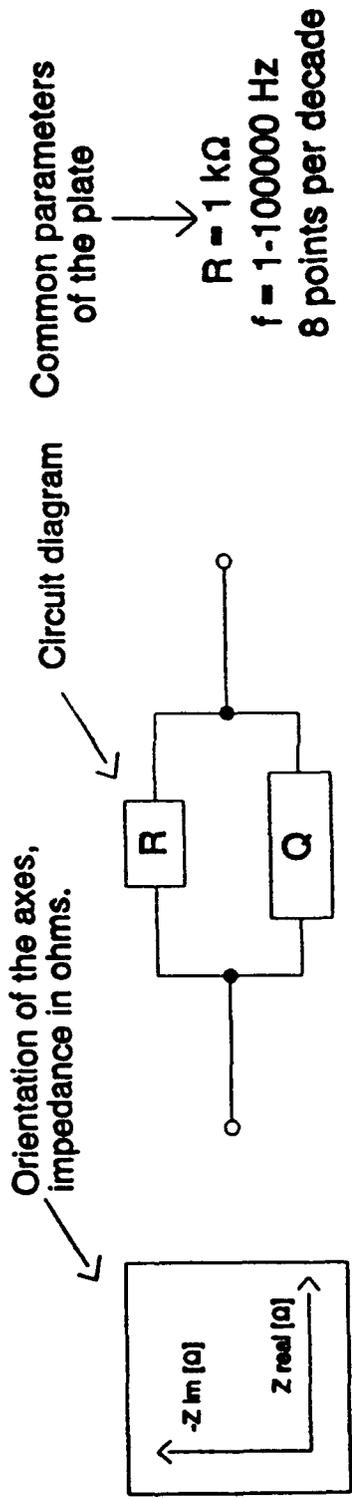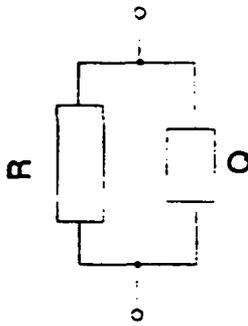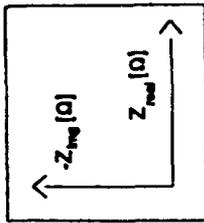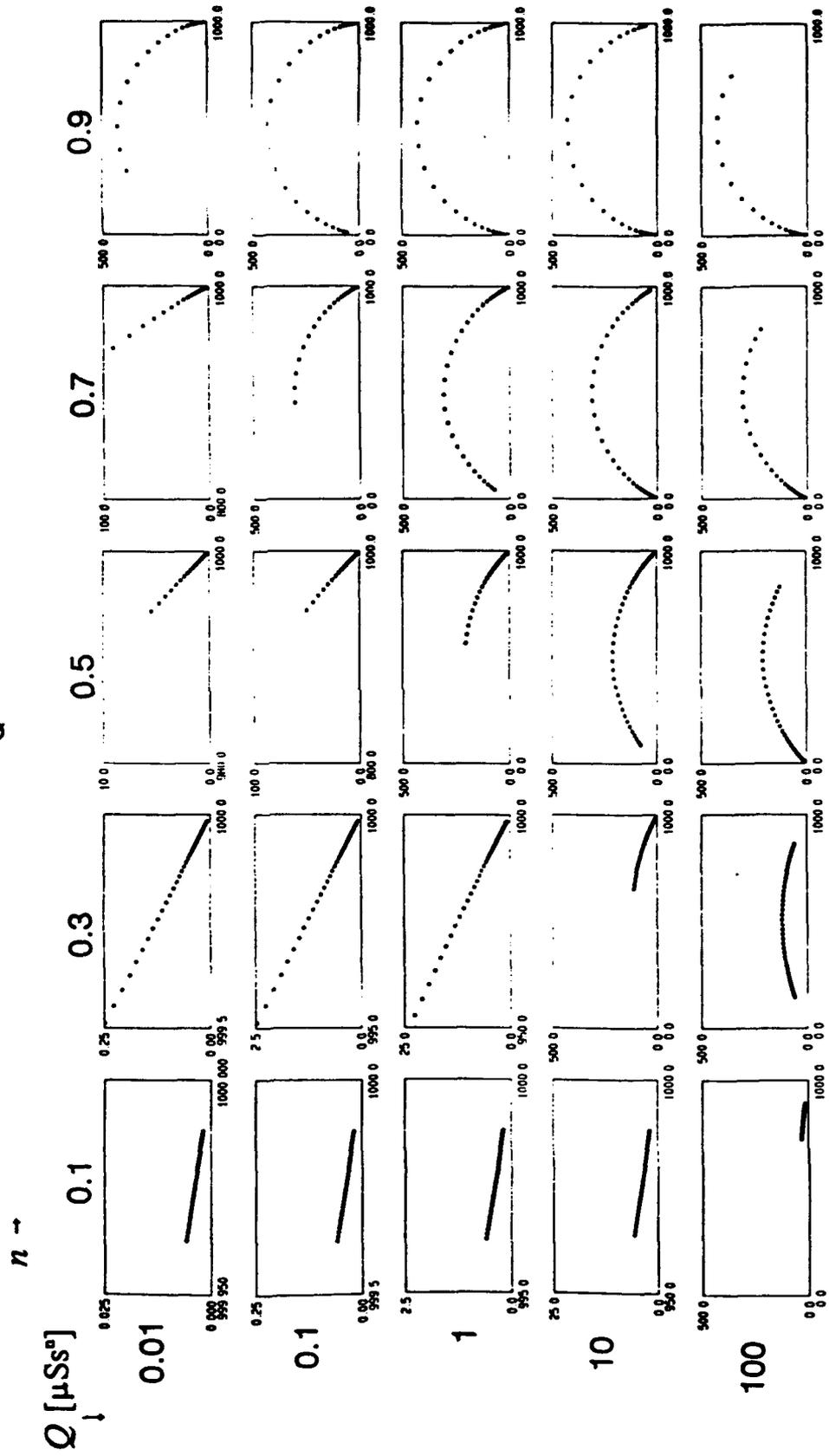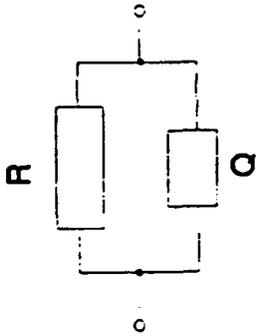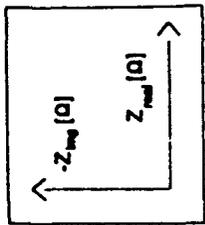
$Q = 1 \ \mu Ss^n$

$f = 1\text{-}100000 \ Hz$

8 points per decade of frequency

$R_1 = 1 \text{ k}\Omega$

$C_1 = 1 \text{ μF}$

$f = 1\text{-}100000 \text{ Hz}$

8 points per decade of frequency

R_2

C_2

R_1

C_1

$-Z_{imag} [\Omega]$

$Z_{real} [\Omega]$

$R_2 [\Omega] \rightarrow$

10 100 1000 10000 100000

$C_2 [\text{μF}]$

0.01

0.1

1

10

100

$B = 10^{-5}\ \mathrm{s}^{1/2}$

$f = 1\text{-}100000\ \mathrm{Hz}$

8 points per decade of frequency

$-Z_{imag}\ [\Omega]$

$Z_{real}\ [\Omega]$

$T\ [\mu Ss^{1/2}] \rightarrow$

$R\ [\Omega]$

| | 0.01 | 0.1 | 1 | 10 | 100 |

10

100
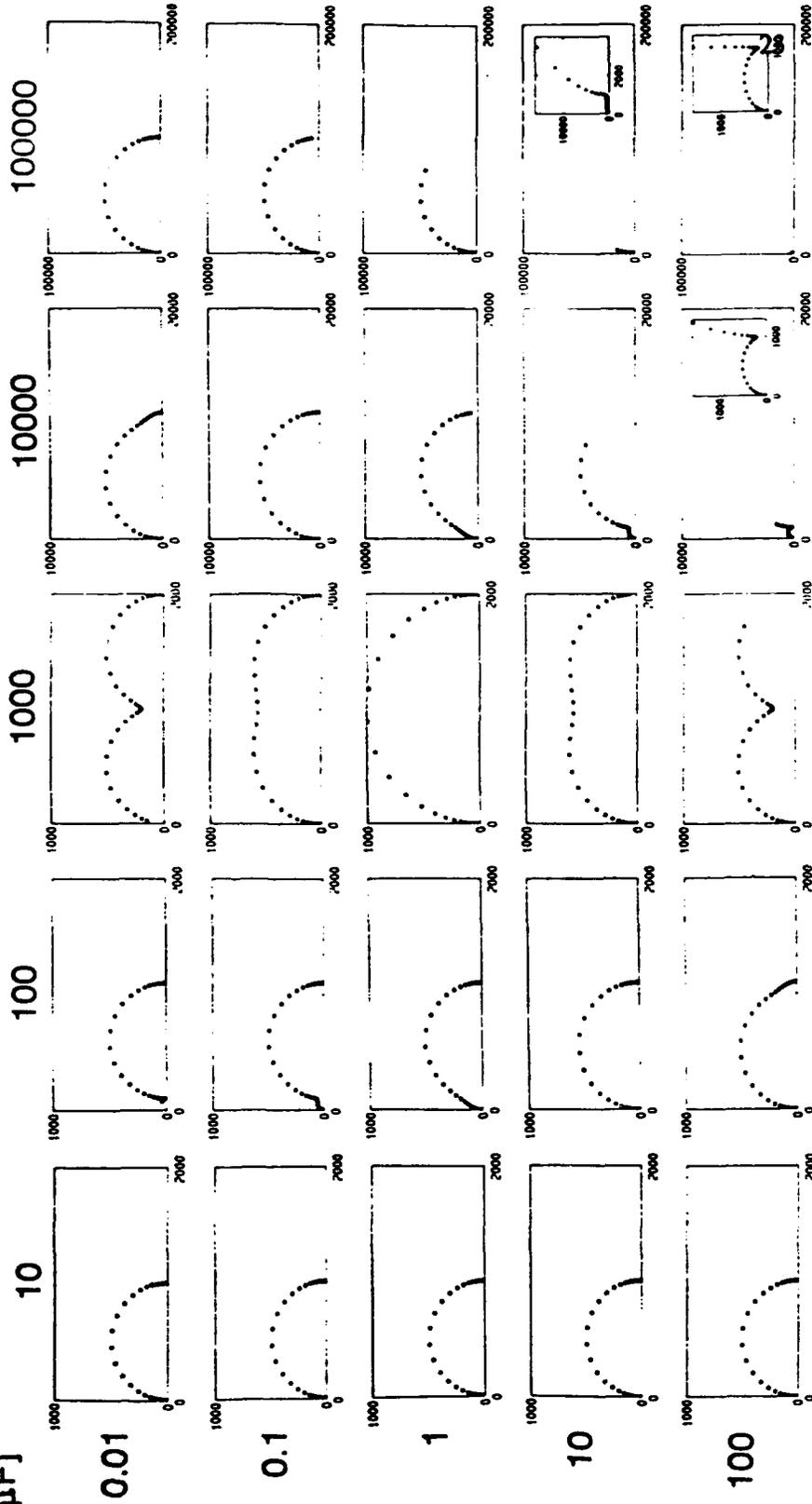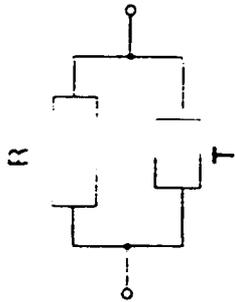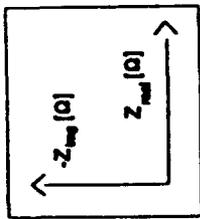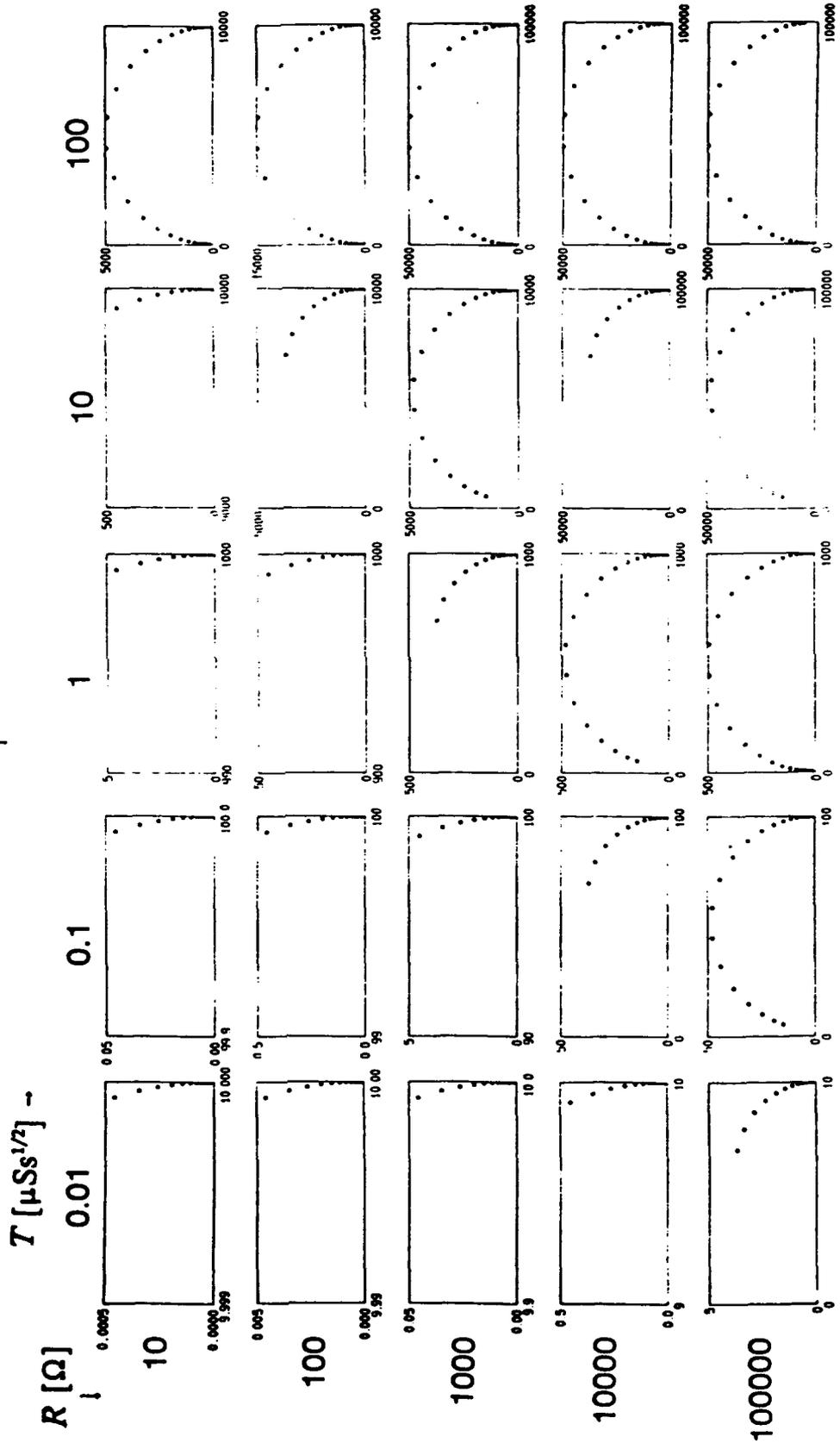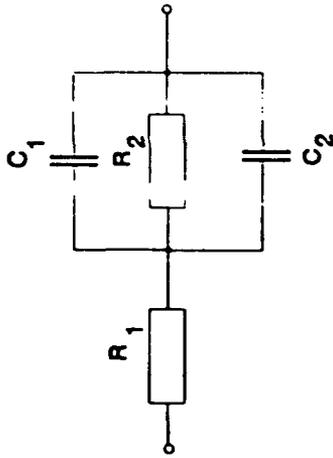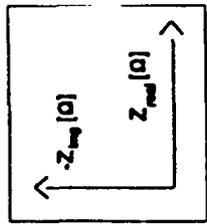
1000

