IMPEDANCE SPECTROSCOPY

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GLOSSARY

Admittance: A complex quantity usually symbolized by $Y = Y' + iY''$. It is the inverse of impedance and is sometimes called complex conductance. Here $i = +(-1)^{0.5}$, and the single and double primes denote in-phase and quadrature components, respectively.

Complex dielectric constant: The ratio of the (complex) dielectric displacement to the small-signal AC electric field that induces the displacement. Conventionally written as $\varepsilon = \varepsilon' - i\varepsilon''$. It is given by $Y/(i\omega C_C)$, where C_C is the capacitance of the empty measuring cell.

Complex forms: Impedance spectroscopy data may be expressed in two different forms. Rectangular: $I = I' + iI''$, where I' and I'' are the real and imaginary parts of I, respectively; or Modulus: $I = |I|e^{i\phi}$, where $|I|$ is the modulus, or absolute value, of I and ϕ is its phase angle, or argument. Note that the complex conjugate of I is $I^* = I' - iI'' = |I|e^{-i\phi}$.

Complex modulus: $M = M' + iM''$. It is the inverse of the complex dielectric constant and is also equal to $i\omega C_C Z$.

Debye length: A characteristic length that determines the extent of a space charge region near a discontinuity. It depends on temperature, dielectric constant, and the valence numbers and bulk concentrations of the mobile charges present. The diffuse double-layer capacitance present near a non-ohmic electrode is inversely proportional to the Debye length.

Immittance: A general term denoting any of the four basic impedance spectroscopy response quantities: Y, Z, ε, or M. $I = I' + iI''$.

Impedance: The ratio of a sinusoidal voltage, applied across two terminals of a measurement cell, to the sinusoidal component of the current flowing between the terminals that results from the applied potential difference. Unless the system is purely resistive, impedance is a complex quantity because the current will have a different phase from the applied voltage: $Z = Z' + iZ''$.

Impedance spectroscopy (IS) is a general term that subsumes the small-signal measurement of the linear electrical response of a material of interest (including electrode effects) and the subsequent analysis of the response to yield useful information about the physicochemical properties of the system. Analysis is generally carried out in the frequency domain, although measurements are sometimes made in the time domain and then Fourier transformed to the frequency domain. IS is by no means limited to the measurement and analysis of data at the impedance level (e.g., impedance vs. frequency) but may involve any of the four basic immittance levels; thus, most generally, IS stands for immittance spectroscopy.

I. Short History of Impedance Spectroscopy

Since impedance spectroscopy (IS) deals directly with complex quantities, its history really begins with the introduction of impedance into electrical engineering by Oliver Heaviside in the 1880s. His work was soon extended by A. E. Kennelly and C. P. Steinmetz to include vector diagrams and complex representation. It was not long before workers in the field began to make use of the Argand diagram of mathematics by plotting immittance response in the complex plane, with frequency an implicit variable. Electrical engineering examples were the circle diagram introduced by C. W. Carter (1925) and the Smith-Chart impedance diagram of P. H. Smith

(1939). These approaches were soon followed in the dielectric response field by the introduction in 1941 of the Cole–Cole plot: a plot of ε'' on the y (or imaginary) axis vs. ε' on the x (or real) axis. Such complex plane plots are now widely used for two-dimensional representation of the response of all four immittance types. Finally, three-dimensional perspective plots that involve a log-frequency axis were introduced to the IS area by the author and his colleagues in 1981; these plots allow complete response at a given immittance level to be shown in a single diagram.

Because IS analysis generally makes considerable use of equivalent circuits to represent experimental frequency response, the whole history of lumped-constant circuit analysis, which particularly flowered in the first third of the century, is immediately relevant to IS. Since then, much work has been devoted to the development of theoretical physicochemical response models and to the definition and analysis of various distributed circuit elements for use in IS-equivalent circuits along with ideal, lumped elements like resistance and capacitance. The preferred analysis method for fitting of IS data to either equivalent circuits or to a mathematical model is complex non-linear least squares fitting (CNLS), introduced to the field in 1977 by Macdonald and Garber. In this procedure, all the parameters of a fitting model are simultaneously adjusted to yield an optimum fit to the data.

Early experimental work in the IS field is discussed in the book on IS listed in the bibliography. Here it will suffice to mention the work of Grahame on electrolyte double-layer response, the technique of AC polarography pioneered by D. E. Smith, and the electrolyte studies of Randles and Somerton, Sluyters and Oomen, R. P. Buck, and J. E. Bauerle. Since the late 1960s, IS has developed rapidly, in large part because of the availability of new, accurate, and rapid measuring equipment.

II. Categories of Impedance Spectroscopy: Definitions and Distinctions

There are two main categories of IS: electrochemical IS (EIS) and everything else. EIS involves measurements and analysis of materials in which ionic conduction strongly predominates. Examples of such materials are solid and liquid electrolytes, fused salts, ionically conducting glasses and polymers, and nonstoichiometric ionically bonded single crystals, where conduction can involve motion of ion vacancies and interstitials. EIS is also valuable in the study of fuel cells, rechargeable batteries, and corrosion.

The remaining category of IS applies to dielectric materials: solid or liquid nonconductors whose electrical characteristics involve dipolar rotation, and to materials with predominantly electronic conduction. Examples are single-crystal or amorphous semiconductors, glasses, and polymers. Of course, IS applies to more complicated situations as well, for example to partly conducting dielectric materials with some simultaneous ionic and electronic conductivity. It is worth noting that although EIS is the most rapidly growing branch of IS, nonelectrochemical IS measurements came first and are still of great value and importance in both basic and applied areas.

In the EIS area in particular, an important distinction is made between supported and unsupported electrolytes. Supported electrolytes are ones containing a high concentration of indifferent electrolyte, one whose ions generally neither adsorb nor react at the electrodes of the measuring cell. Such an added salt can ensure that the material is very nearly electroneutral everywhere, thus allowing diffusion and reaction effects for a low-concentration ion of interest to dominate the AC response of the system. Support is generally only possible for liquid electrochemical materials; it is often, but not always, used in aqueous electrochemistry. Solid electrolytes are unsupported in most cases of interest, electroneutrality is not present, and Poisson's equation strongly couples charged species. Because of this difference, the formulas or models used to analyze supported and unsupported situations may be somewhat or completely different.

Another important distinction is concerned with static potentials and fields. In a material-electrode system without an applied static external potential difference (p.d.), internal p.d.s and fields are, nevertheless, generally present, producing space-charge layers at interfaces. For solids such regions are known as Frenkel layers and arise from the difference in work function between the electrode and the material. Because the static fields and charge concentrations in the material are inhomogeneous, exact small-signal solutions for the impedance of the system are impossible and numerical methods must be used.

