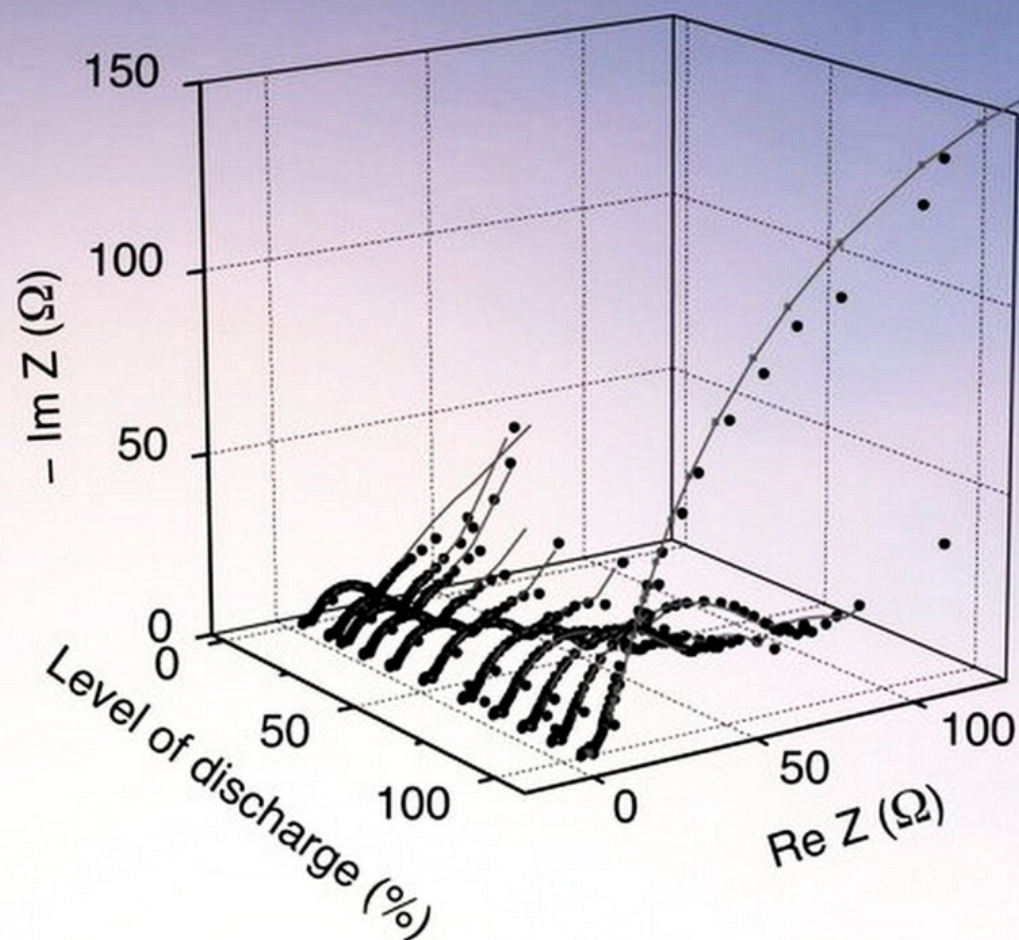


Edited By
Evgenij Barsoukov and J. Ross Macdonald

Impedance Spectroscopy

Theory, Experiment, and Applications

Third Edition



IMPEDANCE SPECTROSCOPY

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Preface to the Third Edition

Previous editions of this book have been used by generations of researchers as primary reference on impedance spectroscopy. This third extended edition updates the book to include the results of the last 10 years of research as well as to add new areas that are now extensively using impedance spectroscopy.

Changes have most affected Section 3.2 where a completely new overview of commercial impedance systems is provided and Section 4.2.4, which includes completely new section dedicated to Poisson–Nernst–Planck (PNP) fitting models. Significant additions have been done to Section 4.3.4 that covers impedance response of electrochromic materials and devices and Section 4.3.5 that covers fast processes in gigahertz–terahertz region in disordered materials. A new Section 4.4.7 is now covering in detail reaction mechanism analysis of passive metals. Chapters on electrochemical power sources, supercapacitors, and fuel cells have been significantly refreshed and augmented with new materials.

Two completely new topics have been added to the book, with Section 4.6 covering dielectric relaxation spectroscopy of polymers and Section 4.7 on impedance spectroscopy of electrical structure of biological cells and tissues. Authors are confident that with these updates and additions, this book will give a solid foundation for anyone entering the field of impedance spectroscopy and will serve as a trusted reference to those already well on the way.

October 2016

EVGENIJ BARSOUKOV
Dallas, Texas

Preface to the Second Edition

The principal audience that will benefit from this book are M.Sc. and Ph.D. students with specialization in physical chemistry, electrochemistry, or physics, as well as researchers and engineers in the field of electrochemistry, particularly in areas of semiconductors, solid electrolytes, corrosion, solid state devices, and electrochemical power sources. Impedance spectroscopy has firmly established itself as one of the most informative and irreplaceable investigation methods in these areas of research. In addition, the book provides a valuable source of information and resource for established researchers and engineers working in one or more of the said fields.