10000

100000

$R_1 = 1\ \mathrm{k\Omega}$

$C_1 = 1\ \mathrm{\mu F}$

$f = 1\text{-}100000\ \mathrm{Hz}$

8 points per decade of frequency

C_1 R_2 C_2 R_1

$-Z_{imag}\,[\Omega]$

$Z_{real}\,[\Omega] \longrightarrow$

$C_2\,[\mathrm{\mu F}] \rightarrow$

0.01   0.1   1   10   100

$R_2\,[\Omega]$

10

100
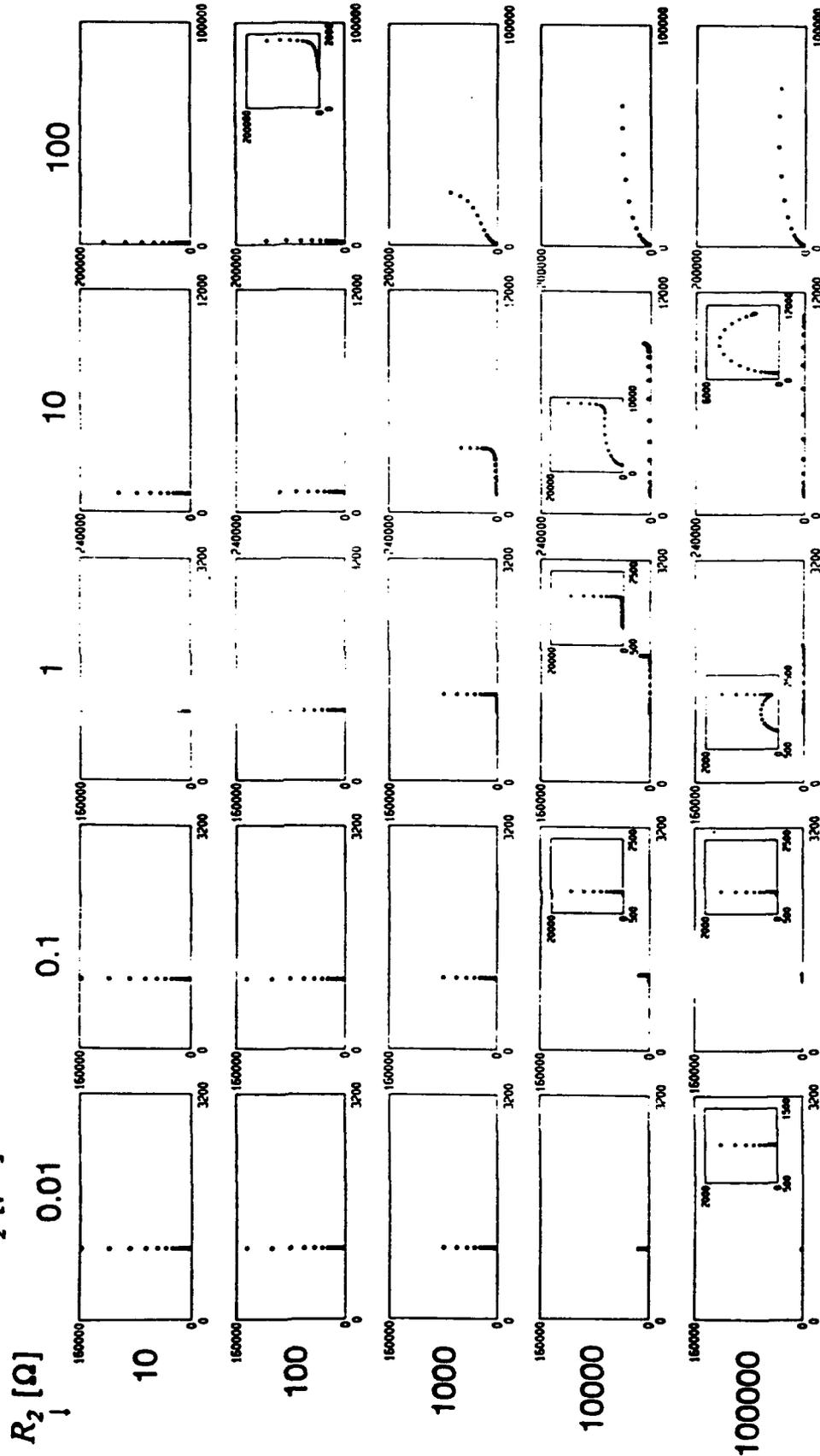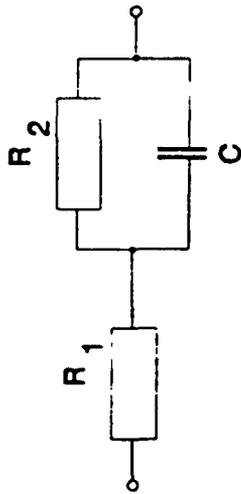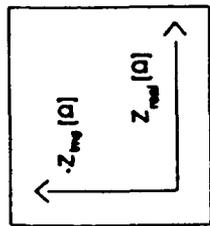
1000