In an electrolytic cell such static space-charge regions are only absent when the external static p.d. is adjusted so that the charge on the working electrode is zero—the point of zero charge (PZC)—a flat-band condition. Such adjustment is impossible for systems with two symmetrical electrodes because an applied static p.d. increases the space-charge region at one electrode while reducing it at the other. But the use of a working electrode of small area and a large-area counter electrode ensures that the overall impedance of the system is little influenced by what happens at

the counter electrode; in this situation the PZC can be achieved for the working electrode. In general, the current distribution near this electrode is frequency dependent and thus makes a frequency-dependent contribution to the overall impedance of the system, which is dependent on electrode geometry and character.

Figure 1 shows a flow diagram for a complete IS study whose goal is characterization of important properties of the material-electrode system from its electrical response, one of the major applications of IS. The experimental data is denoted by $Z_e(\omega)$, the impedance predicted by a theoretical fitting model by $Z_t(\omega)$, and that of a possible electrical equivalent circuit by $Z_{ec}(\omega)$, where $\omega = 2\pi f$ and f is frequency. When an appropriate detailed model for the physicochemical processes present is available, it should certainly be used for fitting. Otherwise, one would employ an equivalent electrical circuit whose elements and connectivity were selected, as far as possible, to represent the various mass and charge transport physical processes thought to be of importance for the particular system.

Note that a complete IS analysis often involves more than a single set of measurements of immittance vs. frequency. Frequently, full characterization requires that such sets of measurements be carried out over a range of temperatures and/or other externally controlled experimental variables. IS characterization may be used to yield basic scientific and/or engineering information on a wide variety of materials and devices, ranging from solid and liquid electrolytes to dielectrics and semiconductors, to electrical and structural ceramics, to magnetic ferrites, to polymers and protective paint films, and to secondary batteries and fuel cells. Other important applications of IS, not further discussed herein, have been made in the biological area, such as studies of polarization across cell membranes and of animal and plant tissues. Finally, the analysis techniques of IS are not limited to electrical immittance but apply as well to measurements of mechanical and acoustic immittance.

III. Elements of Impedance Spectroscopy

A. MEASUREMENT METHODS

Although IS measurements are simple in principle, they are often complicated in practice. Part of the difficulty arises because the resistive and capacitive components of IS response have ranges, when one considers different materials, electrodes, and temperatures, that span 10 or more orders of magnitude. Measurements require comparison with standard values of these components and are thus only as accurate as the standards. Second, the IS frequency range may extend over 12 orders of magnitude or more: from as low as 10 μHz for adequate resolution of interfacial processes, up to 10 MHz or higher, sometimes needed to characterize bulk response of the material of interest.

Although IS measurements on solids or dielectric liquids usually involve cells with two identical plane, parallel electrodes, the situation is often much more complicated for measurements on liquid electrolytes. There, one usually employs one or more small working electrodes, a very small reference electrode, and a large counter electrode. Such an arrangement ensures that everything of interest (related to immittance) happens at or near the working electrode(s). Further, a rotating-disc working electrode is frequently used to control hydrodynamic conditions near the electrode.

Because the kinetics of electrode reactions often depend strongly on the static (dc) potential difference between the working electrode and the bulk, or,
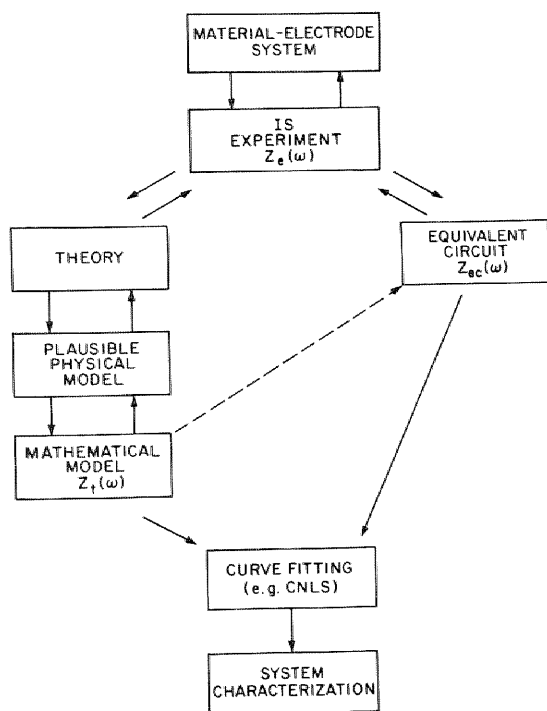

FIG. 1.   Flow diagram for the measurement and characterization of a material-electrode system. (Reprinted by permission of John Wiley & Sons, Inc., from "Impedance Spectroscopy—Emphasizing Solid Materials and Systems." J. R. Macdonald, ed. Copyright © 1987, John Wiley & Sons, Inc.)

equivalently, the working electrode and the reference electrode, a potentiostat is needed to fix this p.d. to a known and controllable value. The simultaneous application of both ac and dc signals to a three- or four-electrode cell makes it particularly difficult to obtain accurate frequency-response results above 50 kHz or so.

Although a calibrated double-beam oscilloscope, or the use of Lissajous figures with a single-beam instrument, can be used to determine immittance magnitude and phase, such measurements are generally insufficiently accurate, are time consuming, and apply only over a limited frequency range. A superior alternative is the use of audio-frequency or high-frequency bridges. Several such bridges are discussed in the IS book. Of particular interest is the Berberian—Cole bridge, which can cover a wide frequency range and can allow potentiostatic dc bias control. Another important technique using a bridge and special error reduction procedures has recently been developed by Schöne and co-workers that allows potentiostatic control and yields very accurate impedance results up to 3 MHz. But manual balancing of a bridge is often disadvantageous because of its slowness, especially for corrosion studies where the properties of the system itself may be slowly changing.

Manual balancing is avoided in various automated network analyzers and impedance analyzers now commercially available. But the measuring instrument that has virtually revolutionized IS measurements and principally led to the burgeoning growth of the field in the past 20 years is the frequency-response analyzer (FRA). Typical examples are FRAs produced by Solartron and by Zahner. Although space does not allow a full description of their many features, such instruments allow potentiostatic control for three- or four-terminal measurements, they are highly digitized, they incorporate automatic frequency sweeps and automatic control of the magnitude of the applied ac signal, they can yield 0.1% accuracy, and they carry out measurements automatically.