The book should enable understanding of the method of impedance spectroscopy in general, as well as detailed guidance in its application in all mentioned areas. It is the only book in existence that brings expert reviews of all main areas of impedance applications together. This book covers all subjects needed by a researcher to identify whether impedance spectroscopy may be a solution to his/her particular needs and to explain how to set up experiments and how to analyze their results. It includes both theoretical considerations and the know-how needed to begin work immediately. For most subjects covered, theoretical considerations dealing with modeling, equivalent circuits, and equations in the complex domain are provided. Best measurement methods for particular systems are discussed, and sources of errors are identified along with suggestions for improvement. The extensive references to scientific literature provided in the book will give a solid foundation in the state of the art, leading to fast growth from a qualified beginner to an expert.

The previous edition of this book became a standard textbook on impedance spectroscopy. This second extended edition updates the book to include the results of the last two decades of research and adds new areas where impedance spectroscopy has gained importance. Most notably, it includes completely new chapters on batteries, supercapacitors, fuel cells and photochromic materials. A new chapter on commercially available measurements systems reflects the reality of impedance spectroscopy as a mainstream research tool.

July 2004

EVGENIJ BARSOUKOV
Dallas, Texas

Preface to the First Edition

Impedance spectroscopy (IS) appears destined to play an important role in fundamental and applied electrochemistry and materials science in the coming years. In a number of respects, it is the method of choice for characterizing the electrical behavior of systems in which the overall system behavior is determined by a number of strongly coupled processes, each proceeding at a different rate. With the current availability of commercially made, high-quality impedance bridges, and automatic measuring equipment covering the millihertz to megahertz frequency range, it appears certain that impedance studies will become increasingly popular as more and more electrochemists, materials scientists, and engineers understand the theoretical basis for impedance spectroscopy and gain skill in the interpretation of impedance data.

This book is intended to serve as a reference and/or textbook on the topic of IS, with special emphasis on its application to solid materials. The goal was to produce a text that would be useful to both the novice and the expert in IS. To this end, the book is organized so that each individual chapter stands on its own. It is intended to be useful to the materials scientist or electrochemist, student, or professional, who is planning an IS study of a solid-state system and who may have had little previous experience with impedance measurements. Such a reader will find an outline of basic theory, various applications of IS, and a discussion of experimental methods and data analysis, with examples and appropriate references. It is hoped that the more advanced reader will also find this book valuable as a review and summary of the literature up to the time of writing, with a discussion of current theoretical and experimental issues. A considerable amount of the material in the book is applicable not only to solid ionic systems but also to the electrical response of liquid electrolytes as well as to solid ones, to electronic as well as to ionic conductors, and even to dielectric response.

The novice should begin by reading Chapter 1, which presents a broad overview of the subject and provides the background necessary to appreciate the power of the technique. He/she might then proceed to Chapter 4, where many different applications of the technique are presented. The emphasis in this chapter is on presenting specific applications of IS rather than extensive reviews; details of how and why the technique is useful in each area are presented. To gain a fuller appreciation of IS, the reader could then proceed to Chapters 2 and 3, which present the theory and measuring and analysis techniques.

For someone already familiar with IS, this text will also be useful. For those familiar with one application of the technique, the book will provide both a convenient source for the theory of IS, as well as illustrations of applications in areas possibly unfamiliar to the reader. For the theorist who has studied IS, the applications discussed in Chapter 4 pose questions the experimentalist would like answered; for the experimentalist, Chapters 2 and 3 offer different (and better!) methods to analyze IS data. All readers should benefit from the presentation of theory, experimental data, and analysis methods in one source. It is our hope that this widened perspective of the field will lead to a more enlightened and therefore broadened use of IS.

In format and approach, the present book is intended to fall somewhere between the single-author (or few-author) text and the "monograph" of many authors and as many chapters. Although the final version is the product of 10 authors' labors, considerable effort has been made to divide the writing tasks so as to produce a unified presentation with consistent notation and terminology and a minimum of repetition. To help reduce repetition, all authors had available to them copies of Sections 1.1–1.3, 2.2,

and 3.2 at the beginning of their writing of the other sections. We believe that whatever repetition remains is evidence of the current importance to IS of some subjects, and we feel that the discussion of these subjects herein from several different viewpoints is worthwhile and will be helpful to the readers of the volume.

March 1987

J. ROSS MACDONALD
Chapel Hill, North Carolina

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Fundamentals of Impedance Spectroscopy

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1.1 BACKGROUND, BASIC DEFINITIONS, AND HISTORY

1.1.1 The Importance of Interfaces

Since the end of World War II, we have witnessed the development of solid-state batteries as rechargeable energy storage devices with high power density; a revolution in high-temperature electrochemical sensors in environmental, industrial, and energy efficiency control; and the introduction of fuel cells to avoid the Carnot inefficiency inherent in noncatalytic energy conversion. The trend away from corrosive aqueous solutions and toward solid-state technology was inevitable in electrochemical energy engineering, if only for convenience and safety in bulk handling. As a consequence, the characterization of systems with solid–solid or solid–liquid interfaces, often involving solid ionic conductors and frequently operating well above room temperature, has become a major concern of electrochemists and materials scientists.