10000

100000

$R_1 = 1\ k\Omega$

$f = 1\text{-}100000\ Hz$

8 points per decade of frequency

$R_1 = 1\ \text{k}\Omega$

$C = 1\ \mu\text{F}$

$n = 0.4$

$f = 1\text{-}100000\ \text{Hz}$

8 points per decade of frequency

$-Z_{Img} [\Omega]$

$Z_{real} [\Omega]$

$R_2 [\Omega] \rightarrow$

$Q_i [\mu Ss^n]$

R_2 Q R_1 C

10   100   1000   10000   100000

0.01   0.1   1   10   100
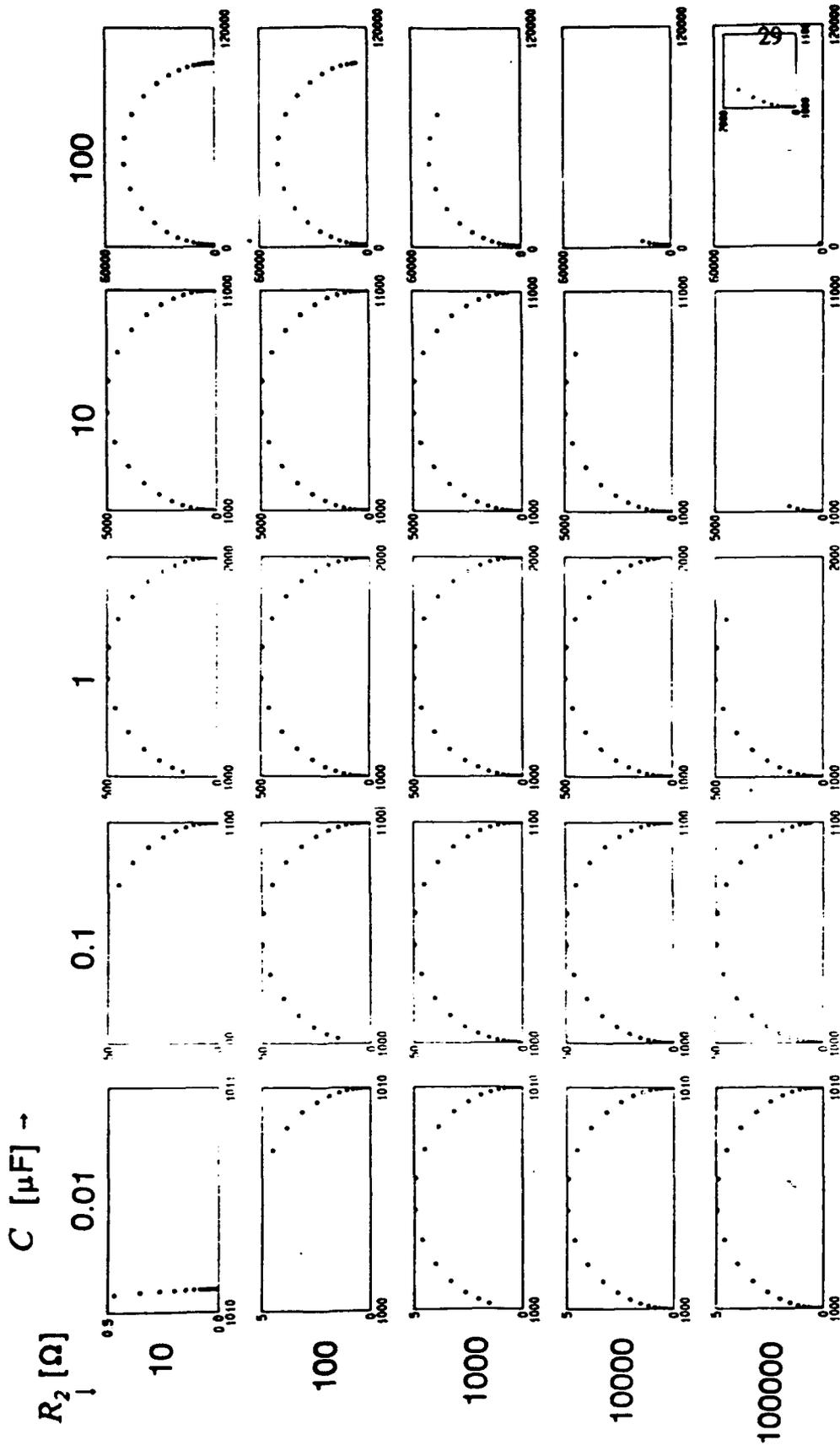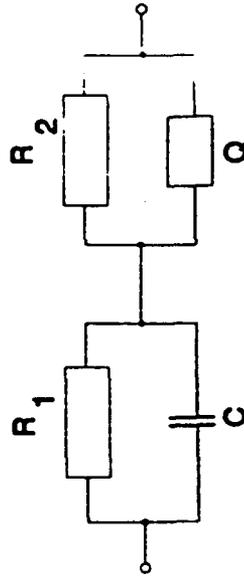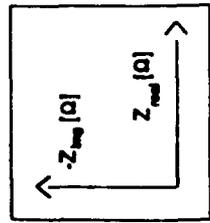
$R_1 = 1\ k\Omega$
$C = 1\ \mu F$
$n = 0.5$
$f = 1\text{-}10000\ Hz$
8 points per decade of frequency
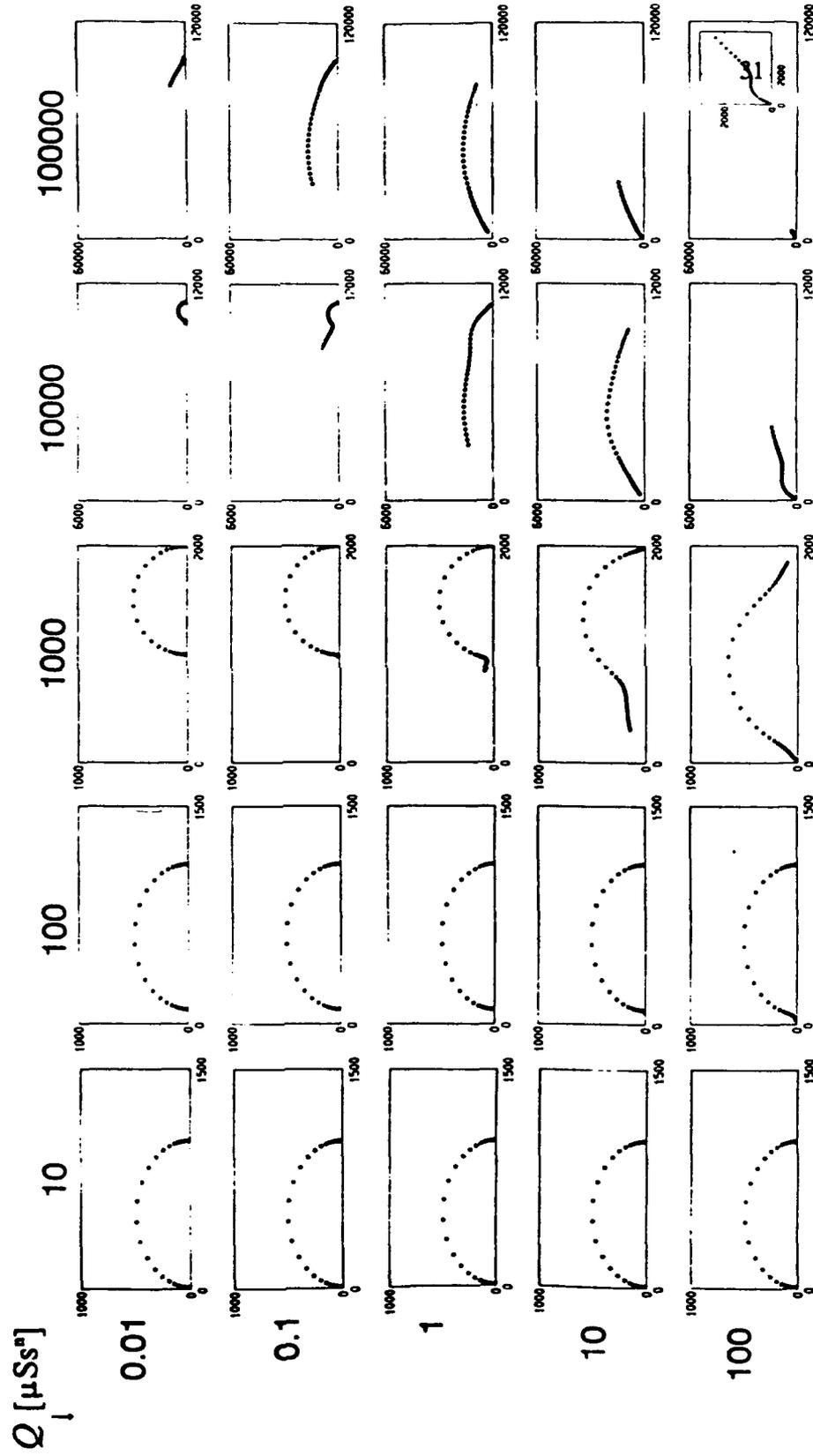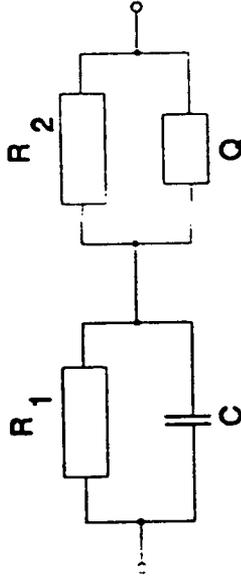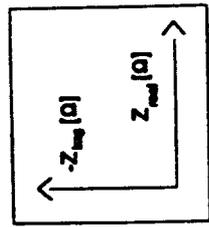
$R_1 = 1\ \mathrm{k\Omega}$
$C = 1\ \mathrm{\mu F}$
$n = 0.6$
$f = 1\text{-}100000\ \mathrm{Hz}$
8 points per decade of frequency

R_2

Q

R_1

C

$-Z_{imag}\ [\Omega]$

$Z_{real}\ [\Omega]$

$R_2\ [\Omega] \rightarrow$

10 100 1000 10000 100000

$Q\ [\mathrm{\mu S s^n}]$

0.01

0.1

1

10

100
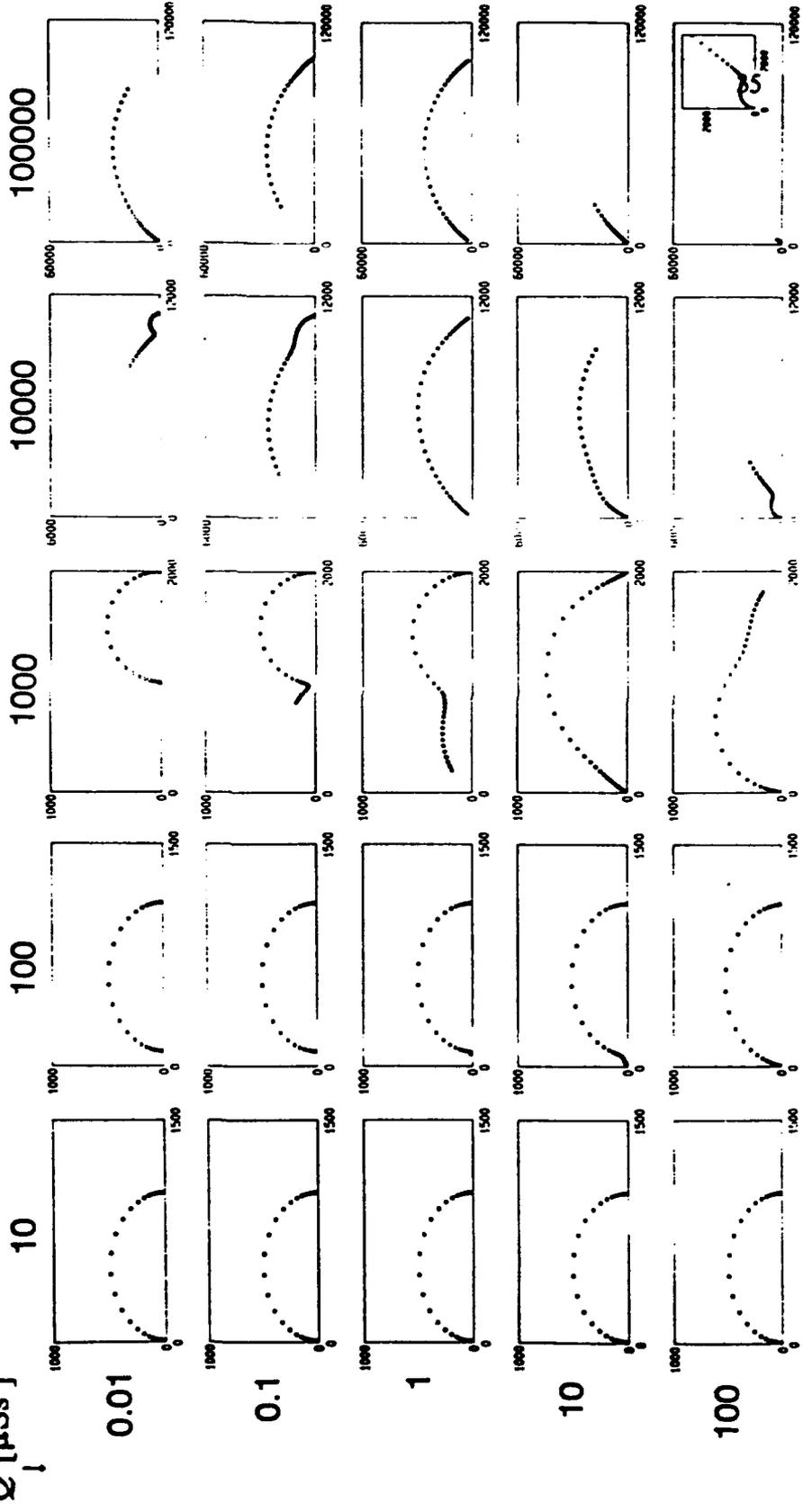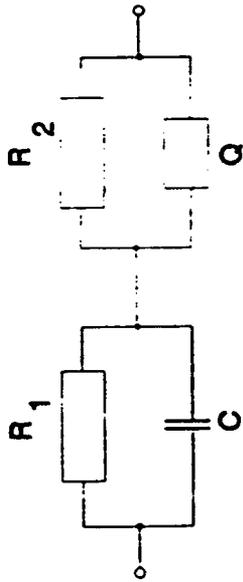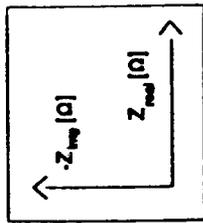
$R_1 = 1\ \text{k}\Omega$

$C = 1\ \mu\text{F}$

$n = 0.7$

$f = 1\text{-}100000\ \text{Hz}$

8 points per decade of frequency

R_2

Q

R_1

C

$-z_{imag}\ [\Omega]$

$z_{real}\ [\Omega]$

$R_2\ [\Omega] \rightarrow$

$Q\ [\mu Ss^n]$

10   100   1000   10000   100000

0.01

0.1

1

10

100

$n = 0.9$

f = 1-100000 Hz

8 points per decade of frequency

Q

R

$-Z_{img}$ [Ω]

Z_{real} [Ω] →

Q [μS s^n] →

0.01   0.1   1   10   100

39

R [Ω]