Although FRAs such as the Solartron 1260 cover a frequency range from 10 μHz to 32 MHz, impedance results using them are not sufficiently accurate above about 50 kHz when potentiostatic control is used. A typical FRA determines impedance by correlating, at each frequency, the cell response with two synchronous signals, one in phase with the applied signal and the other phase-shifted by 90°. This process yields the in-phase and out-of-phase components of the response and leads to the various immittance components. A useful feature is autointegra-

tion, a procedure that averages results over an exact number of cycles, with the amount of such averaging automatically selected to yield statistically consistent results.

B. ANALYSIS AND INTERPRETATION OF DATA

1. Graphics

Before carrying out a detailed analysis of IS immittance data, it is a good idea to examine the data graphically, both to search for any outliers and to examine the structure of the data, structure that will usually reflect, at least in part, the physical processes present that led to the data. From the experimental situation one will generally know whether one is dealing with an intrinsically insulating material, such as a nonconducting or a leaky dielectric, or whether the situation is of intrinsically conducting character: mobile charges dominate the response but may be completely or only partially blocked at the electrodes. For complete blocking, no DC can pass, a case that could be confused with dielectric response. In the intrinsically conducting situation, dielectric effects are generally minimal, and Z and M representations of the data are often most useful. In the nonconducting case, Y and ε are frequently most appropriate, but it is nevertheless a good idea initially to examine plots of the data for all four immittance levels, whatever the conducting/nonconducting situation.

When mobile charges are present, five principal physical processes may influence the data; these are bulk resistive-capacitive effects, electrode reactions, adsorption at the electrodes, bulk generation-recombination effects (e.g., ion-pairing), and diffusion. The double-layer capacitance is the reaction capacitance C_R, and the reaction resistance R_R is inversely proportional to the reaction rate constant. It is important to distinguish C_R from the usually much larger low-frequency pseudocapacitance associated with the diffusion of mobile charge or with adsorption at an electrode. Note that in general a process that dissipates energy is represented in an IS equivalent circuit by a resistance, and energy storage is usually modeled by a capacitance. Detailed CNLS analysis of IS data can lead in favorable cases to estimates of such basic material-electrode quantities as electrode reaction and adsorption rates, bulk generation-recombination rates, charge valence numbers and mobilities, diffusion coefficients, and the (real) dielectric constant of the material.

There are many ways IS data may be plotted. In the IS field, where capacitive rather than inductive

effects dominate, conventionally one plots $-\mathrm{Im}(Z)$ $\equiv -Z''$ on the y-axis vs. $\mathrm{Re}(Z) \equiv Z'$ on the x-axis to give a complex plane impedance plot. Such graphs have (erroneously) been termed Nyquist plots. They have the disadvantage of not indicating frequency response directly, but may, nevertheless, be very helpful in identifying conduction processes present. Another approach, the Bode diagram, is to plot $\log[|Z|]$ and ϕ vs. $\log[f]$. Alternatively, one can plot Z' (or any I') or $-Z''$ (or $-I''$), or the logs of these quantities vs. $\log[f]$.

An important IS building block is Debye response, response that involves a single time constant, τ. A Cole–Cole plot of such response is shown in Fig. 2. The arrow shows the direction of increasing frequency. Debye response can be represented in complex form as $\varepsilon = \varepsilon_\infty + [\varepsilon_0 - \varepsilon_\infty]/[1 + (i\omega\tau)]$ and, in circuit form, involves a capacitance $\varepsilon_\infty C_C$ in parallel with the series combination of a resistor R, modeling dissipative effects, and a capacitor $C \equiv (\varepsilon_0 - \varepsilon_\infty)C_C$, representing stored charge. Finally, the time constant or relaxation time is given by $\tau \equiv RC$.

Three-dimensional perspective plots are particularly useful because they allow complete response to appear on a single graph. Figure 3 shows such plots at the impedance level for the analog of Debye response for a conducting system. By including projections of the 3-D curve of the response in all three perpendicular planes of the plot, one incorporates all relevant 2-D plots in the same diagram. Note that the curve in the back plane, the complex-plane impedance plot, is just the usual Debye semicircle, one with its center on the real axis.

To demonstrate some of the power and weaknesses of 3-D plots, Fig. 4 includes three types of such plots, all for the same EIS data taken on single-crystal Na β-alumina. Graph A is an impedance plot and shows that only two out of the four curves indicate that the lowest frequency point is in error. In this plot, ν denotes frequency f. Clearly, one should not rely on the conventional $\log[f]$ curves alone. Since the diagram shows that much high-frequency data are not resolved by this kind of plot, graph B involves the logarithms of the data. Although high-frequency response now appears, the error in the low-frequency point is nearly obscured by the reduced resolution inherent in a log plot.

Much improved results appear in graph C, a 3-D M plot. Resolution over the full frequency range is greatly increased; the error in the lowest frequency point is clearly shown; a mid-frequency glitch now appears that is not evident in the other plots and arises from a switch of measuring devices without adequate cross-calibration; and nonphysical behavior
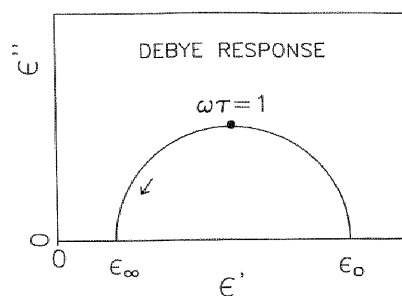

FIG. 2.   Complex-plane plot of the complex dielectric constant for Debye frequency response.
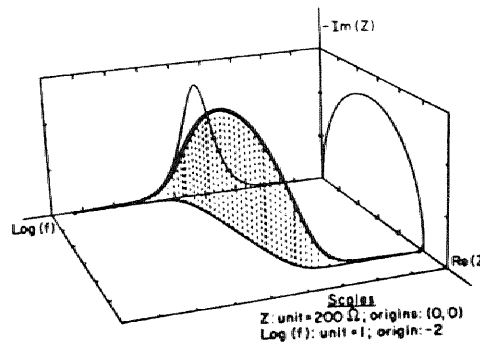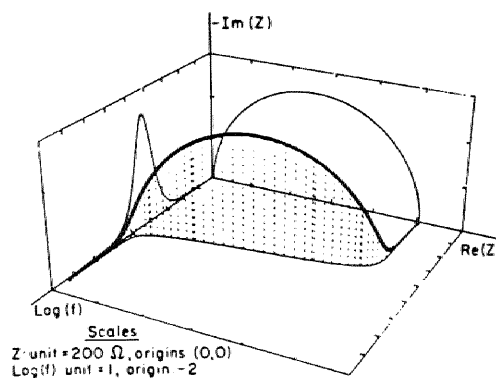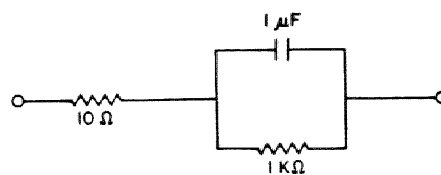

FIG. 3.   A simple circuit and 3-D perspective plots of its impedance response. (Reprinted by permission of John Wiley & Sons, Inc., from "Impedance Spectroscopy—Emphasizing Solid Materials and Systems." J. R. Macdonald, ed. Copyright © 1987, John Wiley & Sons, Inc.)