At an interface, physical properties—crystallographic, mechanical, compositional, and, particularly, electrical—change precipitously, and heterogeneous charge distributions (polarizations) reduce the overall electrical conductivity of a system. Proliferation of interfaces is a distinguishing feature of solid-state electrolytic cells, where not only is the junction between electrode and electrolyte considerably more complex than in aqueous cells but also the solid electrolyte is commonly polycrystalline. Each interface will polarize in its unique way when the system is subjected to an applied potential difference. The rate at which a polarized region will change when the applied voltage is reversed is characteristic of the type of interface: slow for chemical reactions at the triple-phase contacts between atmosphere, electrode, and electrolyte, appreciably faster across grain boundaries in the polycrystalline electrolyte. The emphasis in electrochemistry has consequently shifted from a time/concentration dependency to frequency-related phenomena, a trend toward small-signal alternating current (ac) studies. Electrical double layers and their inherent capacitive reactances are characterized by their relaxation times or more realistically by the distribution of their relaxation times. The electrical response of a heterogeneous cell can vary substantially depending on the species of charge present, the microstructure of the electrolyte, and the texture and nature of the electrodes.

Impedance spectroscopy (IS) is a relatively new and powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of

any kind of solid or liquid material: ionic, semiconducting, mixed electronic–ionic, and even insulators (dielectrics). Although we shall primarily concentrate in this monograph on solid electrolyte materials—amorphous, polycrystalline, and single crystal in form—and on solid metallic electrodes, reference will be made, where appropriate, to fused salts and aqueous electrolytes and to liquid metal and high-molarity aqueous electrodes as well. We shall refer to the experimental cell as an electrode–material system. Similarly, although much of the present work will deal with measurements at room temperature and above, a few references to the use of IS well below room temperature will also be included. A list of acronym and model definitions appears at the end of this work.

In this chapter we aim to provide a working background for the practical materials scientist or engineer who wishes to apply IS as a method of analysis without needing to become a knowledgeable electrochemist. In contrast to the subsequent chapters, the emphasis here will be on practical, empirical interpretations of materials problems, based on somewhat oversimplified electrochemical models. We shall thus describe approximate methods of data analysis of IS results for simple solid-state electrolyte situations in this chapter and discuss more detailed methods and analyses later. Although we shall concentrate on intrinsically conductive systems, most of the IS measurement techniques, data presentation methods, and analysis functions and methods discussed herein apply directly to lossy dielectric materials as well.

1.1.2 The Basic Impedance Spectroscopy Experiment

Electrical measurements to evaluate the electrochemical behavior of electrode and/or electrolyte materials are usually made with cells having two identical electrodes applied to the faces of a sample in the form of a cylinder or parallelepiped. However, if devices such as chemical sensors or living cells are investigated, this simple symmetrical geometry is often not feasible. Vacuum, a neutral atmosphere such as argon, or an oxidizing atmosphere is variously used. The general approach is to apply an electrical stimulus (a known voltage or current) to the electrodes and observe the response (the resulting current or voltage). It is virtually always assumed that the properties of the electrode–material system are time invariant and it is one of the basic purposes of IS to determine these properties, their interrelations, and their dependences on such controllable variables as temperature, oxygen partial pressure, applied hydrostatic pressure, and applied static voltage or current bias.

A multitude of fundamental microscopic processes take place throughout the cell when it is electrically stimulated and, in concert, lead to the overall electrical response. These include the transport of electrons through the electronic conductors, the transfer of electrons at the electrode–electrolyte interfaces to or from charged or uncharged atomic species that originate from the cell materials and its atmospheric environment (oxidation or reduction reactions), and the flow of charged atoms or atom agglomerates via defects in the electrolyte. The flow rate of charged particles (current) depends on the ohmic resistance of the electrodes and the electrolyte and on the reaction rates at the electrode–electrolyte interfaces. The flow may be further impeded by band structure anomalies at any grain boundaries present (particularly if second phases are present in these regions) and by point defects in the bulk of all materials. We shall usually assume that the electrode–electrolyte interfaces are perfectly smooth, with a simple crystallographic orientation. In reality of course, they are jagged, full of structural defects and electrical short and open circuits, and they often contain a host of adsorbed and included foreign chemical species that influence the local electric field.

There are three different types of electrical stimuli that are used in IS. First, in transient measurements a step function of voltage [$V(t) = V_0$ for $t > 0$, $V(t) = 0$ for $t < 0$] may be applied at $t = 0$ to the system, and the resulting time-varying current $i(t)$ measured. The ratio $V_0/i(t)$, often called the indicial impedance or the time-varying resistance, measures the impedance resulting from the step function voltage perturbation at the electrochemical interface. This quantity, although easily defined, is not the usual impedance referred to in IS. Rather, such time-varying results are generally Fourier or Laplace transformed into the frequency domain, yielding a frequency-dependent impedance. If a Fourier transform is used, a distortion arising because of the non-periodicity of excitation should be corrected by using windowing. Such transformation is only valid when $|V_0|$ is sufficiently small that system response is linear. The advantages of this approach are that it is experimentally easily accomplished and that

the independent variable, voltage, controls the rate of the electrochemical reaction at the interface. Disadvantages include the need to perform integral transformation of the results and the fact that the signal-to-noise ratio differs between different frequencies, so the impedance may not be well determined over the desired frequency range.