10

100
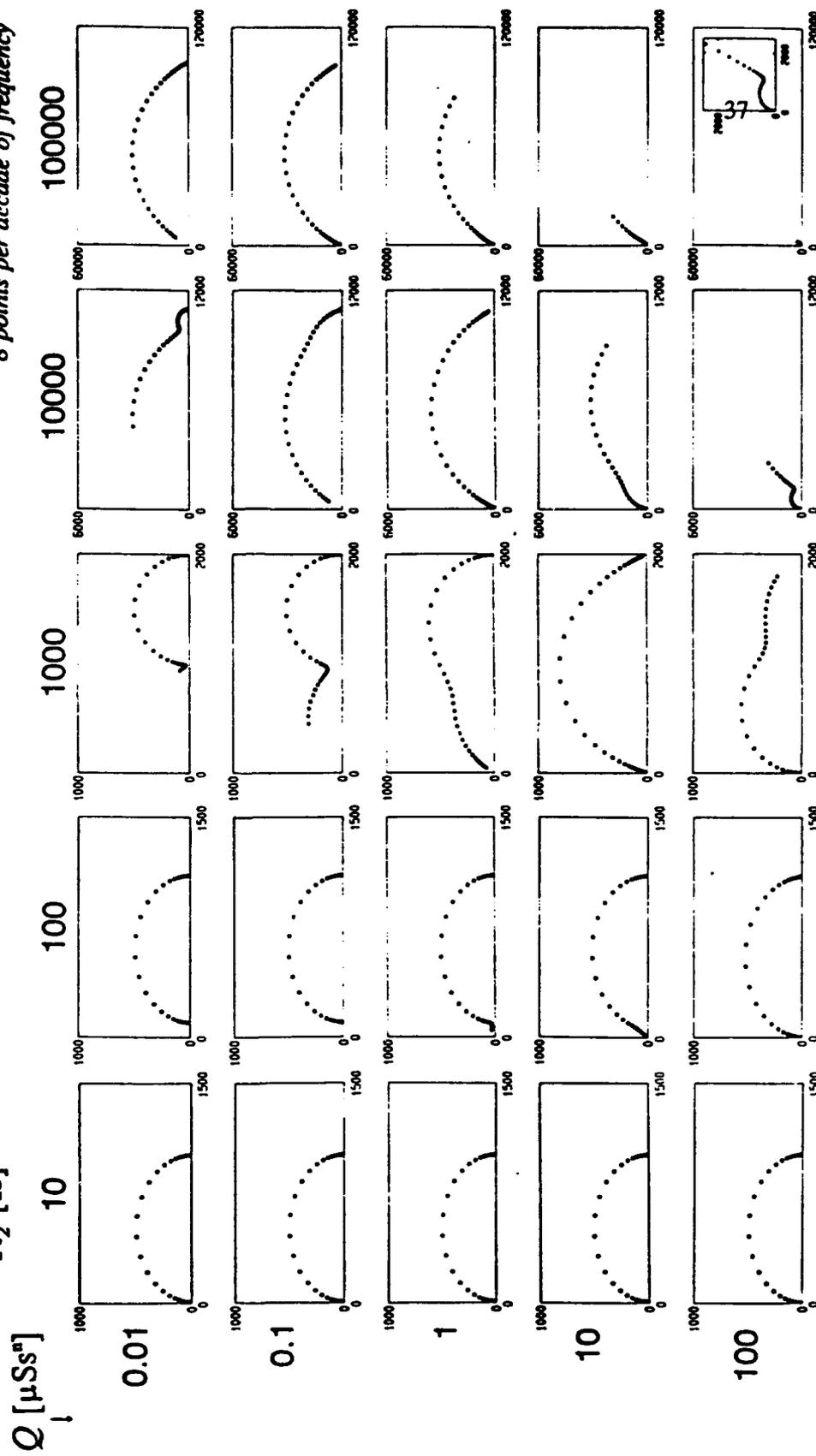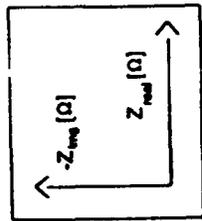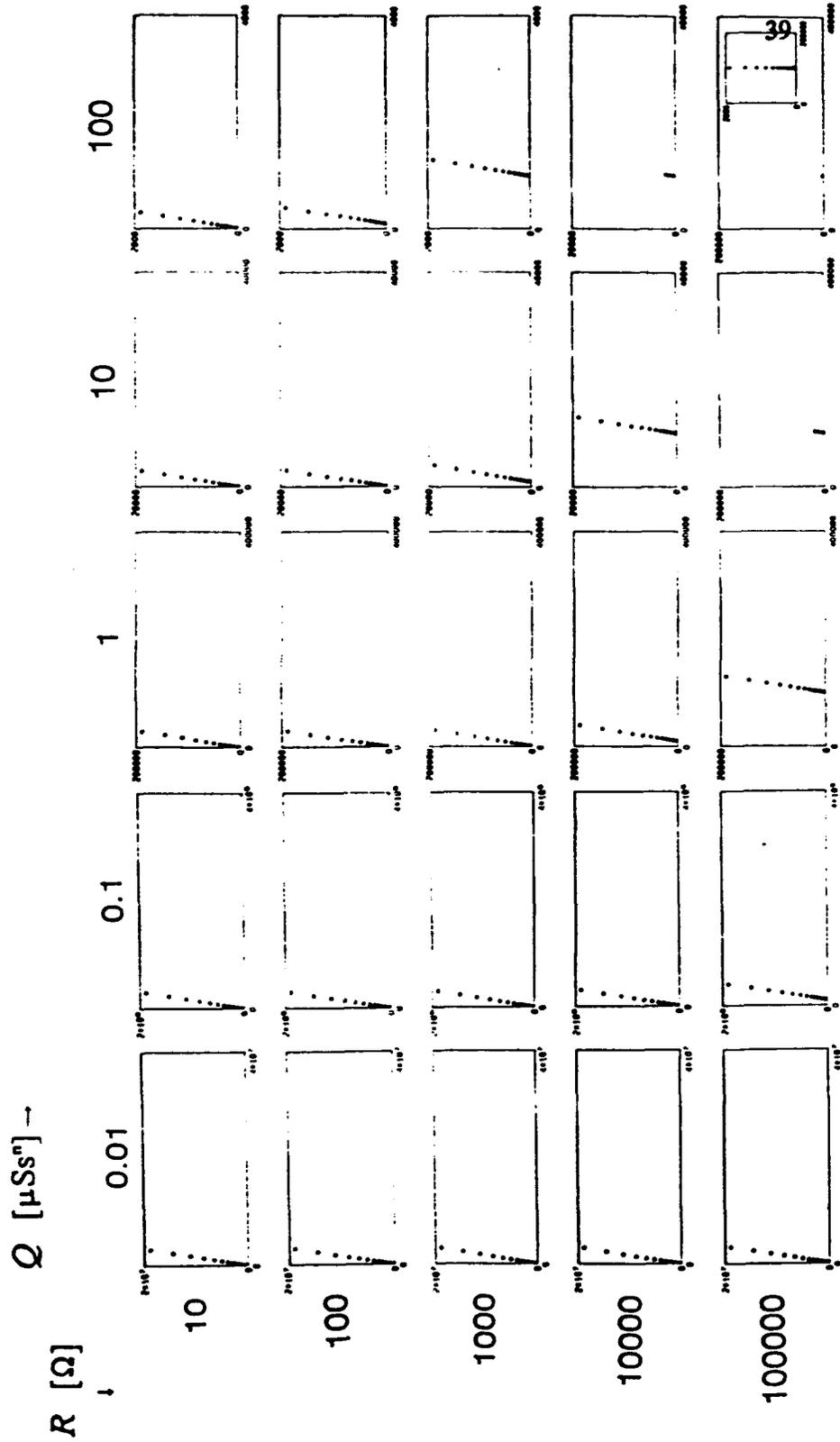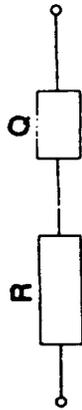
1000

10000

100000

$R_1 = 110\ \Omega$

$Q_1 = 1\ \mu S s^n$

$n_1 = 0.9$

$n_2 = 0.6$

$f = 1\text{-}100000\ Hz$

*8 points per decade of frequency*

R_2 Q_2

Q_1

R_1

$-z_{img}\,[\Omega]$

$z_{real}\,[\Omega] \longrightarrow$

$Q_2\,[\mu S s^n] \longrightarrow$

0.01   0.1   1   10   100

$R_2\,[\Omega]$

10

100

1000

10000

100000
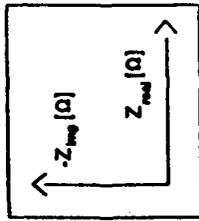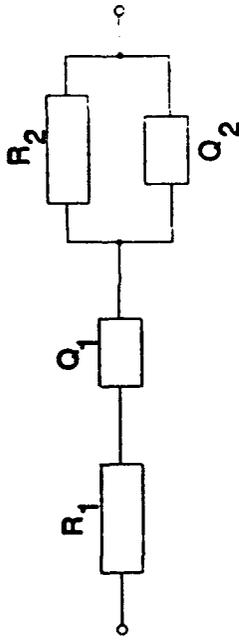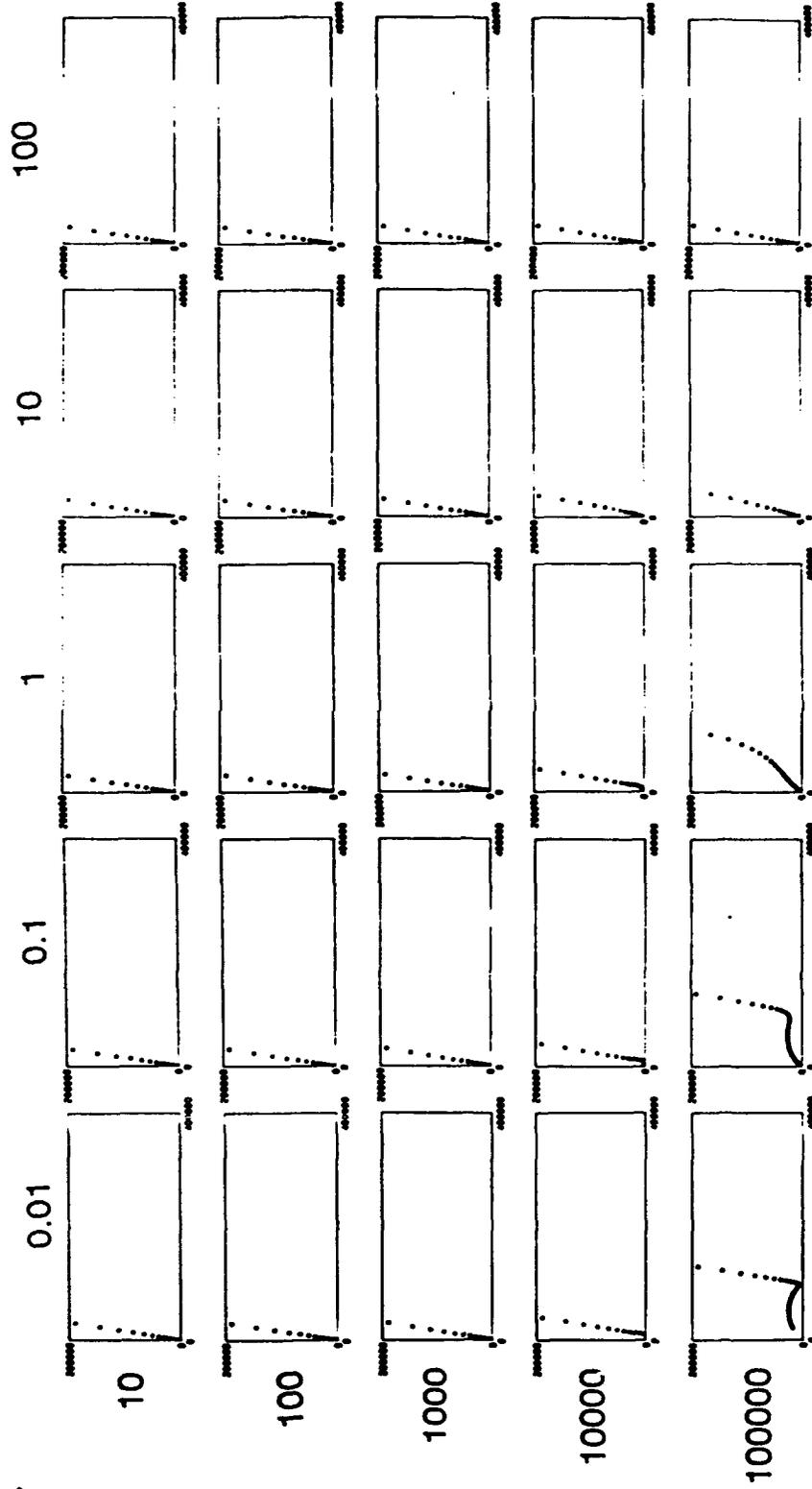
Experimental pitfalls

Counter electrodes

The counter electrodes in impedance measurement carry current flowing through the system. In electrolyte solutions the conductive path between the electrode can be accomplished either by a faradaic process (at DC bias) or by capacitive current (charging and discharging of the electrode/solution interface) at AC conditions. In either case it is desirable that the current density is kept low by increasing area of the electrode, which will prevent buildup of polarization overpotential on the electrodes and allow more current to be passed by a capacitive process.