A

B

C

FIG. 4.   Three-dimensional perspective plots of Na β-alumina data at (A) the impedance level, (B) log impedance level, and (C) complex modulus level. (Reprinted by permission of John Wiley & Sons, Inc., from "Impedance Spectroscopy—Emphasizing Solid Materials and Systems," J. R. Macdonald, ed. Copyright © 1987, John Wiley & Sons, Inc.)
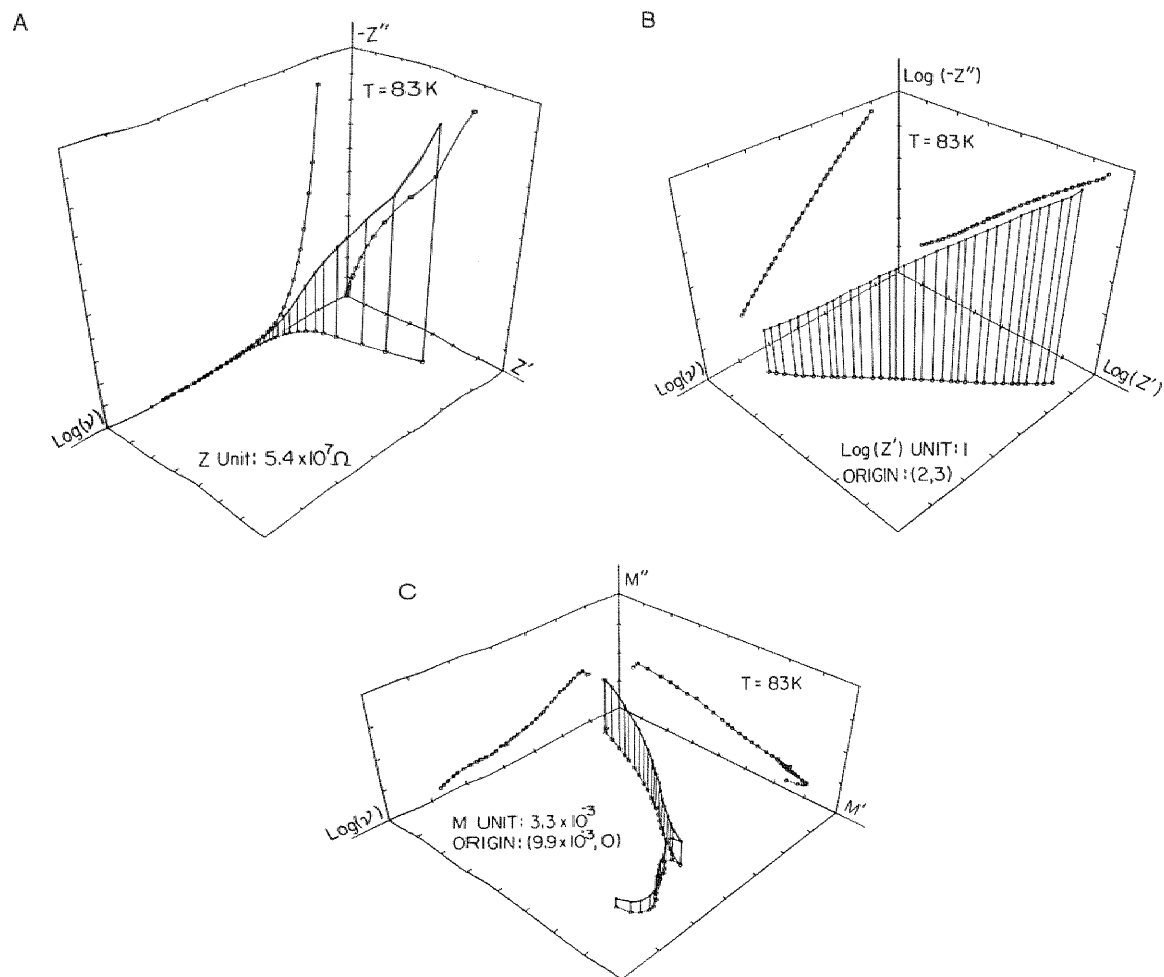
is now apparent at the highest frequencies. These results make it clear that even when 3-D plots are used, it is always desirable to explore the results of different transformations of the data and to pick the one with the best resolution.

2. Complex Nonlinear Least Squares Data-Fitting

a. **Strengths and Weaknesses.** Although graphic examination of IS data is an important analysis step, only in the simplest cases can it be used to obtain even rough estimates of some system parameters. Since good parameter estimates are needed for adequate characterization of the material-electrode

system, a fitting technique such as CNLS must be applied to obtain them. In doing so, the data, at any I level, are fitted to a mathematical model involving the parameters or to the response of an equivalent circuit. Such fitting models are discussed in Section IV, A. Not only does CNLS fitting yield estimates of the parameters of the model, but it also provides estimates of their standard deviations, measures of how well they have been determined by the data fit. These standard deviation values are valuable in deciding which parameters are crucial to the model and which are useless, or at least not well determinable from the data.

CNLS fits are produced by a program that minimizes the weighted sum of squares of the real and

imaginary residuals. A residual is the difference between a data value at a given frequency and the corresponding value calculated from the model. The weights used are the inverses of the estimated error variance for a given real data value and that for the corresponding imaginary value. Weighting is the most subjective part of least squares fitting, yet it can often have crucial effects on the results of such fitting and is thus of prime importance.

Since individual error-variance estimates are usually unavailable, it has been customary to use simplified variance models to obtain values to use in the fitting. The simplest such model is to take all weights equal to one: unity weighting (UWT). Another popular and important choice is to set the error variance of each data value equal to the square of that value. Since the uncertainty of the value is then proportional to the value itself, this defines proportional weighting (PWT). It has recently been shown, however, that such weighting leads to biased parameter estimates; it should be replaced, when the fitting model is well matched to the data, by function-proportional weighting (FPWT), where the calculated rather than the direct data value is employed in the weighting.