Second, a signal $\nu(t)$ composed of random (white) noise may be applied to the interface and measure the resulting current. Again, one generally Fourier transforms the results to pass into the frequency domain and obtain an impedance. This approach offers the advantage of fast data collection because only one signal is applied to the interface for a short time. The technique has the disadvantages of requiring true white noise and then the need to carry out a Fourier analysis. Often a microcomputer is used for both the generation of white noise and the subsequent analysis. Using a sum of well-defined sine waves as excitation instead of white noise offers the advantage of a better signal-to-noise ratio for each desired frequency and the ability to analyze the linearity of system response.

Third, the most common and standard one is to measure impedance by applying a single-frequency voltage or current to the interface and measuring the phase shift and amplitude, or real and imaginary parts, of the resulting current at that frequency using either analog circuit or FFT analysis of the response. Commercial instruments (see Section 3.2) are available, which measure the impedance as a function of frequency automatically in the frequency ranges of about 1 mHz to 1 MHz and which are easily interfaced to laboratory microcomputers. The advantages of this approach are the availability of these instruments and the ease of their use, as well as the fact that the experimentalist can achieve a better signal-to-noise ratio in the frequency range of most interest.

In addition to these three approaches, one can combine them to generate other types of stimuli. The most important of these, ac polarography, combines the first and third techniques by simultaneously applying a linearly varying unipolar transient signal and a much smaller single-frequency sinusoidal signal (Smith [1966]).

Any intrinsic property that influences the conductivity of an electrode–material system, or an external stimulus, can be studied by IS. The parameters derived from an IS spectrum fall generally into two categories: (i) those pertinent only to the material itself, such as conductivity, dielectric constant, mobilities of charges, equilibrium concentrations of the charged species, and bulk generation–recombination rates, and (ii) those pertinent to an electrode–material interface, such as adsorption–reaction rate constants, capacitance of the interface region, and diffusion coefficient of neutral species in the electrode itself.

It is useful and not surprising that modern advances in electronic automation have included IS. Sophisticated automatic experimental equipment has been developed to measure and analyze the frequency response to a small-amplitude ac signal between about 10^{-4} and $>10^6$ Hz, interfacing its results to computers and their peripherals (see Section 3.1). A revolution in the automation of an otherwise difficult measuring technique has moved IS out of the academic laboratory and has begun to make it a technique of importance in the areas of industrial quality control of paints, emulsions, electroplating, thin-film technology, materials fabrication, mechanical performance of engines, corrosion, and so on.

Although this book has a strong physicochemical bias, the use of IS to investigate polarization across biological cell membranes has been pursued by many investigators since 1925. Details and discussion of the historical background of this important branch of IS are given in the books of Cole [1972] and Schanne and Ruiz-Ceretti [1978].

1.1.3 Response to a Small-Signal Stimulus in the Frequency Domain

A monochromatic signal $\nu(t) = V_m \sin(\omega t)$, involving the single-frequency $\nu \equiv \omega/2\pi$, is applied to a cell, and the resulting steady-state current $i(t) = I_m \sin(\omega t + \theta)$ measured. Here θ is the phase difference between the voltage and the current; it is zero for purely resistive behavior. The relation between system properties and response to periodic voltage or current excitation is very complex in the time domain. In general, the solution of a system of differential equations is required. Response of capacitive and inductive elements is given as $i(t) = [dv(t)/dt]C$ and $v(t) = [di(t)/dt]L$ correspondingly, and combination of many such elements can produce an intractable complex problem.

Fortunately, the use of Fourier transformation allows one to simplify significantly the mathematical treatment of this system. The aforementioned differential equations can be transformed into $I(j\omega) = C \cdot \omega \cdot j \cdot V(j\omega)$ and $I(j\omega) = V(j\omega) / (L \cdot \omega \cdot j)$. Here $j \equiv \sqrt{-1}$, which is also often denoted in the literature as "i." For the case of sine-wave excitation as aforementioned, Fourier transforms of voltage and current $V(j\omega)$ and $I(j\omega)$ become $V_m \pi$ and $I_m \pi \cdot \exp(\theta j)$, respectively. It can be easily seen that in frequency domain voltage/current relations can be rearranged to a form similar to Ohm's law for dc current: $I(j\omega) = V(j\omega) / Z(j\omega)$ where for capacitance the complex quantity $Z(j\omega)$ is $1 / (C \cdot \omega \cdot j)$ and for inductance $Z(j\omega)$ is $L \cdot \omega \cdot j$. The complex quantity $Z(j\omega)$ is defined as the "impedance function," and its value at a particular frequency is "impedance" of the electric circuit. For simplicity, $Z(j\omega)$ is usually written as just $Z(\omega)$. Because of this Ohm's law-like relationship between complex current and voltage, the impedance of a circuit with multiple elements is calculated using the same rules as with multiple resistors, which greatly simplifies calculations.

Impedance may be defined not only for discrete systems but also for arbitrary distributed systems as the Fourier transform of the differential equation, defining the voltage response divided by the Fourier transform of the periodic current excitation: $Z(j\omega) = F\{v(t)\} / F\{i(t)\}$. Here the $F\{\}$ operator denotes a Fourier transform. However, Fourier transformation only reduces differential equations to simple Ohm's law-like form under conditions of linearity, causality, and stationarity of the system; therefore impedance is properly defined only for systems satisfying these conditions.

