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AN AUTOMATIC SYSTEM FOR ASSESSING THE ELECTRICAL PERFORMANCE OF ELECTRODES AND BATTERIES

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Summary

A powerful automated system for the measurement of electrode kinetics is described. The system may be applied to many types of electrode process and to the investigation of electrochemical devices.

Nomenclature

a	Anodic Tafel slope
b	Cathodic Tafel slope
$C_T{}^b$	Total concentration of diffusing species
$C_T{}^s$	Surface concentration of diffusing species
C_{dl}	Differential capacity
E_0	Standard potential
D	Diffusion coefficient
i	Current density
j	$\sqrt{-1}$
kf1	Electrochemical rate kSH $\exp[-(E - E_0) \times 2.303/b]$
kb1	Electrochemical rate kb1$' = k$b1$[X^-]^n$
kb1$'$	Electrochemical rate kSH $[X^-]^n \exp[(E - E_0) \times 2.303/a]$
kSH	Standard electrochemical rate
$[MX_n{}^{(2-n)-}]_b$	Bulk concentration of $MX_n{}^{(2-n)-}$
$[MX_n{}^{(2-n)-}]_s$	Surface concentration of $MX_n{}^{(2-n)-}$
R_{ct}	Charge transfer resistance
R_ω	Ohmic resistance
$Z(j\omega)$	Impedance of the interface
$Z_1(j\omega), Z_2(j\omega)$	Impedance for reactions 1 and 2
δ	Diffusion layer thickness
ν	Viscosity
σ	Warburg coefficient
ω_R	Rotation speed of rotating disc
ω	A.C. frequency
$(\partial q/\partial \Gamma)$	Adsorption parameter

Introduction

The investigation of a battery system is usually based on a study of its behaviour under resistive or other types of load. This method of assessing battery performance is equivalent to viewing the battery as a device which has particular electrical characteristics, that is, an effective resistance or impedance at a particular current or potential output. It would therefore be sensible when investigating the electrical performance of a battery to use the most modern techniques of electrical investigation available. A further convenient simplification, in view of the complexity of having two quite different electrodes as the components of a battery, is to be able to investigate the characteristics of the two single electrodes, as is usual in electrode kinetics. This can be achieved by the use of a suitable servo amplifier (potentiostat) and a potential reference probe. Either of the couples comprising the battery can be made up separately in a suitable electrochemical cell, or a potential probe can be inserted into a complete battery.

This paper is an account of a system which works automatically and is capable of carrying out precise electrical measurements, of interpreting and of storing the results. Although the system is capable of making measurements on whole batteries, only single electrode investigations will be discussed, as this area has been that most investigated so far. The method depends on the use of a computer which can control the experiment and, perhaps more important, can carry out the interpretation of the data [1 - 5].

The use of computers in the measurement of the electrical performance of battery couples and in the measurement of electrode kinetics has great advantages. It allows the efficient gathering and storage of experimental data, and also the mathematical handling of the data, so that it can be put into a form useful to the user. This can be carried out separately in a bigger computer after transfer of the data, or in an integrated fashion in the same computer. Both approaches have advantages and are available in the present system. It is tempting to use simpler systems to accumulate data, for example, the microcomputer based Solartron system for impedance measurements. Our experience shows, however, that accumulating limited data without processing in some way is an unsatisfactory method of operation.

Experimental data for a single electrode or a two electrode cell under test can be considered to be the electrical characteristics of a black box. If experimentation is looked at in this way, the emphasis on a particular electrochemical technique is lessened. This approach means, in practice, that the strategy of electrical and control engineering is introduced into the study of electrode kinetics. A further advantage of this approach is the introduction of automation, which means that the equipment can carry out, unattended, complex experiments for long periods.

This paper is an account of such an approach. Although the development is still at an early stage, the progress that has been made is described. The experience gained so far indicates that the method is a very effective way forward, particularly for the study of complex industrial problems

where better data, and the analysis of data on a much wider scale, are required. The method makes the detailed investigations, previously only available in a few university laboratories, easily accessible. The use of the system has also demonstrated that a dramatic reduction in manpower for electrochemical investigations can be achieved by the use of a properly designed computer system.