PWT or FPWT is particularly important because the range of typical IS data can be as large as 10^3 or even 10^6. When UWT is used in fitting such data, only the largest parts of the data determine the parameter estimates, and the smaller values have little or no effect. Alternatively, with PWT or FPWT, which is equivalent to assuming a constant percentage error, small and large data values contribute equally to the final parameter estimates.

Figure 5 presents the results of PWT CNLS fitting of β-PbF$_2$ data using an equivalent circuit with a distributed element, the constant phase element (CPE). Both the original data and the fit results are shown in the 3-D plot. The figure indicates that seven free parameters have been quite well determined by the data, a remarkable result when one considers the apparent lack of much structure in the data themselves.

A detailed physico-chemical model is always preferable to an equivalent circuit for fitting, especially since such models often cannot be expressed in terms of an equivalent circuit involving standard elements. But most IS situations involve many-body problems currently insolvable at the microscopic level. Thus one must usually be satisfied with simpler continuum models, often expressed as equivalent circuits. One weakness of equivalent circuits involving only ideal elements is their ambiguity. The same elements may be interconnected in different ways and yet, with appropriate values, yield exactly the same frequency response at all frequencies. Thus, IS fitting cannot
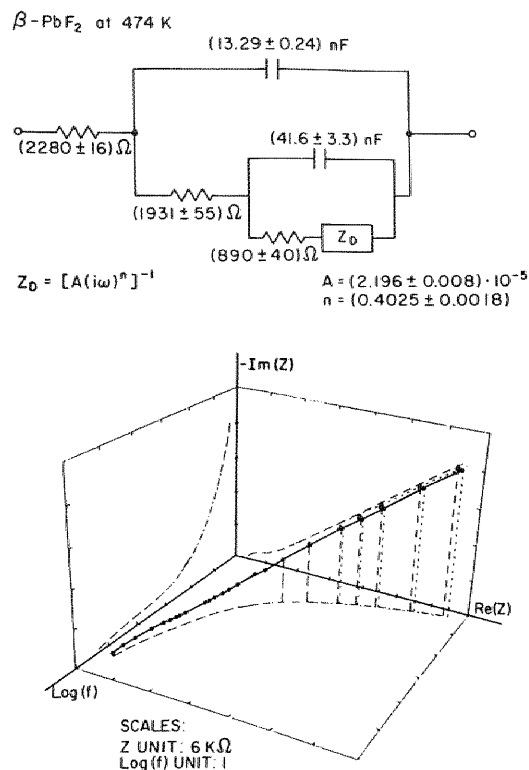

FIG. 5. Three-dimensional perspective impedance plot of β-PbF$_2$ data (——, - - -) and fitted values and curves (— — —); the fitting circuit used and parameter estimates and estimates of their standard deviations. (Reprinted by permission of John Wiley & Sons, Inc., from "Impedance Spectroscopy—Emphasizing Solid Materials and Systems," J. R. Macdonald, ed. Copyright © 1987, John Wiley & Sons, Inc.)

distinguish between the different possible structures, and only other measurements, such as IS fitting of data over a range of temperatures and/or potentials, can help one establish which of the possible circuits is most physically reasonable.

Figure 6 shows all possible potentially equivalent conducting circuits involving two resistances and two capacitances. Specific parameter value choices that make them all have exactly the same response are also indicated. Here the values for circuit D were taken exact, and approximate values for the other elements are denoted with a ~ sign. Let the units of these elements be MΩ for resistances and μF for capacitances. Note that the two RC time constants of circuit A, a series connection, differ by less than 17% and are thus very close together. Can IS procedures resolve such a situation? Figure 7 shows the exact complex-plane response of these circuits at both the
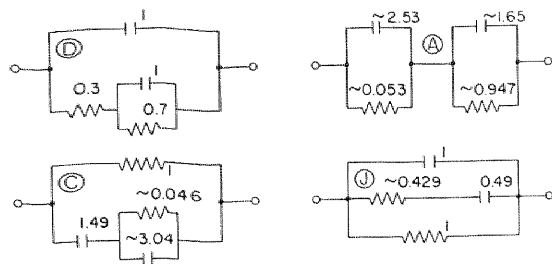
FIG. 6. Four two-time-constant circuits that exhibit the same impedance response over all frequencies. Units are MΩ for resistances and μF for capacitances.

FIG. 7. Complex-plane immittance responses, at the Z and M levels, of the circuits of Fig. 6.

Z and the M levels, compared to single time-constant Debye response. The M curve shows much better separation of the two response regions than does the Z curve. Thus, adequate graphical resolution is indeed possible. Further, it turns out that CNLS fitting of synthetic data calculated from any of these circuits with appreciable proportional random errors added still yields excellent parameter estimates. In fact, with reasonably good data, CNLS can resolve response involving considerably closer time constants than those involved here.

Although several CNLS fitting programs now exist for use on personal computers, two commercially available ones have been especially tailored for the IS field. The first, EQUIVCRT, can be obtained from Dr. B. A. Boukamp, Twente University, P.O. Box 217, 7500 AE Enschede, The Netherlands; the second, LEVM, can be obtained from the Department of Physics and Astronomy, University of North Carolina, Chapel Hill at nominal cost. The programs to some degree complement each other, but LEVM is more general and flexible in many ways and incorporates much more sophisticated weighting possibilities.

b. Recent Developments. Currently, the capability of using various types of weighting involving model predictions instead of data values exists only in LEVM, first released in the summer of 1989. Although weighting such as FPWT is somewhat more complicated than PWT because it varies with each nonlinear least squares iteration as the parameter estimates change during the fitting procedure, its bias reduction potential makes such complexity worthwhile. Although LEVM allows the fitting of real or imaginary parts of the data separately, fitting both together, as in CNLS, ensures that the best use is made of all the data in determining the parameter estimates and is thus preferred when both parts are available.
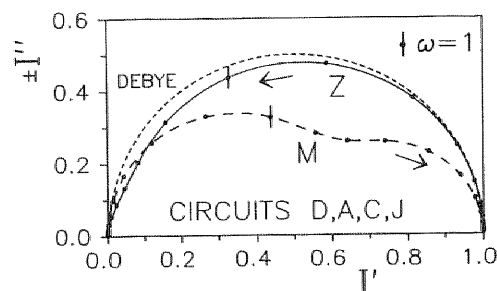
Real IS data often has independent random errors

that have both an additive term and one that depends on the true model predictions. A rather general error-variance model incorporating these possibilities is included in LEVM. For a specific angular frequency ω_j, the real and imaginary parts of v_j, the error variance used in determining the weighting, may be written as

$$v_j' = U^2 + |F'(\omega_j)|^{2\xi}$$

and

$$v_j'' = U^2 + |F''(t_j)|^{2\xi}$$

where U is associated with the additive random errors and ξ is an arbitrary positive fractional exponent.

