CHAPTER 1

Fundamentals of Electrochemical Impedance Spectroscopy

1.1. Concept of complex impedance

The concept of electrical impedance was first introduced by Oliver Heaviside in the 1880s and was soon afterward developed in terms of vector diagrams and complex numbers representation by A. E. Kennelly and C. P. Steinmetz [1, p. 5]. Since then the technique has gained in exposure and popularity, propelled by a series of scientific advancements in the field of electrochemistry, improvements in instrumentation performance and availability, and increased exposure to an ever-widening range of practical applications.

For example, the development of the double-layer theory by Frumkin and Grahame led to the development of the equivalent circuit (EC) modeling approach to the representation of impedance data by Randles and Warburg. Extended studies of electrochemical reactions coupled with diffusion (Gerisher) and adsorption (Eppelboin) phenomena, effects of porous surfaces on electrochemical kinetics (de Levie), and nonuniform current and potential distribution dispersions (Newman) all resulted in a tremendous expansion of impedance-based investigations addressing these and other similar problems [1]. Along with the development of electrochemical impedance theory, more elaborate mathematical methods for data analysis came into existence, such as Kramers-Kronig relationships and nonlinear complex regression [1, 2]. Transformational advancements in electrochemical equipment and computer technology that have occurred over the last 30 years allowed for digital automated

impedance measurements to be performed with significantly higher quality, better control, and more versatility than what was available during the early years of EIS. One can argue that these advancements completely revolutionized the field of impedance spectroscopy (and in a broader sense the field of electrochemistry), allowing the technique to be applicable to an exploding universe of practical applications. Some of these applications, such as dielectric spectroscopy analysis of electrical conduction mechanisms in bulk polymers and biological cell suspensions, have been actively practiced since the 1950s [3, 4]. Others, such as localized studies of surface corrosion kinetics and analysis of the state of biomedical implants, have come into prominence only relatively recently [5, 6, 7, 8].

In spite of the ever-expanding use of EIS in the analysis of practical and experimental systems, impedance (or complex electrical resistance, for a lack of a better term) fundamentally remains a simple concept. Electrical resistance R is related to the ability of a circuit element to resist the flow of electrical current. Ohm's Law (Eq. 1-1) defines resistance in terms of the ratio between input voltage V and output current I:

$$R = \frac{V}{I} \tag{1-1}$$

While this is a well-known relationship, its use is limited to only one circuit element—the ideal resistor. An ideal resistor follows Ohm's Law at all current, voltage, and AC frequency levels. The resistor's characteristic resistance value R [ohm] is independent of AC frequency, and AC current and voltage signals though the ideal resistor are "in phase" with each other. Let us assume that the analyzed sample material is ideally homogeneous and completely fills the volume bounded by two external current conductors ("electrodes") with a visible area A that are placed apart at uniform distance d, as shown in Figure 1-1. When external voltage V is applied, a uniform current I passes through the sample, and the resistance is defined as:

$$R = \rho \frac{d}{A} \tag{1-2}$$

where ρ [ohm cm] is the characteristic electrical resistivity of a material, representing its ability to resist the passage of the current. The inverse of resistivity is conductivity σ [1 / (ohm cm)] or [Sm/cm], reflecting the material's ability to conduct electrical current between two bounding electrodes.

An ideal resistor can be replaced in the circuit by another ideal element that completely rejects any flow of current. This element is referred as an "ideal" capacitor (or "inductor"), which stores magnetic energy created by an applied electric field, formed when two bounding electrodes are separated by a non-conducting (or "dielectric") medium. The AC current and voltage signals though the ideal capacitor are completely "out of phase" with each other, with current following voltage. The value of the capacitance presented in Farads [F] depends on the area of the electrodes A, the distance between the

electrodes d, and the properties of the dielectric reflected in a "relative permittivity" parameter ε as:

$$C = \frac{\varepsilon_o \varepsilon A}{d} \tag{1-3}$$

where ε_0 = constant electrical permittivity of a vacuum ($8.85 \cdot 10^{-14}$ F/cm). The relative permittivity value represents a characteristic ability of the analyzed material to store electrical energy. This parameter (often referred to as simply "permittivity" or "dielectric") is essentially a convenient multiplier of the vacuum permittivity constant ε_0 that is equal to a ratio of the material's permittivity to that of the vacuum. The permittivity values are different for various media: 80.1 (at 20°C) for water, between 2 through 8 for many polymers, and 1 for an ideal vacuum. A typical EIS experiment, where analyzed material characteristics such as conductivity, resistivity, and permittivity are determined, is presented in Figure 1-1.

Impedance is a more general concept than either pure resistance or capacitance, as it takes the phase differences between the input voltage and output current into account. Like resistance, impedance is the ratio between voltage and current, demonstrating the ability of a circuit to resist the flow of electrical current, represented by the "real impedance" term, but it also reflects the ability of a circuit to store electrical energy, reflected in the "imaginary impedance" term. Impedance can be defined as a complex resistance encountered when current flows through a circuit composed of various resistors, capacitors, and inductors. This definition is applied to both direct current (DC) and alternating current (AC).