Whereas it is true that processes occurring on counter electrodes do not interfere with the function of the optimally functioning impedance analyzer, in real life the processes on the electrodes matter. They may increase resistance of the electrodes to the point where the electronics cannot compensate properly. The electrogenerated byproducts also may alter the composition of the studied solutions.

Inert platinum electrodes are most often used. Again, other metals, even corroding ones, could be used, but it is desirable to keep the solution contamination to minimum. Sometimes stainless steel is used in the applications where the price of platinum is restrictive.

Often a platinum mesh is used over a solid platinum flag. One reason is that lesser amount of platinum is needed to produce a mesh electrode with the same properties. The area of the mesh electrode depends on the density of the mesh and is not so much greater as is usually stated. For example an Aldrich 52 mesh platinum (assuming that mesh means 52 wires per linear inch) has a length

of 40.94 cm of Pt wire of radius 0.00524 cm per a square centimeter of area. This gives a total surface area of 1.35 cm^2, which is smaller than that for a 1 cm^2 solid Pt flag electrode, which has an area of 2 cm^2. However, the opposite side of the solid electrode is usually shielded and does not pass as much current. Thus, the areas of the two electrodes are about equal. If the same amount of platinum as is in the mesh electrode were used to make the flag electrode, it would be only 0.035 mm thick, too thin to allow practical handling.

4th electrode to eliminate high frequency problems

Working and counter electrode (another Pd wire, coiled, 1 mm dia, cca 2.5 cm length) were in one compartment of the cell, a reference electrode realized by a reversible hydrogen electrode was in a second compartment of a standard electrochemical cell, with a Luggin capillary close to the working electrode. The electrical connection was of the reference was though a wet, closed ground glass stop cock. Such configuration of a reference electrode is very suitable for most measurements. Because of its resistance and capacitance it introduces a certain time delay to the potentiostat, which causes progressively higher phase shift if impedance is measured at higher frequencies. This problem was dramatically reduced by placing additional electrode, a smooth Pt wire in the working electrode cell compartment and connecting it via a 6.8 microF capacitor to the lead of the reference electrode. This modification was done according to [1--3]. The authors recommend 10 μF resistor, but 6.8 is all what we got. Paper [4] recommends only a 0.1 μF capacitor, whereas [5] uses a 1 μF capacitor.

Figure 36 shows the difference in a Bode plot obtained with and without this modification. It should be noted that the data evaluated for a particular system with and without such modification at the unaffected lower frequencies are identical.
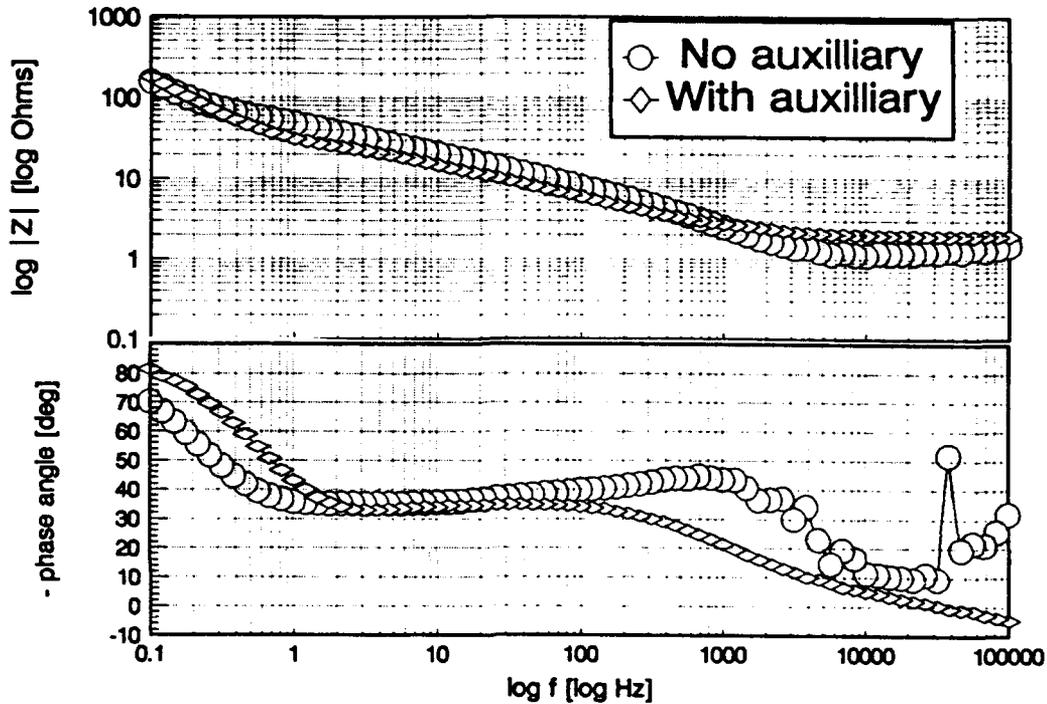
Figure 36

The Solartron impedance analyzer is connected to a 4–electrode "electrochemical interface" which is, in fact, an ordinary potentiostat. It has some awkward way of entering information for scanning, therefore a basic program (PSTAT.BAS), wide infra, was written. It allow the scan. It should be kept in mind that in almost any impedance measurement of an electrochemical system, the electrochemical cell will be connected to a potentiostat. It is very important to assure that all the electrodes are correctly connected to the cell. Not only erroneous results will be obtained, the electrodes in the cell can be destroyed in the process. The potentiostat is a device that maintains along the path between

working and reference electrode a desired potential by actually applying (somewhat higher, to compensate for the IR drop) potential between the counter electrode and the working electrode. Should the reference electrode become disconnected (even a bubble in the Luggin capillary can cause this), the potentiostat will apply its highest possible voltage to achieve desired reading between the reference and working. This voltage is about 15 V for the Solartron and similar potentiostats and can be even higher. Such a voltage, applied between the working and counter electrode can cause lot of damage to previously meticulously cleaned electrode. There is even another subtle, but important danger. Platinum, often used as a counter electrode and usually quite ignored in the whole process, can anodically dissolve in the solution and can be deposited from the solution onto the working electrode. We have observed in our laboratory an episode in which a current surge through a cell with a gold working electrode in 1 mol/l sulfuric acid was observed. It happened presumably because of imperfect connection of the reference electrode. Previously very clean voltammogram of the gold electrode became distorted and features typical for platinum have appeared.

The prevention is to maintain good connections between electrodes and their connectors, which are often, for convenience, alligator clips. The clips tend to corrode and should be periodically replaced and often cleaned with emery cloth. It is also a good practice to read, before the potentiostat is actually switched on, the resting potential of the cell. When the electrodes are properly connected, the reading should be stable, without much drift, and should be of the value typically observed for such a system. When using Z–Plot for measurements, the resting potential can be displayed by choosing potentiostat (F5) from the setup menu. While the potentiostat menu is displayed, the digital meter on the 1286 is activated and the window displays the cell potential. Note that due to certain

peculiarity of the system, the potential displayed has opposite sign than the one we would expect (it reads the potential of the reference electrode *vs.* the working electrode, whereas we report potentials of the working electrode vs. any reference.) this peculiarity is, however, taken into account in Z–Plot. Thus, any potential entered into the program will have the sign of the working electrode.

Potential sweep with the Solartron electrochemical interface 1286

Free standing program.

The entry of sweep parameters is rather awkward and makes the 1286 without proper software essentially unsuitable for potential scan. I have written a program in basic (P_STAT.BAS, AT_WILL.BAS and ALONE.BAS), that can perform simple scan. The programs are on my computer on C: drive in sub directory HBASIC. The P_STAT.BAS or AT_WILL.BAS should be run when scanning feature is called from Z–Plot. ALONE.BAS is a free standing program that can be used independently of Z–Plot, whenever scanning on 1286 is desired. The 1286 scanning capability allows potential scan program that consist of four segments. My BASIC program conveniently uses the initial potential of the first segment as the STARTING POTENTIAL. The first segment ends (and the second starts) with UPPER POTENTIAL (Figure 37).
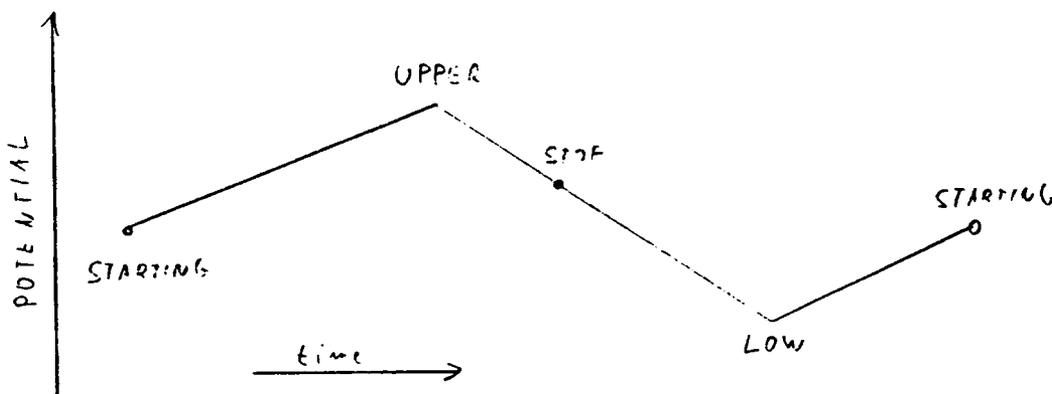
Figure 37

End of second segment (beginning of third) is the STOP POTENTIAL (2nd segment). End of the third segment (and beginning of fourth) is the LOW POTENTIAL. Finally, the fourth segment begins with the LOW POTENTIAL

and ends with the STARTING POTENTIAL. Thus, four segments constitute one full cycle. The potentiostat also need information about duration of each individual segment, but it is calculated by the program from the entered scan rate.

Experimental consideration: To do voltammetry, an X–Y recorder will be connected, via a T–splitter to the BNC connectors on the back of the potentiostat. The same connectors are used to carry also the signal to the analyzer. As this can introduce some error, if the recorder/leads loading/capacitance are excessive, it should be a good practice to disconnect the recorder cables from the back of the potentiostat, for any work that does not routinely call for the use of a recorder.

Version AT_WILL

The AT_WILL program is similar to P_STAT, but it allows running a number of sweeps at will, and return to ZPLOT is initiated after a proper response from the program menu.

Examples:

Polarize (for a palladium work) in the potential range 0.1 V to 1.6 V. Begin at 0.5 V, stop coming from cathodic side at 0.5 V. Perform three complete sweeps. The settings will be:

> Initial: 0.5, Upper: 1.6, Stop potential (2nd segment) [does not matter here, since the stop will happen at the initial potential, so enter e.g., 0.9 V], Lower potential 0.1 V. Number of segments: 12 (3 cycles are required, full cycle has 4 segments). Potential after the sweep stops: 0.5 V.

Polarize is a sweep from 0.5 V to 1.6 V, sweep back to 0.9 and stop. The settings will be:

Initial: 0.5, Upper 1.6, Stop potential 0.9 V, Lower potential: [The sweep will never reach that value, but it has to be entered], e.g., 0.3 V, end potential: 0.9 V. Number of segments: 2.

Polarize from 0.5 to 0.9 V and stop. The setting will be:

Initial: 0.5 V, Upper: 0.9 V, Stop [value does not matter but some has to be entered], 0.5 V, Lower [value does not matter but some has to be entered], 0.3 V, Segments: 1.