The method

The qualitative investigation of battery performance and the detailed investigation of electrode kinetics are not greatly separated in the system. Many methods have been developed for the study of the kinetics of electrode reactions. Figure 1 shows the methods which have been chosen in the

CONTROLLED DIFFUSION LAYER EXPERIMENT
(i.e. Rotating Disc)

$i - E$ Non-stationary	$i - E$ Stationary	$Z(w) - E$ Small Amplitude Perturbation	$i - t$ Small Amplitude Perturbation	$i - t$ Large Amplitude Perturbation	$E - t$ Large Amplitude Perturbation

Laplace Transform

Library of Reaction Models

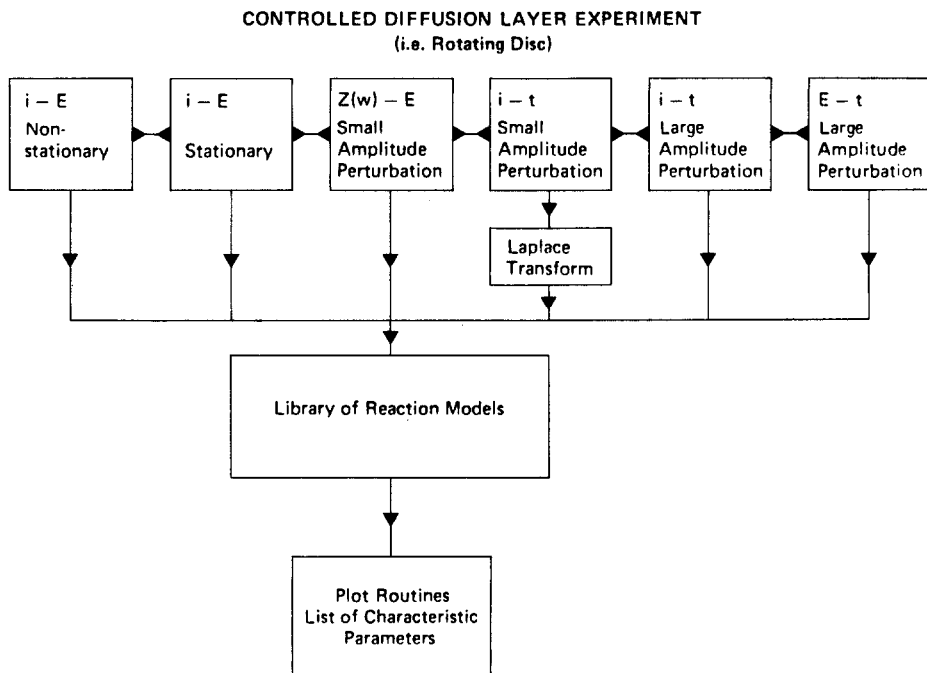Plot Routines
List of Characteristic Parameters

Fig. 1. Electrochemical methods accessible to the present equipment.

present work [1 - 5]. These have been chosen for their general nature and their intrinsic usefulness. Under computer control all can be implemented equally easily. A useful combination for assessing the d.c. and a.c. losses in an electrode, however, is the steady state $i-E$ curve, the $Z(\omega)-E$ curves and the large amplitude potential pulse response. The combination of these three methods is regularly used in this laboratory.

The electrical methods shown in Fig. 1 involve measuring and generating potential signals which vary as a function of time. This combination is

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eminently suitable for computer exploitation, but experience shows that
it is preferable to incorporate dedicated, well-designed instruments where
this is possible. Square potential and current pulses and linear potential
signals are generated by the computer. Although sinusoidal signals could also
be generated by this route, these are generated and analysed by an E.M.I.
S.E. 2450 Transfer Function Analyser. This has been found to be a superb
instrument for this purpose.