The concept of electrical impedance was first introduced by Oliver Heaviside in the 1880s and was soon developed in terms of vector diagrams and complex representation by A. E. Kennelly and especially C. P. Steinmetz. Impedance is a more general concept than resistance because it takes phase differences into account, and it has become a fundamental and essential concept in electrical engineering. IS is thus just a specific branch of the tree of electrical measurements. The magnitude and direction of a planar vector in a right-hand orthogonal system of axes can be expressed by the vector sum of the components a and b along the axes, that is, by the complex number $Z = a + jb$. The imaginary number $j \equiv \sqrt{-1} \equiv \exp(j\pi/2)$ indicates an anticlockwise rotation by $\pi/2$ relative to the x -axis. Thus, the real part of Z , a , is in the direction of the real axis x , and the imaginary part b is along the y -axis. An impedance $Z(\omega) = Z' + jZ''$ is such a vector quantity and may be plotted in the plane with either rectangular or polar coordinates, as shown in Figure 1.1.1. Here the two rectangular coordinate values are clearly

$$\text{Re}(Z) \equiv Z' = |Z| \cos(\theta) \quad \text{and} \quad \text{Im}(Z) \equiv Z'' = |Z| \sin(\theta) \quad (1)$$

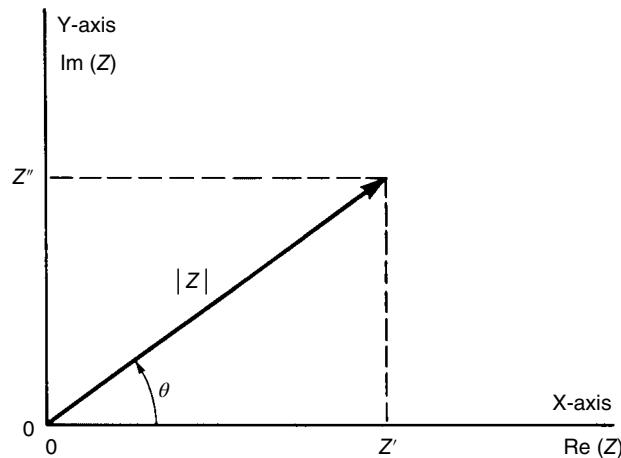


FIGURE 1.1.1 The impedance Z plotted as a planar vector using rectangular and polar coordinates.

with the phase angle

$$\theta = \tan^{-1} \left(\frac{Z''}{Z'} \right) \quad (2)$$

and the modulus

$$|Z| = \left[(Z')^2 + (Z'')^2 \right]^{1/2} \quad (3)$$

This defines the Argand diagram or complex plane, widely used in both mathematics and electrical engineering. In polar form, Z may now be written as $Z(\omega) = |Z| \exp(j\theta)$, which may be converted to rectangular form through the use of the Euler relation $\exp(j\theta) = \cos(\theta) + j \sin(\theta)$. It will be noticed that the original time variations of the applied voltage and the resulting current have disappeared and the impedance is time invariant (provided the system itself is time invariant).

In general, Z is frequency dependent, as defined previously. Conventional IS consists of the (nowadays often automated) measurement of Z as a function of ν or ω over a wide frequency range. It is from the resulting structure of the $Z(\omega)$ versus ω response that one derives information about the electrical properties of the full electrode–material system.

For nonlinear systems, that is, most real electrode–material systems, IS measurements in either the time or the frequency domain are useful and meaningful in general only for signals of magnitude such that the overall electrode–material system response is electrically linear. This requires that the response to the sum of two separate input-measuring signals applied simultaneously be the sum of the responses of the signals applied separately. A corollary is that the application of a monochromatic signal, one involving $\sin(\omega t)$, results in no, or at least negligible, generation of harmonics in the output, that is, components with frequencies $n\nu$ for $n = 2, 3, \dots$. Both solid and liquid electrochemical systems tend to show strong nonlinear behavior, especially in their interfacial response, when applied voltages or currents are large. But so long as the applied potential difference (p.d.) amplitude V_m is less than the thermal voltage, $V_T \equiv RT/F \equiv kT/e$, about 25 mV at 25°C, it can be shown that the basic differential equations that govern the response of the system become linear to an excellent approximation. Here k is Boltzmann's constant, T the absolute temperature, e the proton charge, R the gas constant, and F the faraday. Thus if the applied amplitude V_m is appreciably less than V_T , the system will respond linearly. Note that in the linear regime, it is immaterial as far as the determination of $Z(\omega)$ is concerned whether a known $\nu(\omega t)$ is applied and the current measured or a known $i(\omega t)$ applied and the resulting voltage across the cell measured. When the system is nonlinear, this reciprocity no longer holds.

1.1.4 Impedance-Related Functions

The impedance has frequently been designated as the ac impedance or the complex impedance. Both these modifiers are redundant and should be omitted. Impedance without a modifier always means impedance applied in the frequency domain and usually measured with a monochromatic signal. Even when impedance values are derived by Fourier transformation from the time domain, the impedance is still defined for a set of individual frequencies and is thus an ac impedance in character.