Scan from 0.5 V to 0.3 V and stop at 0.9 V, going from cathodic side. The settings will be:

Initial: 0.5 V, Upper 0.3 V, Stop potential: 0.9 V, Lower potential [does not matter but has to be entered], e.g., 1.6 V. Segments: 2.

Note that in the last example the upper potential had lower value than the lower potential. This is correct − it is a way how to change the direction of polarization. The values for the Lower and Upper potential determine the span of the sweep. The values of the start and stop potential cannot be outside this range, or equal to the limit values. The values have to be within ± 10 V. The program itself does not prevent entry of incorrect values. The instrument itself will display an error code, but in al the likely hood a sweep will actually proceed, with the values that were previously correctly entered.

Running the program from within Z–Plot

Z–Plot allows to be suspended during its execution of a batch program and another program can be run from DOS. Upon finishing of this program (i.e., its return to DOS), execution of next line of the batch program will resume. If the external feature of Z–Plot is used, the information about pause time, and pause polarization is passed to the external program as numbers; they are not used as actual pause of potential information.

To invoke the P_STAT.BAS program from within Z–Plot, start Z–Plot as follows:

cd\zplot

zplot/ext test

(ext is the program switch, test is a small batch file that invokes a BASICA program and loads P_STAT.BAS program in it. By replacing test with at_will, the program at_will will be invoked instead.)

With the program started in this manner, every time a valid line (i.e., a line that does not begin with a zero for pause time) will switch to P_STAT.BAS program. Once P_STAT.BAS is executed, program will continue with the task specified on that line.

Example:

The line: 1 Sec Potential 1.5 V OXIDE15.ZET   PD7TIME1.Z

will start P_STAT.BAS (The time 1 Sec is arbitrary, it is not a pause, it just has to be a no–zero value. Similarly, the potential 1.5 V is not applied to the cell.) After the P_STAT.BAS program ends, Z–plot will perform a task specified in setup file OXIDE15.ZET and store the data in file PD7TIME1.Z. If a following

line in the batch file is valid (begins with a non—zero number) another P_STAT.BAS file will be invoked.

Hints for P_STAT.BAS program: The program is listed as an appendix of this text. Sensible modifications can improve its performance or alter parameters that are not suitable for a particular task. Take care not to alter the original version so that you can always fall back on a working copy should anything with the programming go wrong.

Z—Plot is suspended during running the external program until the external program leaves to DOS. Hence, it is possible to modify the program or restart it, should you make a mistake. Type Ctrl—Break and BASIC program will stop. It is possible to start it again (by RUN) if you type in a wrong scan values, edit the program and run it afterwards or, not to run the program at all. Should it happen that you do not want to use a particular scan during the batch processing, use Ctrl—Break and then type SYSTEM. This will end the BASICA program, return the computer to DOS and consequently, return to Z—PLOT.

Using the IBM 8088 machine to run the Solarton instrumentation

1.   Configurations already done:

For operation an IEEE GPIB (general purpose interface bus) board has to be present in the computer. This has been accomplished by taking an unused board from the COMTEX 386 computer (!!! Comtex does not have the card).

For operation of the board it is required that a driver (a computer program) called GPIB.COM be installed on the computer and used during boot–up. It is installed by including a line in the CONFIG.SYS file: device=c:\pc–gpib\gpib.com. This means that the CONFIG.SYS is in PC–GPIB sub directory. There are also some utility programs related to GPIB in this sub directory. The version of GPIB.COM installed on this computer came from PV. It allows to handle commands of the type IEEE 422.2 (it is the "dot two" part, that is important), which is required by the ZPLOT.PROGRAM. All this has been already done so there is no need to get involved with this part of installation, nor an attempt to make changes to the setup should be made.

CONFIG.SYS

This program looks as follows:

        buffers=10

        files=10

        country=039

        device=c:\pc–gpib\gpib.com

These settings should not be changed because overall change in total memory (which is small, only 500 kbytes) could be decreased and programs might not work.

AUTOEXEC.BAT

Looks as follows:

```
@echo off
PATH C:\DOS;C:\UTIL;C:\BAT
prompt $p$g
get_dat
time
date
save_dat
```

This computer does not have clock and when it starts on its own, it starts with time 00 hours, January 1, 1980. Since it is essential that files we generated have correct dates, the AUTOEXEC.BAT file contains lines requiring entry of time and data (see appendix for the detail). After the time and date is entered, it is also saved in small files in main sub directory. These files are recalled upon next boot. Thus, even is time/date are not entered (do not do this), the time/date will be closer to reality than the 1980 default value.

Key diskette

ZPLOT will not operate without so called a key diskette, that has to be present in drive B upon starting ZPLOT. It is a blue diskette, marked as such. Do not erase anything from the diskette and do not borrow it for other purposes. It cannot be replaced except by paying money for a new program.

Data storage

It will be desirable to copy the *.Z data obtained from impedance measurement and present on a hard disk on a floppy and tread them on another computer (This one does not have a math co processor so it cannot be used for EQUIVCRT anyway). The PC has two floppy drives: A is a 360 kByte 5 1/4 drive and can be used for copying and disk formation with no known problems. Disk B can write and read from a 720 kbytes 3 1/2 disk (know as double sided double density, labeled usually DD). However, it cannot format the disk to 720 k, but only to 360 k. Thus, do not format 3–1/4 disks on this computer, format them elsewhere. There are two types of 3–1/4 disks, the double density (720 kbytes) and high density (1.44 Mbytes, usually labeled HD). Both can be formatted to 720 kbytes, but doing this with HD disks is wasteful. Drives on our other computers will in default attempt to format a 3–1/4 disk in 1.44 Mbyte. To format a DD disk to 720 kbytes in a HD drive should be done by a command

format b: /f:720   (or format a: /f:720)

Data storage on IBM 8088 machine.

ZPLOT allows storage of data on a disk. For convenience there is a sub directory on the C drive called DATA, that should be used for temporary data storage. Use this sub directory for saving your results. To save a file with the name PD1–106, is should be typed as c:\data\PD1–106. Note, that the files stored as data will have automatically added to their name suffix z: PD1–106.Z.

If you do not specify during storage, while running Z plot a sub directory, all data (with the extension after the dot in the filename .Z) will be stored in directory ZPLOT. This is fine, except it puts files together with the operating files and makes it difficult to clean up the directory if data need to be eventually removed.

Retrieval of the data after finished impedance run

Assuming that you stored your data in a sub directory c:\data, you should, once in DOS, switch to that directory (cd\data), remove the key diskette in the B drive, put you data storage diskette in B and copy all your data (copy *.* b:). When it appears that all you created is now on the floppy disk, you should consider delete your old data from the sub directory \data. Make sure that you do not delete data that belong to somebody else.

Visualization of ZPLOT files

Plotting of raw impedance data cannot be a substitute for their evaluation according to a suitable model. Nevertheless, certain experience can be achieved after reading Bode or Argand plots, so plotting of data has its place. In particular, plotting of data as a function of a changing parameter (time, bias potential), can provide quick insight whether impedance is a function of this parameter, or not.

GT (Graph Tools program)

This program is in sub directory GT and will start by command GT. It is a nice graphics program. The manual for it is, unfortunately, in DeKalb, so you have to figure out its function by experimenting with it.

ZPLOT data files *.Z contain values in columns: frequency, real, imaginary, vector length, phase angle, resistor/error code. To plot an X–Y plot of real/vs. imaginary using GT, the following should be done.

Start the program and do:

ADD, GRAPH, XY

In the window for a file name (where data for graph are contained), enter the file name as, e.g., C:\zplot\iridium.z/C2/C3

This command will recall file iridium.z, located in appropriate directory/drive and will use its column 2 (C2) as first variable (X on the graph), and C3 as the second variable. By typing CONTINUE and REDRAW a graph will show. By changing axes, labels, etc, a nice graph can be obtained.

To print, choose, PRINT, and follow menu. The graph will be printed on the HP laser printer. Since it involves lot of graphics, it can take a while. The light on the printer will be blinking if it is receiving data.

NOTE: the printer memory size is marginally smaller than is needed for the printing and it can run out. This will cause printer error. Most of the graph can be retrieved by taking the printer OFFLINE and manually ejecting the page. The program can be overcome by printing in portrait (rather than landscape) format and/or by making the image on the screen smaller (fewer addressed bites).

Merging of data files for quick visualization of results into a 3–dimensional plots.

A 3–Dimensional plot can be created from combined ZPLOT files. To combine the files, a QuickBasic program called ZCON2.BAS can be used (see appendix ZCON2.BAS for the program listing). You will be editing contents of the actual program file to suit your needs. To prevent inadvertent changes of the original file, make a copy of it. Such us (from within directory c:>\QB)

<p style="text-align:center">copy ZCON2.BAT USER.BAT</p>

Start program QuickBasic (cd\qb45 for the 4.5 version) by typing QB within sub directory C:\QB45. Load your file (USER.BAT) and make the needed changes as can be gleaned from the ZCON2.BAS appendix. Do not attempt to modify the original ZCON2.BAS. It is possible to make changes of this file within the editing window of QuickBasic and once edited, it can be from this window also run. But it cannot be saved. It is protected against unintentional changes.

Once the changes to your file (e.g., "USER.BAS") are made, RUN the program from within QuickBasic. To do so, use mouse and click on RUN in the upper part of the window. If all goes well, a merged file of you data sets will be created. Once the file is created, it can be plotted in GraphTool. To plot phase angle vs. log f as a function of applied potential, from a file pallad.3D, you would choose: ADD, GRAPH, 3D. In the file name window, type:

<p style="text-align:center">c:\zplot\pallad.3D/t/c2/c7/c6</p>

the switches mean t:trajectory (as opposed to a mesh, 3D plot), C2 – column 2 containing log f, C7 – column 7, containing information on applied potential, C6, phase angle.

Again, changing scales, adding labels, etc., will create a nice graph.

Measurement of open–circuit potential

NOTE: There is a little confusion in the vernacular of electrochemistry. I call as the "open circuit potential" a potential the cell has when it is not connected to anything (realistically, it is connected to a high–impedance voltmeter). It is true, though, that such potential may be changing with time. VIB calls this potential "zero current potential," whereas in her terms an open circuit potential is an ideal potential the system WOULD attain after (long) time, when everything is at equilibrium (albeit dynamic equilibrium).

It is possible to use the 1286 potential to measure the open–circuit or resting potential of a cell (or any other system) connected to between its two reference electrode.

Within ZPLOT software, the measurement can be made by choosing the setup menu (F1) from the main menu, and then potentiostat/galvanostat (F5). Once in the p–stat setup menu, the meter on 1286 is activated and the fluorescent display will show the cell potential. As is with all readings (potential and current), when the cell is connected to operate correctly under ZPLOT, the sign of the read value has to be inverted. Although the current part of the display will show some values (often quite high) they have no meaning in respect to the cell current. There is no current flowing through the cell.

Construction of electrodes

(Contribution by Viola I. Birss)

Most of the electrodes, especially those involving noble metal wires or gauzes, are constructed in a standard way:

1. Obtain approximately a 2cm length of the metal to be embedded in glass tubing, It is recommended that the wire be degreased in acetone ultrasonically for a short time. Likewise, metal gauze should also be degreased.

2. Select the appropriate length and diameter (to fit into your cell top) of SOFT–GLASS TUBING from the appropriate drawer in SB204. The tubing should be clean. To clean glassware, soak for 24 hours in chromic acid cleaning solution, followed by 24 hours in distilled water. NOTE: Pyrex cannot be used for the electrodes as it will not seal well to metal.

3. Give tubing and metal to glassblower, reminding him that you have degreased the metal and cleaned the tubing. Also give him a diagram of the electrode design, if· he does not already know. He will spot weld your metal wire to either Ni or Ag wire, which he has, and then will seal the soft glass around the metal wire, maximizing how much of it protrudes out from the glass.