Figure 2 shows a functional diagram of the organisation of a system
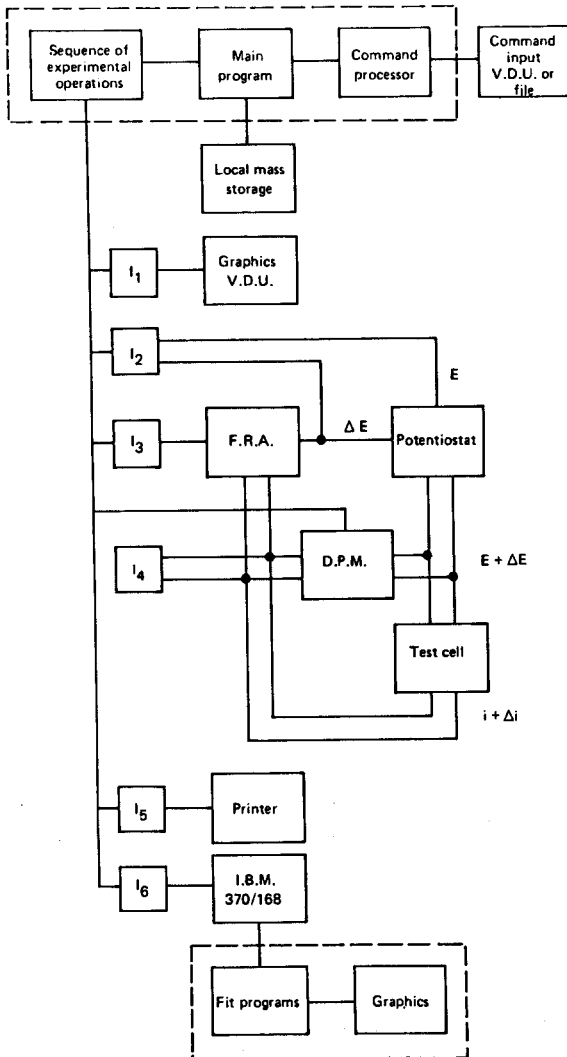which will implement the methods of Fig. 1. The boxes surrounded by

Fig. 2. The layout of a scheme to implement the methods of Fig. 1 by minicomputer.
The dashed boxes enclose software functions. Key: I_1 - I_6, Interfaces; DAC, Digital–anal-
ogue convertors; ADC, Analogue–digital convertors; DPM, Digital voltmeter; FRA,
Frequency response analyser, E.M.I. S.E. 2450.

a dashed line are software operations and those surrounded by a full line essentially enclose hardware functions. When a command is input the command processor orders the functions which are to be carried out and the result is stored locally. Subsequently, the data are sent in batch fashion to the I.B.M. 370/168 computer.

In addition it is necessary to have a means of controlling the steady state diffusional state of the system, by flow or rotation or some other similar technique [6]. This can be reasonably primitive as the primary investigation tool in this system is the electrical response.

Library of reaction schemes

The electrical performance parameter curves and the electrode kinetic investigations are made in the same equipment, using the same data. With a computing system the most complicated calculations can be implemented as a matter of course, as the details are invisible to the user. An important part of any investigation is to have the ability to interpret the data as a reaction scheme. A large amount of work has been carried out [7] on the calculation of various reaction schemes. Almost parallel developments have taken place in polarography [8], linear potential sweep methods [9, 10], double potential pulse methods [11], and in a.c. polarography [12] and in the a.c. method [13 - 15].

These are recent or representative examples. This field is now so extensive that it would need a longer article to cover it adequately. Most of these theoretical treatments are, however, too inflexible for the present purpose, as they are single calculations for a particular reaction scheme and usually involve complicated algebraic expressions [14, 15]. A way around this problem has been suggested by Rangarajan [16] who has presented a matrix formulation for the impedance, for example, which allows a uniform method of solution for a large number of reaction schemes, which lead to linear sets of equations.

That is the basis for the method of calculation given in this paper. Using computer subroutine packages which are available, on large and small computers it is not even necessary to carry out any algebra or the manipulation of matrices. As shown here, once the problem is formulated in matrix form directly from the diffusion equations and boundary conditions, the numerical calculation is straightforward. An idea of how a typical problem is formulated in the computer is given in the *Appendix*.