Impedance is by definition a complex quantity and is only real when $\theta = 0$ and thus $Z(\omega) = Z'(\omega)$, that is, for purely resistive behavior. In this case the impedance is completely frequency independent. When Z' is found to be a variable function of frequency, the Kronig–Kramers (Hilbert integral transform) relations (Macdonald and Brachman [1956]), which holistically connect real and imaginary parts with each other, ensure that Z'' (and θ) cannot be zero over all frequencies but must vary with frequency as well. Thus it is only when $Z(\omega) = Z'$, independent of frequency, so $Z' = R$, an ordinary linear resistance, that $Z(\omega)$ is purely real.

There are several other measured or derived quantities related to impedance that often play important roles in IS. All of them may be generically called immittances. First is the admittance,

TABLE 1.1.1 Relations between the Four Basic Immittance Functions

	M	Z	Y	ϵ
M	M	μZ	μY^{-1}	ϵ^{-1}
Z	$\mu^{-1}M$	Z	Y^{-1}	$\mu^{-1}\epsilon^{-1}$
Y	μM^{-1}	Z^{-1}	Y	$\mu\epsilon$
ϵ	M^{-1}	$\mu^{-1}Z^{-1}$	$\mu^{-1}Y$	ϵ

$\mu \equiv j\omega C_c$, where C_c is the capacitance of the empty cell.

$Y \equiv Z^{-1} \equiv Y' + jY''$. In the complex domain where ν , i , and Z are all taken complex, we can write $\nu = Zi$ or alternatively $i = Y\nu$. It is also customary in IS to express Z and Y in terms of resistive and capacitance components as $Z = R_s(\omega) - jX_s(\omega)$ and $Y = G_p(\omega) + jB_p(\omega)$, where the reactance $X_s \equiv [\omega C_s(\omega)]^{-1}$ and the susceptance $B_p \equiv \omega C_p(\omega)$. Here the subscripts s and p stand for “series” and “parallel.”

The other two quantities are usually defined as the modulus function $M = j\omega C_c Z = M' + jM''$ and the complex dielectric constant or dielectric permittivity $\epsilon = M^{-1} \equiv Y/(j\omega C_c) \equiv \epsilon' - j\epsilon''$. In these expressions $C_c \equiv \epsilon_0 A_c/l$ is the capacitance of the empty measuring cell of electrode area A_c and electrode separation length l . The quantity ϵ_0 is the dielectric permittivity of free space, 8.854×10^{-12} F/m. The dielectric constant ϵ is often written elsewhere as ϵ^* or $\hat{\epsilon}$ to denote its complex character. Here we shall reserve the superscript asterisk to denote complex conjugation; thus $Z^* = Z' - jZ''$. The interrelations between the four immittance functions are summarized in Table 1.1.1.

The modulus function $M = \epsilon^{-1}$ was apparently first introduced by Schrama [1957] and has been used appreciably by McCrum *et al.* [1967], Macedo *et al.* [1972b], and Hodge *et al.* [1975, 1976]. The use of the complex dielectric constant goes back much further but was particularly popularized by the work of Cole and Cole [1941], who were the first to plot ϵ in the complex plane.

Some authors have used the designation *modulus spectroscopy* to denote small-signal measurement of M versus ν or ω . Clearly, one could also define admittance and dielectric permittivity spectroscopy. The latter is just another way of referring to ordinary dielectric constant and loss measurements. Here we shall take the general term *IS* to include all these other very closely related approaches. Thus IS also stands for *immittance spectroscopy*. The measurement and use of the complex $\epsilon(\omega)$ function is particularly appropriate for dielectric materials, those with very low or vanishing conductivity, but all four functions are valuable in IS, particularly because of their different dependence on and weighting with frequency.

1.1.5 Early History

IS is particularly characterized by the measurement and analysis of some or all of the four impedance-related functions Z , Y , M , and ϵ , and the plotting of these functions in the complex plane. Such plotting can, as we shall see, be very helpful in interpreting the small-signal AC response of the electrode-material system being investigated. Historically, the use of Z and Y in analyzing the response of electrical circuits made up of lumped (ideal) elements (R , L , and C) goes back to the beginning of the discipline of electrical engineering. An important milestone for the analysis of real systems, that is, ones distributed in space, was the plotting by Cole and Cole [1941] of ϵ' and ϵ'' for dielectric systems in the complex plane, now known as a Cole–Cole plot, an adaption at the dielectric constant level of the circle diagram of electrical engineering (Carter [1925]), exemplified by the Smith–Chart impedance diagram (Smith [1939, 1944]). Further, Z and Y have been widely used in theoretical treatments of semiconductor and ionic systems and devices since at least 1947 (see, e.g., Randles [1947], Jaffé [1952], Chang and Jaffé [1952], Macdonald [1953a], and Friauf [1954]). Complex plane plots have sometimes been called Nyquist diagrams. This is a misnomer, however, since Nyquist diagrams refer to transfer function (three- or four-terminal) response, while conventional complex plane plots involve only two-terminal input immittances.

On the experimental side, one should mention the early work of Randles and Somerton [1952] on fast reactions in supported electrolytes; no complex plane plotting appeared here. But complex plane plotting of G_p/ω versus C_p was used by Macdonald [1955] for experimental results on photoconducting alkali halide single crystals. Apparently the first plotting of impedance in the impedance plane for aqueous electrolytes was that of Sluyters [1960] (theory) and Sluyters and Oomen [1960] (experiment). The use of admittance plane plotting for accurate conductivity determination of solid electrolytes was introduced by Bauerle [1969], the first important paper to deal with IS for ionic solids directly. Since then, there have been many pertinent theoretical and experimental papers dealing with IS and complex plane plots. Many of them will be cited later, and we conclude this short survey of early history pertinent to IS with the mention of three valuable reviews: Sluyters-Rehbach and Sluyters [1970], Armstrong *et al.* [1978], and Archer and Armstrong [1980]. The first and second of these deal almost entirely with liquid electrolytes but are nevertheless somewhat pertinent to IS for solids.