When $U = 0$, $\xi = 1$, and F is a data value, one has PWT; whereas when F is a model prediction the result is FPWT. Another widely used weighting, modulus weighting, follows when the same values of U and ξ are used but both F' and F'' in the above equations are replaced by $|F|$. It is usually inconsistent, however, with the types of errors likely to be present and generally leads to appreciably more bias in parameter estimates even than PWT. CNLS fitting yields a standard deviation S_f of residuals, which is a measure of the overall goodness of fit. For proportional random errors having a proportionality constant of σ_r. S_f is an unbiased estimate of σ_r for FPWT, is nearly so for PWT, and is appreciably biased on the low side for FMWT and MWT, types of modulus weighting.

When the data involve one or more inductive-type loops, such as arise from adsorption of a mobile charge at an electrode, it is desirable to use a nonzero U along with PWT or FPWT or to use modulus weighting. Otherwise, because values of the imaginary part of the data may become very small and even pass through zero in the loop region, PWT or FPWT alone can strongly overemphasize the effect of these values near zero and thus lead to poor fitting.

Although U and ξ may be given fixed values dur-

ing CNLS fitting, a way has been found to incorporate them as free parameters in LEVM least squares fitting. When this is done, the data themselves determine the most appropriate weighting for their fit, thus removing an appreciable part of the subjective element present in prior weighting approaches. Further, Monte Carlo fitting studies have shown that the statistical uncertainties of U and ξ in CNLS fits with them both taken free, or with only ξ free, are usually quite small compared to their estimates, and their biases are even smaller. Thus, their fit estimates may be used with confidence.

Although for much IS data one would expect that ξ would be close to unity, this need not always be the case. Consider, for example, a set of real data arising from the sum of the radioactive decay of two different species. Now the statistics of such decay follows a Poisson process, one for which $\xi = 0.5$. The radioactive background count will also involve such a process. Thus the appropriate variance model would involve $U = 0$ and three terms, each with $2\xi = 1$. The first two would be the two exponential decays and the last, the background. In such a fitting situation, where ξ is known absolutely it should be held fixed at its proper value.

IV. Applications

A. BASIC ANALYSIS OF MATERIAL PROPERTIES AND ELECTRODE EFFECTS

1. Bulk and Reaction Response

Although IS is of great value for the characterization of the electrical properties of material-electrode systems, its use for this purpose requires that connections be known between model and/or equivalent circuit parameters and the basic characterization parameters. One must be able to pass from estimates of macroscopic quantities, such as resistances and capacitances, to estimates of average microscopic quantities. Here only a brief overview will be given of some of the large amount of theoretical IS-related work of the past 40 years. More details appear in the IS book.

Because of the charge decoupling present in a supported situation, it is often an excellent approximation to treat the effects of the various physical processes present independently. On the other hand, for unsupported conditions where strong coupling is present, a unified treatment of all the processes together is necessary. The most complete such theory, which incorporates all five of the processes mentioned in Section III.B.1, was published by Frances-

chetti and Macdonald in 1978. It is a continuum (i.e., averaged, not microscopic) theory, includes intrinsic and extrinsic charge effects, and applies to either ionic or electronic conduction conditions. Even though it strictly applies only to flat-band conditions, its results are still sufficiently complicated that only in simplified cases does it lead to response that may be modeled by an equivalent circuit.

It is useful, particularly in the EIS area, to separate the electrical processes present into bulk- and electrode-related groups whenever possible. The first group includes bulk resistance and dielectric effects and the homogeneous reactions associated with dissociation and recombination of the charges present. It is generally associated with response effects at the high end of the frequency range, while electrode effects usually occur near the low end, possibly at very low frequencies. Bulk resistance and capacitance are extensive quantities, dependent on the effective separation between electrodes.

The second group involves what happens in the neighborhood of the electrodes (within a few Debye lengths of them) and is thus intensive. No charge is transferred to an electrode if it is completely blocking for all mobile charges. The next simplest EIS situation is that where a mobile metallic ion is of the same species as the atoms of a metallic electrode: a parent-ion electrode. Then, in a symmetrical-electrode situation there is a sink/source of ions at each electrode, since electron transfer at an electrode can transform ions into atoms and vice versa, depending on the polarity of the electric field at the electrode. Such a reaction can be written

$$\text{Me} \rightleftharpoons \text{Me}^{z+} + ze^-$$

where Me denotes a metal atom and z the number of electrons transferred. An example of a symmetrical cell of this type is Ag|AgCl|Ag.

Particularly important for the aqueous electrolyte area is the redox electrode, where charge crosses the interface at the electrode only in the form of electrons. The species Red and Ox are usually soluble in the electrolyte, satisfy

$$\text{Red}^{(z-n)+} \rightleftharpoons \text{Ox}^{z+} + ne^-$$
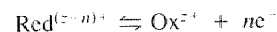
and involve the forward and reverse reaction rate constants k_f and k_r, respectively. If $z = n$, the Red species is uncharged and may diffuse in the electrode, or may evolve if it is a gas.

2. Distributed Circuit Element Response

a.   Diffusion.   Since diffusion is not localized at a point in space but is distributed over a finite region, it leads to electrical response characteristic of a dis-

tributed circuit element (DCE). Such elements cannot be described by means of a finite number of ideal elements such as resistances and capacitances. Here, the response of several DCEs important to IS will be discussed.

In addition to possible diffusion of uncharged species within an electrode, diffusion of mobile species in the electrolyte may contribute significantly to the impedance of a IS system. Generally, diffusion response is neither intensive nor extensive. At sufficiently high frequencies, diffusion effects are confined to the immediate neighborhood of the electrode (or within a hydrodynamic boundary layer at a rotating electrode) and so are intensive; whereas at low enough frequencies, diffusion occurs throughout the material between electrodes, and the response becomes extensive as the frequency decreases and the effective diffusion length l_d, proportional to $(\omega)^{-0.5}$, becomes comparable to the size of the cell.

The diffusion impedance, appropriate when there is a fast electrode reaction, is of the form

$$Z_W(\omega) = Z_W(0)[\tanh\{i(l/l_d)^2\}^{0.5}]/\{i(l/l_d)^2\}^{0.5}$$

where l is the separation between symmetrical electrodes and $Z_W(0)$ is a resistance proportional to l and thus is extensive. Such response is known as finite-length Warburg behavior. At high enough frequencies that the tanh term goes to unity, $Z_W(\omega)$ becomes proportional to the intensive quantity l_d and is termed (ordinary) Warburg response.