Figure 3 shows the reaction schemes which are available in the present system. These have been chosen to represent common reaction types; many other reaction schemes which lead to sets of linear equations can be calculated by a trivial extension of the present method. It is necessary to calculate both the steady state and the relaxation response. This is an aspect which has been neglected in some previous treatments.
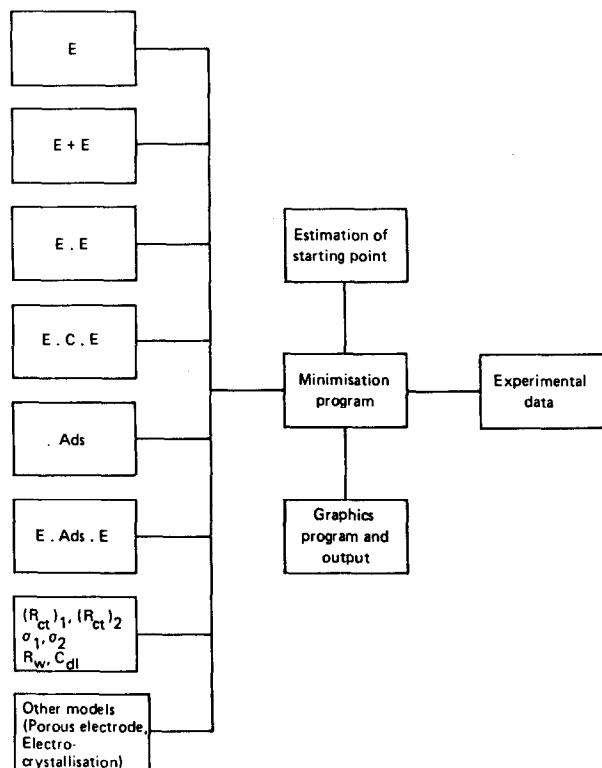
Fig. 3. Scheme to demonstrate the data analysis system which is carried out in the IBM 370/168 section of Fig. 2. The analysis is based on the steady state (i–E) and impedance ($Z(w)$–E) calculations presented here.

Also noted diagrammatically in Fig. 3 is the important step of being able to compare, efficiently, experiment and theory. In the present computer system this is carried out using well designed subroutines which minimise the difference between experiment and theory by varying selected parameters. The parameters which determine the electrode kinetic behaviour for the reaction schemes presented in the theory section are given in Table 1. The art of the researcher is to select the parameters which, on chemical grounds, can be used to effect the correspondence between experiment and theory.

Application of the method

The examples will be chosen from the types of chemical situation that commonly occur in batteries. These are the active metal deposition– dissolution, and the active–passive types of reaction. Only limited investigations have been made in this area [1 - 5]. As implied by Fig. 3, there are two approaches to the problem of using electrochemical data obtained auto-
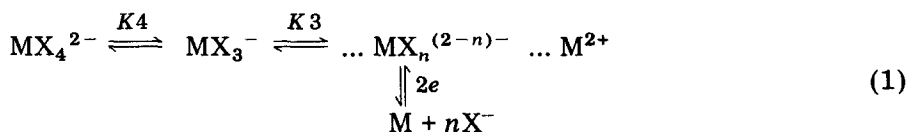
TABLE 1

Reaction parameters

E	δ, D_A, D_B, kf1, kb1
E + E	δ, D_A, D_B, kf1, kb1, D_C, D_D, kf2, kb2
E.E	δ, D_A, D_B, D_C, kf1, kb1, kf2, kb2
E.C.E.	δ, D_A, D_B, D_C, kf1, kb1, kf2, kb2, kk, kkk
Ads	δ, D_A, k_a, k_d, $(\partial q/\partial \Gamma_A)$
E.Ads.E	δ, D_A, D_B, D_C, kf1, kb1, k_a, k_d, $(\partial q/\partial \Gamma_B)$

matically. The first method is to use the data in an empirical fashion, in the manner of chemical spectroscopy. That is a mode of analysis such as the box marked $(R_{ct})_2$, etc., in which sets of parameter curves which describe the electrical properties of the electrode system or battery under test, are the output (see *Appendix*). These parameters can give information about the physical factors affecting the battery performance.