1.2 ADVANTAGES AND LIMITATIONS

Although we believe that the importance of IS is demonstrated throughout this monograph by its usefulness in the various applications discussed, it is of some value to summarize the matter briefly here. IS is becoming a popular analytical tool in materials research and development because it involves a relatively simple electrical measurement that can readily be automated and whose results may often be correlated with many complex materials variables: from mass transport, rates of chemical reactions, corrosion, and dielectric properties, to defects, microstructure, and compositional influences on the conductance of solids. IS can predict aspects of the performance of chemical sensors and fuel cells, and it has been used extensively to investigate membrane behavior in living cells. It is useful as an empirical quality control procedure, yet it can contribute to the interpretation of fundamental electrochemical and electronic processes.

A flow diagram of a general characterization procedure using IS is presented in Figure 1.2.1. Here CNLS stands for complex nonlinear least squares fitting (see Section 3.2.2). Experimentally obtained impedance data for a given electrode–materials system may be analyzed by using an exact mathematical model based on a plausible physical theory that predicts theoretical impedance $Z_t(\omega)$ or by a relatively empirical equivalent circuit whose impedance predictions may be denoted by $Z_{ec}(\omega)$. In case either of the relatively empirical equivalent circuit or of the exact mathematical model, the parameters can be estimated and the experimental $Z_e(\omega)$ data compared with either the predicted equivalent circuit impedance $Z_{ec}(\omega)$ or the theoretical impedance $Z_t(\omega)$. Such fitting is most accurately accomplished by the CNLS method described and illustrated in Section 3.2.2.

An analysis of the charge transport processes likely to be present in an experimental cell (the physical model) will often suggest an equivalent circuit of ideal resistors and capacitors (even inductors or negative capacitors in some instances) and may account adequately for the observed IS response. For example, Schouler *et al.* [1983] found that the effects of densification by sintering a polycrystalline electrolyte will reduce the magnitude of the resistance across the grain boundaries and simultaneously decrease the surface area associated with the interface capacitance. These components will clearly be electrically in parallel in this situation. Their combination will be in series with other similar subcircuits representing such processes as the ionization of oxygen at the electrodes.

In another example, the oxidation–reduction reaction for the Zn^{2+} couple in an aqueous solution with a dropping mercury electrode (Sluyters and Oomen [1960]) can be represented by a reaction resistance R_R , arising from the transfer of electrons between the electrode and the solution, in parallel with a capacitor C_R associated with the space-charge diffuse double layer near the electrode surface. It is not difficult to calculate the theoretical impedance for such a circuit in terms of the parameters R_R and C_R . From an analysis of the parameter values in a plausible equivalent circuit as the experimental conditions are changed, the materials system can be characterized by analysis of its observed impedance response, leading to estimates of its microscopic parameters such as charge mobilities, concentrations, and electron transfer reaction rates.

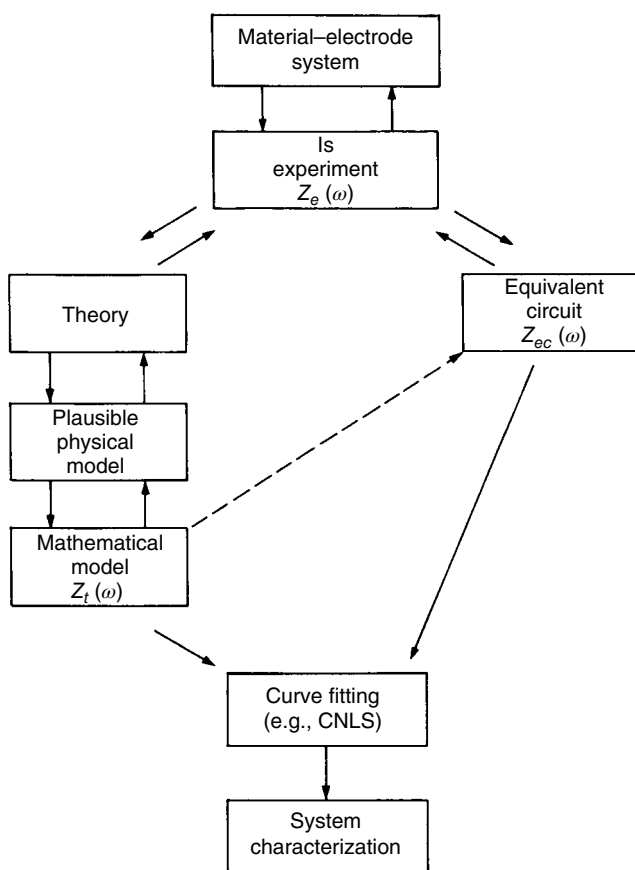


FIGURE 1.2.1 Flow diagram for the measurement and characterization of a material–electrode system.