As the electrode reaction rate decreases toward zero, a more complicated expression for $Z_W(\omega)$ must be used, but it reduces to the form

$$Z_W(\omega) = Z_C[\text{ctnh}\{i(l/l_d)^2\}^{0.5}]/\{i(l/l_d)^2\}^{0.5}$$

when the electrode is completely blocking (open circuit diffusion). Here Z_C is given by $(l/l_d)^2/\omega C_{DOC}$ and C_{DOC}/C_C is the effective low-frequency limiting dielectric constant associated with the process.

For general unsupported situations, those with positive and negative charged species mobile and having diffusion coefficients of D_n and D_p and valence numbers of z_n and z_p,

$$(l_d)^2 = (4D_nD_p/\omega)[(z_n + z_p)/(z_nD_n + z_pD_p)]$$

No diffusion effects appear when only charge of a single sign is mobile; this often is an excellent approximation for solid electrolytes.

For supported conditions, matters are different. Consider a single species with diffusion coefficient D and valence number z (possibly zero). Then $(l_d)^2 = 4D/\omega$, a result that follows from the above expression when one sets $D_n = D_p = D$ and $z_n = z_p = z$. Further, when both positive and negative charges are

mobile, diffusion under unsupported conditions leads to a single expression involving tanh, as above, but for supported conditions, as in the redox case, two such terms appear, one for each species—in keeping with the lack of coupling between the species.

b. Other DCEs. A characteristic signature of diffusion is $(i\omega)^{\pm 0.5}$ response, but IS data more often exhibits CPE response $(i\omega\tau)^{-\psi}$, where $0 \leq \psi \leq 1$. But such response is not physically realizable over all frequencies, and so other DCEs have been introduced that approximate such behavior over a limited frequency range. They may be written as impedances or complex dielectric constants, depending upon which l level is appropriate. Here they will be given at the Z level.

An empirical DCE of the above type is Havriliak–Negami (HN) response, written as

$$Z_{HN}(\omega) = R_{HN}/[1 + (i\omega\tau)^\alpha]^\beta$$

where $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$. It reduces to Cole–Davidson response when $\alpha = 1$ and to Cole–Cole response (termed ZC response at the Z level) when $\beta = 1$. The first of these yields an asymmetric arc in a complex-plane plot and the second one a symmetric arc. Both shapes appear often in practice, and ZC fitting is frequently used to represent data that yield an arc of a semicircle with its center below the real axis. Such behavior is usually ascribed to the presence of a distribution of some physical quantity in space, time, or energy. Rough electrodes are one example. Although fitted values of α and/or β often show appreciable temperature dependence, there exists no theory yielding such dependence for HN response.

Another important DCE is that of Kohlrausch–Williams–Watts (KWW) response. It yields a stretched exponential in the time domain, response proportional to $\exp[-t/\tau]^\psi$, with $0 \leq \psi \leq 1$. Here there are, if anything, too many different theories yielding such response, but again they do not predict the temperature dependence of ψ. The corresponding frequency response is very difficult to calculate accurately, but an excellent approximation for it is available in LEVM. Complex plane plots of KWW response yield an asymmetric arc for any $\psi < 1$ until $\psi = 1$, when a Debye semicircle appears.

Another DCE category is associated with the presence in a material of a distribution of activation energies (DAE). Such distributions are likely in IS materials and may be expected even in single crystals when there are many competing possibilities for the individual motion of mobile charges. Both Gaussian and exponential distributions have been considered in

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detail and can lead to either symmetric or asymmetric complex-plane arcs. But only an exponential DAE yields CPE-like fractional-exponent frequency response over a finite frequency region. This exponent, ϕ, is not limited to the range from 0 to 1 but satisfies $-\infty < \phi < \infty$. Further, unlike the other DCEs considered, an exponential DAE predicts temperature dependence of ϕ in good agreement with many experimental results.

3. Equivalent Circuits

Many different equivalent circuits have been proposed over the years for IS fitting, and no one circuit structure is appropriate for all situations. Figure 8 shows a circuit, however, that has been found useful for a variety of materials and experimental conditions. Bulk properties are represented by C_g, the geometrical capacitance, and R_∞, the high-frequency limiting resistance. C_R, associated with an electrode reaction, is the double-layer capacitance (possibly including both a compact inner-layer capacitance and a diffuse double-layer capacitance), and R_R is the reaction resistance. Finally, C_A and R_A are associated with adsorption at an electrode. The Z_D elements, when present, are DCEs. Also, not all the other elements need be present; for example, in the absence of adsorption C_A and R_A would not appear.

For an unsupported, fully dissociated material with charges of only a single sign mobile, the Fig. 8 circuit with all Z_Ds absent has been found to yield an accurate representation of the impedance resulting from a flat-band theoretical analysis of the situation. Since only Rs and Cs are involved, ambiguity is present, and many other circuit structures with the same elements and the same frequency response are

possible. Nevertheless, the present hierarchical ladder-network connection is more physically reasonable than the others for homogeneous material. It ensures that bulk charging and conduction effects take place before reaction/adsorption ones. For polycrystalline materials, however, circuits involving series rather than hierarchical connection of parallel RC subcircuits are often found appropriate.

For the conditions above, no diffusion DCE element is present. The $Z_W(\omega)$ one discussed earlier appears, however, in the Z_{D3} position when charges of both signs are mobile and at least one of them reacts at an electrode. When static fields are present in the material, either intrinsic and/or externally produced, numerical analysis of the nonlinear transport equations governing the IS response shows that the Fig. 8 circuit still applies to good approximation but elements such as C_R and R_R then depend appreciably on the static p.d. present. Finally, the circuit of Fig. 8 has often been found appropriate for the fitting of data for supported conditions as well as unsupported ones.

B. Uses of IS for Evaluation and Control of Electrochemical Processes of Industrial Interest and Importance

1. Corrosion and Surface Protection

Corrosion of metallic structural materials leads to immense damage each year (an estimate for the United States for 1988 is 200 billion dollars); thus its control and amelioration are of tremendous economic importance. EIS has played and is playing a valuable role in quantifying and mitigating corrosion effects. For example, it has been successfully applied to complicated corrosion systems to determine corrosion rates as well as the mechanisms and efficiency of corrosion inhibitors. The use of EIS has broadened the range of corrosion phenomena that can be studied using electrochemical techniques and has been particularly valuable in evaluating the corrosion behaviors of polymer-coated metals and anodized aluminum alloys. In addition, it has been incorporated into a quality control test for anodized aluminum surfaces and for chromate-conversion-coated aluminum alloys.