Deposition—dissolution reactions

The theory appropriate to these reactions is associated with the C.E. box in Fig. 3.

The two important features of these reactions, which effectively determine the electrode kinetics, are the fate of the electrons and the presence of complexing. The kinetics of electron transfer for a number of two electron transfer reactions have been considered in some detail in previous publications [4, 17 - 19]. The methods which can be used to deal with complexing have also been discussed [1, 20, 21]. In this work the interpretation of the data is based on the reaction scheme

$$MX_4{}^{2-} \underset{}{\overset{K4}{\rightleftharpoons}} MX_3{}^{-} \underset{}{\overset{K3}{\rightleftharpoons}} \dots MX_n{}^{(2-n)-} \dots M^{2+}$$
$$\Big\Updownarrow 2e$$
$$M + nX^{-}$$

(1)

and the set of equations which describes the expected electrical consequences of this reaction scheme can easily be calculated from the methods used in the *Library of Reaction Schemes* section. For a reaction scheme, the parameters which determine the behaviour are similar to those which describe an E reaction with the addition of $K1$ - Kn which describes the C part. The parameters are then kf1, kb1$'$, C_T^b, C_M^b, n, D_T, D_M, δ, $K1$ - Kn.

There are a number of ways of dealing with this situation. What we have done is to fix $K1$ - Kn, E_0, n, D and to fit the current–potential for kf1, kb1$'$ and the impedance data for kf1, kb1$'$, R_ω, C_{dl}. The i–E and $Z(\omega)$–E data should be consistent and give information in C_{dl} about the real surface, which is an invaluable quantity in battery system investigations.

Because of the importance of the reaction scheme, the set of equations is given in the *Appendix*.

The solutions of these equations include all the previous methods of dealing with complex discharge, for example, the variation of the exchange current density or the variation of the value of the current at fixed potential with anion concentration. By this means it has been possible to follow the instantaneous electrode kinetics and the variation with time of discharge from a number of complexes. These measurements represent a significant improvement over the methods which have been used previously to investigate, for example, the reactions of nickel in ammonia-containing solution [22] and for a number of other systems such as gold [23], rhodium [24], palladium [25]. These are used as examples, as it is no longer necessary to consider battery reactions and plating reactions separately, and the method deals with deposition and dissolution equally. This is of great advantage for a detailed investigation of rechargeable battery systems.

A further example which has been investigated is the deposition-dissolution of Zn in near neutral solution [17 - 19]. This has applications to the characteristics of the Leclanché cell [26].

Active–passive reactions

Three situations which have been investigated recently will be briefly mentioned here. The dissolution of lead in sulphuric acid, the dissolution [27 - 29] of mercury in hydrochloric acid and the dissolution of titanium in sulphuric acid [30]. The $R_{ct}-E$, $C_{dl}-E$, $\sigma-E$, $R_{\omega}-E$ parameter curves (see *Appendix*) allow precise identification of the active region, and the encroachment of passive behaviour, as a function of time, potential, or concentration of the electrolyte.

The case of Pb dissolution in H_2SO_4 is interesting. Some sample results of a potential scan and the resulting parameter curves are shown in Fig. 4. As shown particularly by the $\sigma-E$ curve the active dissolution of Pb is confined to a narrow potential range. Negative to about -500 mV the H_2 evolution reaction dominates the electrical behaviour. These results are only presented as an example, to identify the main effects in the data. In a practical investigation one would be interested in the time and concentration, electrode structure, and temperature dependence of these parameters.

The characteristics of Pb dissolution have been investigated previously using more conventional methods [27, 28]. An attempt has been made to set up a model for the passive behaviour of Pb [29], and to compare it with Hg dissolution. A start has been made in translating the measurements of Fig. 4, which were obtained with a smooth electrode, to sections of battery plate [31]. This should allow the electrical characteristics of battery plates to be compared in a much more satisfactory way and allow some progress to be made in this difficult area of investigation.