The disadvantages of IS are primarily associated with possible ambiguities in interpretation. An important complication of analyses based on an equivalent circuit (e.g., Bauerle [1969]) is that ordinary ideal circuit elements represent ideal lumped-constant properties. Inevitably, all electrolytic cells are distributed in space, and their microscopic properties may be also independently distributed. Under these conditions, ideal circuit elements may be inadequate to describe the electrical response. Thus, it is often found that $Z_e(\omega)$ cannot be well approximated by the impedance of an equivalent circuit involving only a finite number of ordinary lumped-constant elements. It has been observed by many in the field that the use of distributed impedance elements (e.g., constant-phase elements (CPEs) (see Section 2.2.2.2)) in the equivalent circuit greatly aids the process of fitting observed impedance data for a cell with distributed properties.

There is a further serious potential problem with equivalent circuit analysis, not shared by the direct comparison with $Z_t(\omega)$ of a theoretical model: what specific equivalent circuit out of an infinity of possibilities should be used if one is necessary? An equivalent circuit involving three or more circuit elements can often be rearranged in various ways and still yield exactly the same $Z_{ec}(\omega)$. For the different interconnections, the values of the elements will have to be different to yield the same $Z_{ec}(\omega)$ for all ω , but an essential ambiguity is present. An example is presented in Figure 1.2.2. In these circuits the impedance Z_i is arbitrary and may be made up of either lumped elements, distributed elements, or a combination of these types. Examples of other circuits that demonstrate this type of ambiguity will be presented in Section 2.2.2.3. Which one of two or more circuits that all yield exactly the same $Z_{ec}(\omega)$ for all ω should be used for physicochemical analysis and interpretation? This question cannot be answered for a single set of $Z_e(\omega)$ data alone. An approach to its solution can only be made by employing

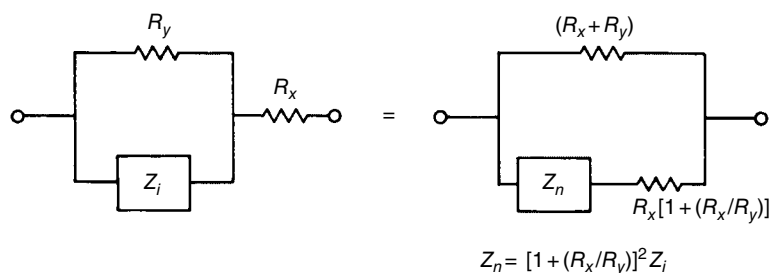


FIGURE 1.2.2 An example of different circuits with the same overall impedance at all frequencies.

physical intuition and by carrying out several $Z_e(\omega)$ sets of measurements with different conditions, as discussed in Section 2.2.2.3.

1.2.1 Differences between Solid-State and Aqueous Electrochemistry

The electrochemist who works with aqueous electrolytes has available to him/her at least one major stratagem not accessible to those who work with solid electrolytes. If he/she is interested in the interfacial behavior of a particular charged species, he/she is usually free to add to the solution an excess of a second electrolyte, the ions of which are neither adsorbed nor react at the interface but which by sheer numbers are able to screen the interior of the electrolyte from any electric field and cause nearly all the potential drop to occur within a few angstroms of the interface. The investigator is thus (at least by assumption) freed from having to take into account the effect of a nonuniform electric field on the transport of the electroactive species through the bulk electrolyte and need not (again by assumption) puzzle over the fraction of the applied signal that directly governs the exchange of ions or electrons between the electrode surface and the adjacent layer of electrolyte. The added electrolyte species that thus simplifies the interpretation of the experimental results is termed the *indifferent* or *supporting electrolyte*, and systems thus prepared are termed *supported systems*. Solid electrolytes must necessarily be treated as unsupported systems, even though they may display some electrical characteristics usually associated with supported ones. The distinction between unsupported and supported situations is a crucial one for the interpretation of IS results.

It is thus unfortunate that there has been a tendency among some workers in the solid electrolyte field to take over many of the relatively simple theoretical results derived for supported conditions and use them uncritically in unsupported situations, where the supported models and formulas rarely apply adequately. For example, the expression for the Warburg impedance for a redox reaction in a supported situation is often employed in the analysis of data on unsupported situations where the parameters involved are quite different (see, e.g., Sections 2.2.3.2 and 2.2.3.3).

There are a few other important distinctions between solid and liquid electrolytes. While liquid electrolytes and many solid electrolytes have negligible electronic conductivity, quite a number of solid electrolytes can exhibit substantial electronic conductivity, especially for small deviations from strict stoichiometric composition. Solid electrolytes may be amorphous, polycrystalline, or single crystal, and charges of one sign may be essentially immobile (except possibly for high temperatures and over long time spans). On the other hand, all dissociated charges in a liquid electrolyte or fused salt are mobile, although the ratio between the mobilities of positive and negative charges may differ appreciably from unity. Further, in solid electrolytes, mobile ions are considered to be able to move as close to an electrode as permitted by ion-size steric considerations. But in liquid electrolytes, a compact inner or Stern layer composed of solvent molecules, for example, H_2O , immediately next to the electrode, is usually present. This layer may often be entirely devoid of ions and only has some in it when the ions are specifically adsorbed at the electrode or react there. Thus capacitive effects in electrode interface regions can be considerably different between solid and liquid electrolyte systems.