4. Upon receipt of electrode from glassblower, suspend electrode in water overnight (e.g., in graduated. cylinder), never allowing the weight of the

electrode to rest on the wire (this will weaken the glass/metal seal). Check the next day for electrode leakage. Any water or vapor in the glass tubing implies leakage and the electrode will need to be reconstructed,

5. To increase the lifetime of your electrode, drop small chips of wax (in 'glass—blowing drawer) into tubing to rest near the metal/glass seal. Heat very gently in cool Bunsen burner flame (orange) until wax melts. Allow it to harden while holding the electrode vertically, Also, it is wise to epoxy the wire to the rim of the top of the glass tube, so that as leads and clips are attached to the wire, this does not allow the wire to move inside the glass tube, thus minimizing the stresses at the glass/metal seal.

6. Store electrodes in ca. 10–20% sulfuric acid, in general.

NOTE: Tips about the construction or other types of electrodes, e.g., those which can be used to support metal discs or plates, are given in the theses of Shevalier, Lian and Waudo and are also available from current members of our research group.

Acknowledgment

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Appendix:

BASIC program (BASICA) for computer controlled cyclic voltammetry on Solartron 1286
The listed program is the P_STAT.BAS. Program ALONE.BAS is identical, with line
number 2040 removed.

```
1      CLEAR  ,59400!        ' BASIC Declarations
2      IBINIT1 = 59400!
3      IBINIT2 = IBINIT1 + 3   ' Lines 1 through 6 MUST be included in your program.
4      BLOAD "C:\HBASIC\bib.m",IBINIT1
5      CALL IBINIT1(IBFIND,IBTRG,IBCLR, ...ETC.)
6      CALL IBINIT2(IBGST, ...ETC)
7      REM Optionally include the following declarations in your program.
8      REM They provide appropriate mnemonics by which
9      REM to reference commonly used values.  Some mnemonics (GET%, ERR%,
10     REM END%, ATN%) are preceded by "B" in order to distinguish them from
11     REM BASIC keywords.
12     REM
13     REM GPIB Commands
14     UNL% = &H3F     ' GPIB unlisten command
15     UNT% = &H5F     ' GPIB untalk command
16     GTL% = &H1      ' GPIB go to local
17     SDC% = &H4      ' GPIB selected device clear
18     PPC% = &H5      ' GPIB parallel poll configure
19     BGET% = &H8     ' GPIB group execute trigger
20     TCT% = &H9      ' GPIB take control
21     LLO% = &H11     ' GPIB local lock out
22     DCL% = &H14     ' GPIB device clear
23     PPU% = &H15     ' GPIB ppoll unconfigure
24     SPE% = &H18     ' GPIB serial poll enable
25     SPD% = &H19     ' GPIB serial poll disable
26     PPE% = &H60     ' GPIB parallel poll enable
27     PPD% = &H70     ' GPIB parallel poll disable
28     REM
29     REM GPIB status bit vector
30     REM global variable IBSTA% and wait mask
31     BERR% = &H8000  ' Error detected
32     TIMO% = &H4000  ' Timeout
33     BEND% = &H2000  ' EOI or EOS detected
34     SRQI% = &H1000  ' SRQ detected by CIC
35     RQS% = &H800    ' Device needs service
36     CMPL% = &H100   ' I/O completed
37     LOK% = &H80     ' Local lockout state
38     REM% = &H40     ' Remote state
39     CIC% = &H20     ' Controller-In-Charge
40     BATN% = &H10    ' Attention asserted
41     TACS% = &H8     ' Talker active
42     LACS% = &H4     ' Listener active
43     DTAS% = &H2     ' Device trigger state
44     DCAS% = &H1     ' Device clear state
```

45   REM

```
46    REM Error messages returned in global variable IBERR%
47    EDVR% =  0     ' DOS error
48    ECIC% =  1     ' Function requires board to be CIC
49    ENOL% =  2     ' Write function detected no Listeners
50    EADR% =  3     ' Interface board not addressed correctly
51    EARG% =  4     ' Invalid argument to function call
52    ESAC% =  5     ' Function requires board to be SAC
53    EABO% =  6     ' I/O operation aborted
54    ENEB% =  7     ' Non-existent interface board
55    EOIP% = 10     ' I/O operation started before previous operation completed
56    ECAP% = 11     ' No capability for operation
57    EFSO% = 12     ' File system operation error
58    EBUS% = 14     ' Command error during device call
59    ESTB% = 15     ' Serial poll status byte lost
60    ESRQ% = 16     ' SRQ remains asserted
61    REM
62    REM EOS mode bits
63    BIN% = &H1000   ' Eight bit compare
64    XEOS% = &H800   ' Send EOI with EOS byte
65    REOS% = &H400   ' Terminate read on EOS
66    REM
67    REM Timeout values and meanings
68    TNONE% =   0    ' Infinite timeout (disabled)
69    T10US% =   1    ' Timeout of 10 us (ideal)
70    T30US% =   2    ' Timeout of 30 us (ideal)
71    T100US% =  3    ' Timeout of 100 us (ideal)
72    T300US% =  4    ' Timeout of 300 us (ideal)
73    T1MS% =    5    ' Timeout of 1 ms (ideal)
74    T3MS% =    6    ' Timeout of 3 ms (ideal)
75    T10MS% =   7    ' Timeout of 10 ms (ideal)
76    T30MS% =   8    ' Timeout of 30 ms (ideal)
77    T100MS% =  9    ' Timeout of 100 ms (ideal)
78    T300MS% = 10    ' Timeout of 300 ms (ideal)
79    T1S% =    11    ' Timeout of 1 s (ideal)
80    T3S% =    12    ' Timeout of 3 s (ideal)
81    T10S% =   13    ' Timeout of 10 s (ideal)
82    T30S% =   14    ' Timeout of 30 s (ideal)
83    T100S% =  15    ' Timeout of 100 s (ideal)
84    T300S% =  16    ' Timeout of 300 s (ideal)
85    T1000S% = 17    ' Timeout of 1000 s (maximum)
86    REM
87    REM Miscellaneous
88    S% = &H8        ' Parallel Poll sense bit
89    LF% = &HA       ' Line feed character
90    REM
91    REM Application program variables passed to
92    REM GPIB functions
93    REM
94    CMD$ = SPACE$(10)      ' command buffer
95    RD$ = SPACE$(255)      ' read data buffer
96    WRT$ = SPACE$(255)     ' write data buffer
97    BNAME$ = SPACE$(7)     ' board name buffer
```

```
98    BDNAME$ = SPACE$(7)    ' board or device name buffer
```

```
99     FLNAME$ = SPACE$(50)    ' file name buffer
100    '
110    REM The previous code was supplied with the National IEEE board
120    REM software as program DECL.BAS
130    '
140 '
1050 '
1060 '  *********************************************************
1070 '  *                                    *
1080 '  *          PROGRAM : P_STAT.BAS              *
1090 '  *                                    *
1100 '  *    SCANNING OF POTENTIAL ON A 1286 INTERFACE        *
1110 '  *                                    *
1120 '  *           Petr Vanysek              *
1130 '  *         Univeristy of Calgary          *
1140 '  *                                *
1150 '  *            14 October 1993           *
1160 '  *                                *
1170 '  *                                *
1180 '  *                                *
1190 '  *********************************************************
1220    PRINT ""
1230    PRINT ""
1240    PRINT "****************************************************************"
1250    PRINT "*                                            *"
1260    PRINT "*    This program allows a potential scan between      *"
1270    PRINT "*  certain values.                          *"
1280    PRINT "*                                          *"
1290    PRINT "*                                          *"
1300    PRINT "* THERE ARE SIX INPUT VARIABLES:                   *"
1310    PRINT "*        — Staring potential                *"
1320    PRINT "*        — Upper limit                      *"
1330    PRINT "*        — Lower limit                      *"
1340    PRINT "*        — Final potential                  *"
1350    PRINT "*        — Scan rate                        *"
1360    PRINT "*        — Number of segments                 *"
1370    PRINT "*          (4 segments/cycle, allow specify end of   *"
1380    PRINT "*          sweep)                         *"
1390    PRINT "*                                        *"
1400    PRINT "****************************************************************"
1410    PRINT ""
1420    BDNAME$ = "DEV6"
1430    CALL IBFIND (BDNAME$,POT%)            '1286 Potentiostat
1440    CALL IBSRE (POT%,V%)            'set Remote enable
1450    BDNAME$ = "GPIB0"
1460    CALL IBFIND (BDNAME$,ZEN%)            'Zenith National IEEE board
1470 '  **********************************************************
1480 '  *                                    *
1490 '  *  INITIALIZATION OF THE 1286                   *
1500 '  *                                *
1510 '  **********************************************************
1520    WRT$ = "RR 3" : CALL IBWRT (POT%,WRT$)    'Sets resistor to 10 ohms
```

1530   WRT$ = "ON 0" : CALL IBWRT (POT%,WRT$)   'On mode – Polarization pot

```
1540   WRT$ = "BY 1" : CALL IBWRT (POT%,WRT$)      'Stand-by mode CE o/c
1550   WRT$ = "TR 3" : CALL IBWRT (POT%,WRT$)      'Sets meter to sync
1560   WRT$ = "RU 1" : CALL IBWRT (POT%,WRT$)      'DVM run
1570   V1 = .5        'Initial potential
1580 INPUT " Initial potential  (V):" , V1
1590   V2 = 1.6       'Upper potential
1600 INPUT " Upper potential limit (V): " , V2
1610   V3 = .1             'Lower potential
1620 INPUT " Lover potential limit (V): " , V3
1630   V4 = .5           'Final potential
1640 INPUT " Stop potential (2nd segment) (V): " , V4
1650   T1 = .1           'Scan rate in V/s
1660 INPUT " Scan rate (V/s): " , T1
1670   CYC = .75          'Number of cycles
1680 INPUT " Number of segments (cycle = 4 segments): " , CYC
1690 PV = -V1             'Set initial polarization potential
1700 PS = -V1             'Final potential
1710 INPUT " Potential which will be applied after sweep stops (V): ", PS1
1720 PS=-PS1
1722 INPUT " Sensing resistor value (4 for CV, 3 for |Z|): ", SR1
1723 IF SR1=4 GOTO 1730
1724 IF SR1=3 GOTO 1730
1725 GOTO 1722
1730   VA = - V1         'Potential of first segment
1740   VB = - V2         'Potential of upper segment
1750   VC = - V4         'Stop potential
1760   VD = - V3         'Potential of lower segment
1770   TA = ABS(VB-VA)/T1
1780   TB = ABS(VC-VB)/T1
1790   TC = ABS(VD-VC)/T1
1800   TD = ABS(VA-VD)/T1
1810   PRINT TA, TB, TC, TD
1820   WRT$= "PV" + STR$(PV) : CALL IBWRT(POT%,WRT$)
1830   WRT$= "VA" + STR$(VA) : CALL IBWRT(POT%,WRT$)
1840   WRT$= "VB" + STR$(VB) : CALL IBWRT(POT%,WRT$)
1850   WRT$= "VC" + STR$(VC) : CALL IBWRT(POT%,WRT$)
1860   WRT$= "VD" + STR$(VD) : CALL IBWRT(POT%,WRT$)
1870   WRT$= "TA" + STR$(TA) : CALL IBWRT(POT%,WRT$)
1880   WRT$= "TB" + STR$(TB) : CALL IBWRT(POT%,WRT$)
1890   WRT$= "TC" + STR$(TC) : CALL IBWRT(POT%,WRT$)
1900   WRT$= "TD" + STR$(TD) : CALL IBWRT(POT%,WRT$)
1910   WRT$= "SM" + STR$(CYC) : CALL IBWRT(POT%,WRT$)
1912   WRT$= "RR" + STR$(SR1) : CALL IBWRT(POT%,WRT$)
1920   WRT$= "SV4" : CALL IBWRT(POT%,WRT$)      'SRQ generated upon sweep
end
1930   WRT$= "PW 1" : CALL IBWRT(POT%,WRT$)
1940   WRT$= "SW 1" : CALL IBWRT(POT%,WRT$)
1950   MASK%=&H800 : CALL IBWAIT(POT%,MASK%)   'WAITING FOR SRQ
1960   WRT$= "PV" + STR$(PS) : CALL IBWRT(POT%,WRT$)
1970   WRT$= "PW 1" : CALL IBWRT(POT%,WRT$)
1980   WRT$ = "TR 1" : CALL IBWRT (POT%,WRT$)   'Sets meter to recycle
1990   WRT$ = "RU 1" : CALL IBWRT (POT%,WRT$)   'DVM run
```

```
2000   FOR J=1 TO 1000   ' Time delay for the instrument to accept a command
```

```
2010   GOTO 2020
2020   NEXT
2030   CALL IBLOC(POT%)
2040   SYSTEM   ' Could be removed for NO—BATCH processing as is in ALONE.BAS
2050   END
```