Catalytic electrodes and redox reactions

Couples of this type have possibilities in storage batteries. One that has been investigated by the methods of this paper is the Cl^-/Cl_2 couple on a
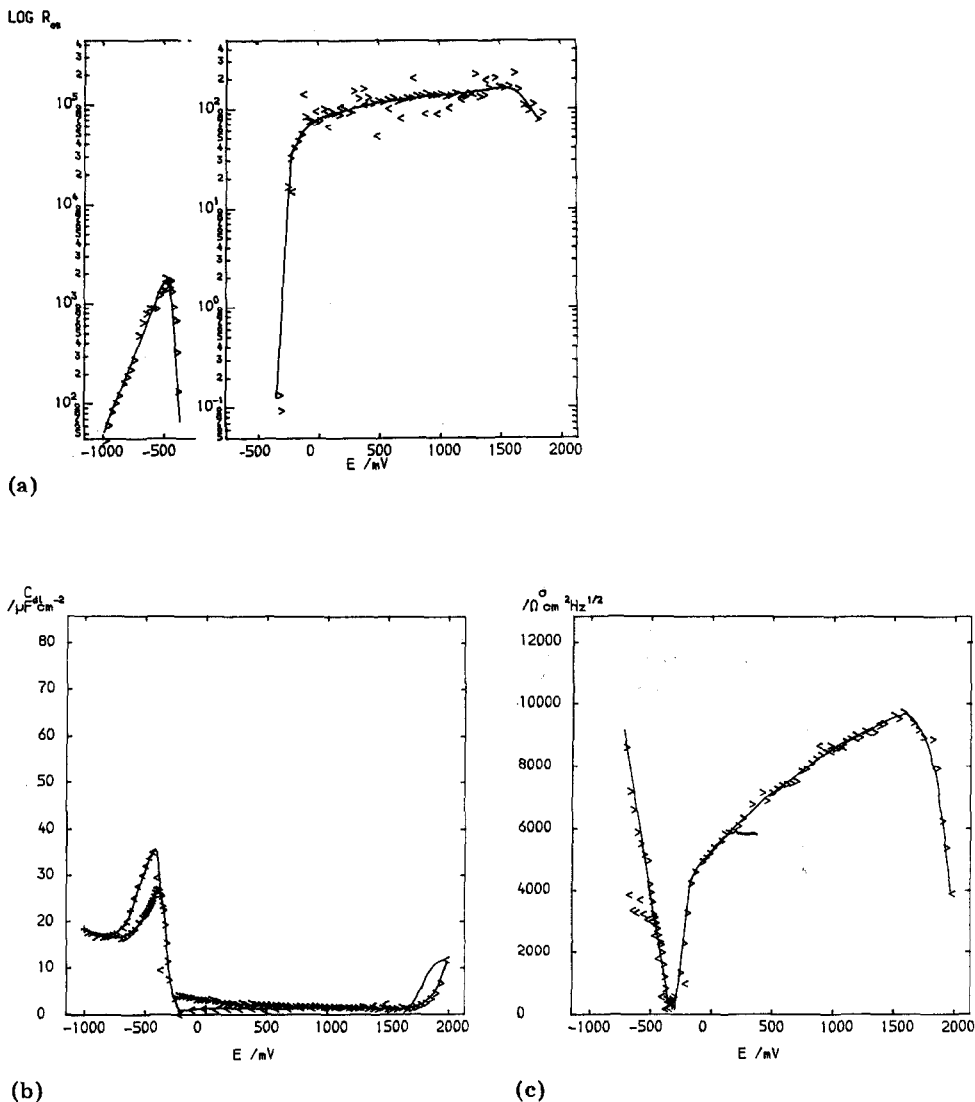
Fig. 4. Example of an experimental result for the dissolution of Pb in 5M H_2SO_4. The parameter curves, based on an analysis of the impedance, are (a) log $R_{ct}-E$, (b) $C_{dl}-E$, (c) $\sigma-E$.