The application of EIS techniques has resulted in a great deal of information on methods of corrosion protection that are difficult or impossible to study with traditional dc techniques, such as conversion and polymer coatings, anodic films, and inhibitors. Not only can EIS measurements provide greater sensitivity and more information about the processes investigated than can conventional dc methods, they
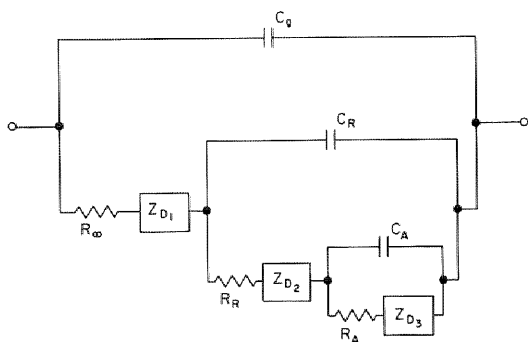

FIG. 8. An equivalent circuit of hierarchical structure useful in fitting much IS data. (Reprinted from "Interface Effects in the Electrical Response of Non-Metallic Conducting Solids and Liquids," J. R. Macdonald, *IEEE Trans. on Electrical Insulation*, Vol. EI-15, pp. 65–82, Fig. 3. Copyright © IEEE 1981.)

are particularly appropriate when impedances are high and/or when low-conductivity media are used.

EIS measurement and analysis has been used to provide fast and sensitive information on the protection properties of chromated galvanized steel. Such measurements may be used as a quality control procedure, since the charge transfer resistance has been found to be well related to the corrosion rate. EIS has been used to detect corroding areas of large structures accurately and has been applied for corrosion monitoring of steel reinforcing bars in concrete to yield a nondestructive estimate of the amount of corrosion damage.

Since the roughness of an electrode surface is reflected in the results of EIS measurements involving the electrode, EIS may be used to identify surface inhomogeneities produced by corrosion. It provides (averaged) information on surface morphology on a much smaller scale than does even electron micrography. EIS has been employed as a means of nearly continuous evaluation of localized corrosion processes such as pitting, crevice corrosion, stress corrosion, cracking and fatigue corrosion, abrasion, and corrosion under a porous surface layer.

EIS measurements over a relatively wide frequency range have been found to yield valuable detailed information about the properties of aluminum oxide layers formed under different anodizing and sealing conditions. Discrimination was possible between properties of the dense barrier layer and the porous outer layer, and changes arising from aging and from the effects of natural environmental conditions were reflected in the results.

An EIS monitor has been used for the detection of paint degradation under atmospheric exposure. A model is being developed to help predict the lifetime of protective organic coatings on steel based on short laboratory tests. The model includes the steps of defect formation, transport of corrodents, loss of adhesion, and corrosion. EIS helps elucidate how these four processes interact and depend on coating processes and environmental effects.

Although IS analysis should properly be carried out only on time-invariant data—data obtained from a system whose properties are independent of time—some of these properties are often not time-invariant during measurement of a corroding system. If the change is slow compared to the required measurement time and/or if it is approximately linear in time, improved results may be obtained by making a set of measurements from low to high frequencies immediately followed by one from high to low frequencies. Averaging of the results will then eliminate much of the variation with time.

A test of time invariance can be made by analyzing the data with the Kramers–Kronig (K–K) relations, integral transforms connecting real to imaginary parts of the data and vice versa. They are only applicable for time-invariant systems. All useful fitting models and equivalent circuits are minimum phase and so automatically satisfy the K–K relations. Thus, a good fit is evidence of time invariance. Strong failure of the K–K relations for a given set of data is immediate evidence of unwanted time variation, and, unlike CNLS fitting, no model or circuit is required to carry out such a test. But be warned that K–K analysis requires a lot of computation and can be difficult to apply accurately.

2. Batteries and Fuel Cells

EIS studies have been made of the kinetics of the insertion reaction in solid-state batteries based on such reactions. A single EIS experiment allows information to be obtained about the electrode-interface reaction and diffusion in the electrolyte or electrode. Measurements at different battery voltages to determine the dependence of the results on the charge of the battery have led to increased understanding of the discharge process and thence to improved battery design.

An interesting EIS study has been carried out on electrochemically impregnated Ni electrodes from four different manufacturers of Ni/H cells. The EIS measurements were made in KOH electrolyte, and large differences were found in the impedance behavior of the electrodes from the different manufacturers. The results indicated a probable correlation between impedance parameters and cell life and performance.

EIS studies of molten carbonate fuel cells have increased the understanding of processes going on under operating conditions of the cell. In particular, they have helped identify and elucidate the reactions that occur both at the anode and at the cathode.

3. Other Devices and Techniques

Electrolyte-insulator-semiconductor sensors meld integrated circuit technology with traditional chemical technology. They can be used to monitor pH changes, for example, and can be constructed with ion-selective membranes to make them sensitive to a specific ion. IS measurements and analysis can yield, in favorable cases, information on the electrical characteristics of the electrolyte, the insulator, the semiconductor, and the various interfaces and on interface states. The IS approach allows very low surface-state densities at the insulator-semiconductor interface to

be determined. Measurements have shown, however, that it is the electrolyte–insulator interface that responds to pH changes.

Solid-electrolyte chemical sensors are electrochemical cells designed to measure the concentration or pressure of chemical species in gases or fluids; for example, zirconia-based solid electrolytes have been used to measure oxygen concentration. Such sensors are employed to measure the oxygen concentration in steel melts and the air–fuel ratio in automobile engines. EIS has been found very useful to study (and to help optimize) electrode materials and appropriate pretreatment preparation for such sensors.

Photoelectrochemical solar cells involve a semiconductor electrode, an electrolyte interface, and a redox reaction in solution. EIS can yield information on surface states and other electrode properties of such devices. It is an important tool for probing the processes occurring at the interface and for finding ways to increase cell conversion efficiency.

In recent years a number of variants on and extensions of IS have been developed. An important one is electrohydrodynamic impedance. Here the speed of a rotating-disk electrode is modulated sinusoidally, resulting in modulation of the mass transport in a liquid electrolyte. Such modulation allows the minimization of the coupling with interfacial kinetics. Modulation of numerous other quantities in an IS experiment is also possible, such as light, temperature, or magnetic field. Thus analysis of other transfer functions, cause and effect relations that go beyond potential and current, can add valuable additional information to IS studies. It is likely that much future development will be concerned with such possibilities.

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