Basic program (BASICA) used for interactive run of voltammetry using Solartron 1286.
The program is adjusted (memory and screen statements) for the use on a 8088 PC with
512 megabytes of memory.

```
1      CLEAR  ,29560!        ' BASIC Declarations
2      IBINIT1 = 29560!
3 – 99  These lines are identical to the previous program
100    '
110    REM The previous code was supplied with the National IEEE board
120    REM software as program DECL.BAS
130    CLS
140    SCREEN 4 ' needed to restore screen from the ZPLOT setting on 8088
1000 '
1010 ' *********************************************************
1020 ' *                                             *
1030 ' *          PROGRAM : AT_WILL.BAS              *
1040 ' *                                    *
1050 ' *     SCANNING OF POTENTIAL ON A 1286 INTERFACE      *
1060 ' *                               *
1070 ' *              Petr Vanysek              *
1080 ' *            Univeristy of Calgary         *
1090 ' *                          *
1100 ' *            22 November 1993          *
1110 ' *                            *
1120 ' *      (modified to operate on the 8088 machine)     *
1130 ' *                            *
1140 ' *********************************************************
1150    PRINT ""
1160    PRINT ""
1170    PRINT "***************************************************************"
1180    PRINT "*                                          *"
1190    PRINT "*     This program allows a potential scan between      *"
1200    PRINT "* certain values.                          *"
1210    PRINT "*                                     *"
1220    PRINT "*                                     *"
1230    PRINT "* THERE ARE EIGHT INPUT PARAMETERS:                *"
1240    PRINT "*        – Staring potential               *"
1250    PRINT "*        – Upper limit                 *"
1260    PRINT "*        – Lower limit                 *"
1270    PRINT "*        – Final potential               *"
1280    PRINT "*        – Scan rate                 *"
1290    PRINT "*        – Potential that will be applied after the    *"
1300    PRINT "*          sweep stops                 *"
1310    PRINT "*        – Sensitivity (=choice of the current sensing  *"
1320    PRINT "*          resistor                 *"
1330    PRINT "*        – Number of segments             *"
1340    PRINT "*          (4 segments/cycle, allow to specify end of  *"
1350    PRINT "*           the sweep)                 *"
1360    PRINT "*                                 *"
1370    PRINT "***************************************************************"
1380    PRINT ""
```

```
1390  BDNAME$ = "DEV6"
1400  CALL IBFIND (BDNAME$,POT%)          '1286 Potentiostat
1410  CALL IBSRE (POT%,V%)               'set Remote enable
1420  BDNAME$ = "GPIB0"
1430  CALL IBFIND (BDNAME$,ZEN%)          'Zenith National IEEE board
1440 ' **********************************************************************
1450 ' *                                         *
1460 ' *   INITIALIZATION OF THE 1286            *
1470 ' *                                         *
1480 ' **********************************************************************
1490  WRT$ = "RR 3" : CALL IBWRT (POT%,WRT$)     'Sets resistor to 10 ohms
1500  WRT$ = "ON 0" : CALL IBWRT (POT%,WRT$)     'On mode – Polarization pot
1510  WRT$ = "BY 1" : CALL IBWRT (POT%,WRT$)     'Stand–by mode CE o/c
1520  WRT$ = "TR 3" : CALL IBWRT (POT%,WRT$)     'Sets meter to sync
1530  WRT$ = "RU 1" : CALL IBWRT (POT%,WRT$)     'DVM run
1540  V1 = .5         'Initial potential
1550  INPUT " Initial potential  (V):" , V1
1560  V2 = 1.6         'Upper potential
1570  INPUT " Upper potential limit (V): " , V2
1580  V3 = .1          'Lower potential
1590  INPUT " Lower potential limit (V): " , V3
1600  V4 = .5          'Final potential
1610  INPUT " Stop potential (2nd segment) (V): " , V4
1620  T1 = .1          'Scan rate in V/s
1630  INPUT " Scan rate (V/s): " , T1
1640  CYC = .75        'Number of cycles
1650  INPUT " Number of segments (cycle = 4 segments): " , CYC
1660  PV = –V1         'Set initial polarization potential
1670  PS = –V1         'Final potential
1680  INPUT " Potential which will be applied after sweep stops (V): ", PS1
1690  PS=–PS1
1700  INPUT "Sensing resistor value (5 or 4 for CV, 3 for |Z|, 2 for Clean): ", SR1
1710  IF SR1=4 GOTO 1760
1720  IF SR1=3 GOTO 1760
1730  IF SR1=2 GOTO 1760
1740  IF SR1=5 GOTO 1760
1750  GOTO 1700
1760  VA = – V1         'Potential of first segment
1770  VB = – V2         'Potential of upper segment
1780  VC = – V4         'Stop potential
1790  VD = – V3         'Potential of lower segment
1800  TA = ABS(VB–VA)/T1
1810  TB = ABS(VC–VB)/T1
1820  TC = ABS(VD–VC)/T1
1830  TD = ABS(VA–VD)/T1
1840  PRINT TA, TB, TC, TD
1850  WRT$= "PV" + STR$(PV) : CALL IBWRT(POT%,WRT$)
1860  WRT$= "VA" + STR$(VA) : CALL IBWRT(POT%,WRT$)
1870  WRT$= "VB" + STR$(VB) : CALL IBWRT(POT%,WRT$)
1880  WRT$= "VC" + STR$(VC) : CALL IBWRT(POT%,WRT$)
1890  WRT$= "VD" + STR$(VD) : CALL IBWRT(POT%,WRT$)
1900  WRT$= "TA" + STR$(TA) : CALL IBWRT(POT%,WRT$)
```

```
1910    WRT$= "TB" + STR$(TB) : CALL IBWRT(POT%,WRT$)
1920    WRT$= "TC" + STR$(TC) : CALL IBWRT(POT%,WRT$)
1930    WRT$= "TD" + STR$(TD) : CALL IBWRT(POT%,WRT$)
1940    WRT$= "SM" + STR$(CYC) : CALL IBWRT(POT%,WRT$)
1950    WRT$= "RR" + STR$(SR1) : CALL IBWRT(POT%,WRT$)
1960    WRT$= "SV4" : CALL IBWRT(POT%,WRT$)      'SRQ generated upon sweep
end
1970    WRT$= "PW 1" : CALL IBWRT(POT%,WRT$)
1980    WRT$= "SW 1" : CALL IBWRT(POT%,WRT$)
1990    MASK%=&H800 : CALL IBWAIT(POT%,MASK%)    'WAITING FOR SRQ
2000    WRT$= "PV" + STR$(PS) : CALL IBWRT(POT%,WRT$)
2010    WRT$= "PW 1" : CALL IBWRT(POT%,WRT$)
2020    WRT$ = "TR 1" : CALL IBWRT (POT%,WRT$)   'Sets meter to recycle
2030    WRT$ = "RU 1" : CALL IBWRT (POT%,WRT$)   'DVM run
2040    FOR J=1 TO 1000    ' Time delay for the instrument to accept a command
2050    GOTO 2060
2060    NEXT
2070    CALL IBLOC(POT%)
2080    INPUT " PRESS 1 TO DO MORE SCANS, PRESS 2 TO DO IMPEDANCE ",
TREE
2090    IF TREE=1 GOTO 1
2100    IF TREE=2 GOTO 2120
2110    GOTO 2080
2120    SYSTEM            ' Could be removed for NO—BATCH processing
2130    END
```

Note for operation on IBM 8088 computer which has less memory. It is necessary to change lines 1 and 2 to read 29560 instead of 59400 to allow operation under the ZPLOT subroutine. Also, somewhere before first text is displayed on the screen, the command SCREEN 4 should be used for a proper choice of text. Prior to November 22, 1993, when the main board on the PC was replaced, the command was SCREEN 1, rather than SCREEN 4. It is likely that some switches were changed on the board or the video card.

To introduce a delay, under 8088, 4.7 MHz machine it seems that 10000 dummy lines (goto to previous) lasts 40 seconds.

Appendix — TIME/DATE programs for the 8088 machine

SAVE_DAT.BAS

This program save time and date in two text files. It was written to operate with the 8088 machine that does not have clock. With this feature the machine will start, if no proper tame/date is entered, with the tame/date of the previous session, which is probably better than the deafualt, 0 hours, on 1.1.1980. It works in conjunction with GET_TIME.BAS and an appropriate AUTOEXEC.BAT file.

```
OPEN "c:\time.txt" FOR OUTPUT AS #1
WRITE #1, TIME$
CLOSE #1
OPEN "c:\date.txt" FOR OUTPUT AS #1
WRITE #1, DATE$
CLOSE #1
END
```

****

GET_TIME.BAS

A counterpart to the above file SAVE_DAT.BAS

```
OPEN "C:\date.txt" FOR INPUT AS #1
INPUT #1, sdate$
CLOSE #1
DATE$ = sdate$
OPEN "C:\time.txt" FOR INPUT AS #1
INPUT #1, stime$
CLOSE #1
TIME$ = stime$
END
```

Program ZCON2.BAS

Combines files generated by ZPLOT to be readable as a set of data by Graph Tools.
Note that the text in italics is annotation only. It is not part of the actual program.

The created file will have data blocks each beginning with a line specifying the number of
line in the set (will vary) and number of columns (7). The seven columns are as follows:
frequency, log frequency, real impedance, imaginary impedance (negative), $|Z|$,
phase angle, parameter entered as the second value in number statement (typically time or
potential.)

NMD$ = "C:\ZPLOT\AL1−2.3d"
*(The above file name should be modified as desired. It is the file name, and a
drive/subdirectory, where the merged file will be located, once it is created.)*
DIM NUM$(40), Y(40)
OPEN NMD$ FOR OUTPUT AS #2
FOR J = 1 TO 34
*(The above line should be modified according to how many files are going to be
merged. It may not be greater than 40. unless the dimension statement above is changed to a
higher value.)*
READ NUM$(J)
READ Y(J)
*(The following list of DATA contains as the first number the distinguishing part of
the data file name, which should be read. The common part of the file name is
expressed in a later statement. The second number is a value which will be written in
the 7th column of the data sets. In this example it is just a distinguishing number.
Typically, it would be replaced by time or applied potential. There are currently 34
lines of data. Fewer than that can be used and the count set in the line before (FOR
J=1 to 34). The rest of the lines can then contain any values from previous
experiments. If more than 34 files are to be merged, more lines will need to be added.)*
DATA 21,0
DATA 22,1
DATA 23,2
DATA 24,3
DATA 25,4
DATA 26,5
DATA 27,6
DATA 28,7
DATA 29,8
DATA 30,9
DATA 31,10
DATA 32,11
DATA 33,12
DATA 34,13
DATA 35,14
DATA 36,15
DATA 37,16
DATA 38,17
DATA 39,18
DATA 40,19

```
DATA 41,20
DATA 42,21
DATA 43,22
DATA 44,23
DATA 45,24
DATA 46,25
DATA 47,26
DATA 48,27
DATA 49,28
DATA 50,29
DATA 51.30
DATA 52,31
DATA 53,32
DATA 54,33
NUM$ = MID$(NUM$, 2, 2)
FILE$ = "C:\ZPLOT\AL8–5" + NUM$(J) + ".Z"
```
(*The above statement contains the common part of the files to be merged. The distinguishing part is specified in the DATA lines above.*)
```
PRINT FILE$
OPEN FILE$ FOR INPUT AS #1
PRINT #2, "73 7"
```
The number 73 should agree with the number of lines in the data files. 73 is the value for log scan from 100000 Hz to 0.1 Hz at 12 steps per decade. If there is fewer lines, the program will not work. If the number is smaller, however, only that number of lines will be read as specified. This could be used in omitting uniformly a set of data (such as low frequencies. The number here (73) must be the same as the number in the following line.
```
FOR I = 1 TO 73
INPUT #1, A, B, C, D, E, F
PRINT #2, USING "+#.####^^^^_ "; A; LOG(A) / LOG(10); B; –1 * C; –1 * D; E;
Y(J)
NEXT
CLOSE #1
NEXT
CLOSE #2
END
```

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