D.S.A. RuO_2 electrode [32 - 34]. The $i-E$ curve and the parameter curves allow the performance of the couple to be assessed. In particular, the variation of the $C_{dl}-E$ curve with time allows the activity of the RuO_2 large, real area electrodes to be monitored. In addition, it becomes possible to investigate the effects of the gas bubbles on the reaction mechanism. Similar measurements can be made for the H^+/H_2 couple and for other gas reactions.

Conclusion

The introduction of potentiostatic and galvanostatic methods in a systematic manner some 20 years ago revolutionised the investigation of battery and corrosion reactions.

The introduction of the computer and more efficient ways of electrical investigation will certainly improve the capability to investigate complex chemical situations by orders of magnitude. Although the developments are still at a relatively early stage, the power of a succesful system such as the present one is great. I can foresee that research and development organisations which do not have such a system in the future will be at a serious disadvantage.

Appendix

Parameter analysis

The method used in this work to characterise the electrical response of an electrochemical system is by means of an equivalent circuit. The measurements made so far indicate that the usual method of analysis based on a redox reaction has been sufficient to account for the behaviour of the systems which were investigated. However more complex situations may arise. The equation for the usual equivalent circuit, involving a charge transfer resistance, R_{ct}, in series with a Warburg impedance, characterised by σ, leads to

$$\frac{1}{Z(\omega) - R_\omega} = \frac{1}{R_{ct} + (1 - j)\sigma\omega^{-1/2}} + j\omega C_{dl}. \tag{2}$$

When two electrochemical reactions occur then

$$\frac{1}{Z(\omega) - R_\omega} = \frac{1}{Z_1(\omega)} + \frac{1}{Z_2(\omega)} + j\omega C_{dl}. \tag{3}$$

It is sometimes possible to simplify the last equation when, for example, $(R_{ct})_1 < \sigma_1$, and $(R_{ct})_2 > \sigma_2$, in a particular ω range. The method that is used in the present equipment is to fit the impedance data at each potential completely. If a single reaction is suspected then parameter curves of R_ω–E, R_{ct}–E, σ–E, C_{dl}–E together with the i–E curves would be reported as the final result of an experiment.

Reaction mechanism analysis

A typical calculation for a common reaction type, eqn. (1), is given here as an example.

For a redox reaction involving MX_n, M and X^-, the steady state concentrations can be deduced from the following sets of equations:

$$-D_{\mathrm{T}}\left(\frac{\mathrm{d}C_{\mathrm{T}}{}^{\mathrm{s}}}{\mathrm{d}x}\right) + k\mathrm{f}1[\mathrm{MX}_n]_{\mathrm{s}} - k\mathrm{b}1'[\mathrm{M}]_{\mathrm{s}} = 0 \tag{4}$$

$$D_{\mathrm{M}}\left(\frac{\mathrm{d}C_{\mathrm{M}}{}^{\mathrm{s}}}{\mathrm{d}x}\right) + k\mathrm{f}1[\mathrm{MX}_n]_{\mathrm{s}} - k\mathrm{b}1'[\mathrm{M}]_{\mathrm{s}} = 0 \tag{5}$$

$$\delta\left(\frac{\mathrm{d}C_{\mathrm{T}}{}^{\mathrm{s}}}{\mathrm{d}x}\right) + C_{\mathrm{T}}{}^{\mathrm{s}} = C_{\mathrm{T}}{}^{\mathrm{b}} \tag{6}$$

$$\delta\left(\frac{\mathrm{d}C_{\mathrm{M}}{}^{\mathrm{s}}}{\mathrm{d}x}\right) + [\mathrm{M}]_{\mathrm{s}} = [\mathrm{M}]_{\mathrm{b}} \tag{7}$$

$$K1[\mathrm{M}^+][\mathrm{X}^-] - [\mathrm{MX}] = 0 \tag{8}$$

$$K2[\mathrm{MX}][\mathrm{X}^-] - [\mathrm{MX}_2] = 0 \tag{9}$$

$$K3[\mathrm{MX}_2][\mathrm{X}^-] - [\mathrm{MX}_3] = 0 \tag{10}$$

$$K4[\mathrm{MX}_3][\mathrm{X}^-] - [\mathrm{MX}_4] = 0 \tag{11}$$

$$[\mathrm{M}^+]_{\mathrm{s}} + [\mathrm{MX}]_{\mathrm{s}} + [\mathrm{MX}_2]_{\mathrm{s}} + [\mathrm{MX}_3]_{\mathrm{s}} + [\mathrm{MX}_4]_{\mathrm{s}} = C_{\mathrm{T}}{}^{\mathrm{s}} \tag{12}$$

$$[\mathrm{M}^+]_{\mathrm{b}} + [\mathrm{MX}]_{\mathrm{b}} + [\mathrm{MX}_2]_{\mathrm{b}} + [\mathrm{MX}_3]_{\mathrm{b}} + [\mathrm{MX}_4]_{\mathrm{b}} = C_{\mathrm{T}}{}^{\mathrm{b}} \tag{13}$$

$$i = 2F[k\mathrm{b}1'[\mathrm{M}]_{\mathrm{s}} - k\mathrm{f}1[\mathrm{MX}_n]_{\mathrm{s}}] \tag{14}$$

where the symbols are defined in the reaction scheme of eqn. (1). Equations (4) - (13) simplify if one complex, say MX_4^{2-}, is in large excess. However, the more general formulation has been retained here. Equations (4) - (13) are solved as simultaneous equations in a single matrix, given $C_{\mathrm{T}}{}^{\mathrm{b}}$, $[\mathrm{M}]_{\mathrm{b}}$, $k\mathrm{f}1$, $k\mathrm{b}1'$, δ, D_{T}, D_{M}, $K1$ - $K4$. For the evaluation of $k\mathrm{f}1$ and $k\mathrm{b}1'$, E_0 can be calculated from the Nernst equation. The theoretical i–E curve then follows from eqn. (14) and the $Z(\omega)$–E curve from the equations

$$\overline{\mathrm{d}i} = \left(\frac{\partial i}{\partial E}\right)\overline{\mathrm{d}E} + \left(\frac{\partial i}{\partial[\mathrm{MX}_n]_{\mathrm{s}}}\right)\overline{\mathrm{d}[\mathrm{MX}_n]_{\mathrm{s}}} + \left(\frac{\partial i}{\partial C_{\mathrm{M}}{}^{\mathrm{s}}}\right)\overline{\mathrm{d}C_{\mathrm{M}}{}^{\mathrm{s}}} \tag{15}$$

$$\overline{\mathrm{d}[\mathrm{MX}_n]_{\mathrm{s}}} = \frac{\overline{\mathrm{d}i}}{2FK\sqrt{pD_{\mathrm{T}}}} \tag{16}$$

$$\overline{\mathrm{d}C_{\mathrm{M}}{}^{\mathrm{s}}} = -\frac{\overline{\mathrm{d}i}}{2F\sqrt{pD_{\mathrm{M}}}} \tag{17}$$

where the quantities with the bar are Laplace transforms defined by

$$\overline{\mathrm{d}i} = \int_0^\infty \mathrm{d}i \exp(-pt)\,\mathrm{d}t. \tag{18}$$

The constancy of the partial differentials with respect to the other quantities is understood. K is a constant relating $[\mathrm{MX}_n]_{\mathrm{s}}$ to $C_{\mathrm{T}}{}^{\mathrm{s}}$. The $Z(\omega)$–E curve is then derived from

$$\frac{1}{Z(p)} = \frac{(\partial i/\partial E)}{1 + k\mathrm{f}1/K\sqrt{pD_\mathrm{T}} + k\mathrm{b}1'/\sqrt{pD_\mathrm{M}}} + p\,C_{\mathrm{dl}}. \tag{19}$$

Acknowledgement

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