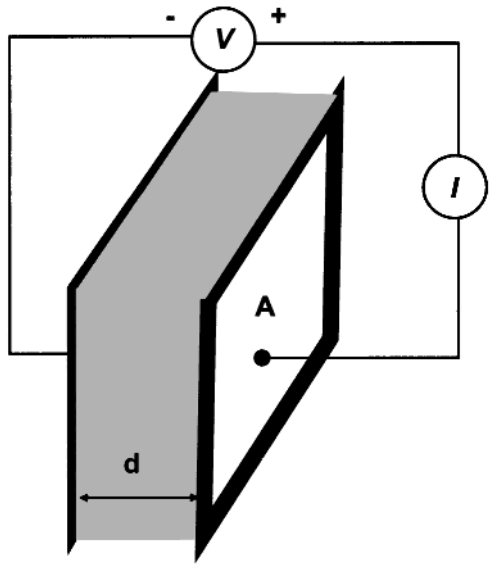

FIGURE 1-1 Fundamental impedance experiment

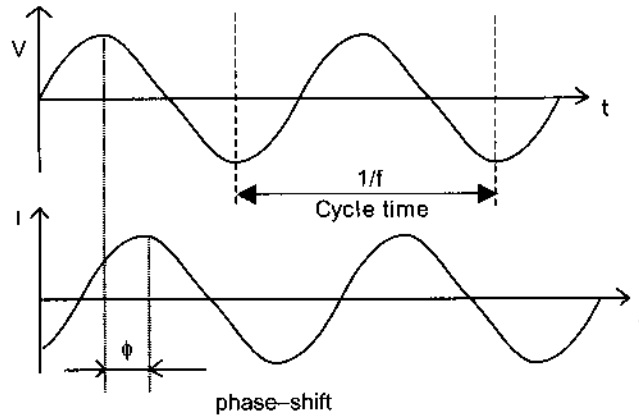

FIGURE 1-2 Impedance experiment: sinusoidal voltage input V at a single frequency f and current response I

In experimental situations the electrochemical impedance is normally measured using excitation AC voltage signal V with small amplitude V_A (expressed in volts) applied at frequency f (expressed in Hz or 1/sec). The voltage signal $V(t)$, expressed as a function of time t, has the form:

$$V(t) = V_A \sin(2\pi ft) = V_A \sin(\omega t) \tag{1-4}$$

In this notation a "radial frequency" ω of the applied voltage signal (expressed in radians/second) parameter is introduced, which is related to the applied AC frequency f as $\omega = 2\pi f$.

In a linear or pseudolinear system, the current response to a sinusoidal voltage input will be a sinusoid at the same frequency but "shifted in phase" (either forward or backward depending on the system's characteristics)—that is, determined by the ratio of capacitive and resistive components of the output current (Figure 1-2). In a linear system, the response current signal $I(t)$ is shifted in phase (ϕ) and has a different amplitude, I_A:

$$I(t) = I_A \sin(\omega t + \phi) \tag{1-5}$$

An expression analogous to Ohm's Law allows us to calculate the complex impedance of the system as the ratio of input voltage $V(t)$ and output measured current $I(t)$:

$$Z^* = \frac{V(t)}{I(t)} = \frac{V_A \sin(\omega t)}{I_A \sin(\omega t + \phi)} = Z_A \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \tag{1-6}$$

The impedance is therefore expressed in terms of a magnitude (absolute value), $Z_A = |Z|$, and a phase shift, ϕ. If we plot the applied sinusoidal voltage signal on the x-axis of a graph and the sinusoidal response signal $I(t)$ on the y-axis, an oval known as a "Lissajous figure" will appear (Figure 1-3A).

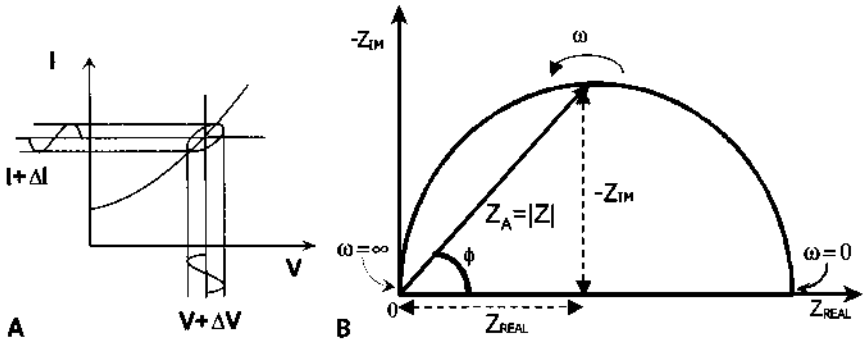

FIGURE 1-3 Impedance data representations: A. Lissajous figure; B. Complex impedance plot

Analysis of Lissajous figures on oscilloscope screens was the accepted method of impedance measurement prior to the availability of lock-in amplifiers and frequency response analyzers. Modern equipment allows automation in applying the voltage input with variable frequencies and collecting the output impedance (and current) responses as the frequency is scanned from very high (MHz-GHz) values where timescale of the signal is in micro- and nanoseconds to very low frequencies (μHz) with timescales of the order of hours.

Using Euler's relationship:

$$\exp(j\phi) = \cos\phi + j\sin\phi \tag{1-7}$$

it is possible to express the impedance as a complex function. The potential $V(t)$ is described as:

$$V(t) = V_A \, e^{j\omega t} \tag{1-8}$$

and the current response as:

$$I(t) = I_A \, e^{j\omega t - j\phi} \tag{1-9}$$

The impedance is then represented as a complex number that can also be expressed in complex mathematics as a combination of "real," or in-phase (Z_{REAL}), and "imaginary," or out-of-phase (Z_{IM}), parts (Figure 1-3B):

$$Z^* = \frac{V}{I} = Z_A e^{j\phi} = Z_A \, (\cos\phi + j\sin\phi) = Z_{REAL} + jZ_{IM} \tag{1-10}$$

and the phase angle ϕ at a chosen radial frequency ω is a ratio of the imaginary and real impedance components:

$$\tan\phi = \frac{Z_{IM}}{Z_{REAL}} \quad \text{or} \quad \phi = \arctan\left(\frac{Z_{IM}}{Z_{REAL}}\right) \tag{1-11}$$

1.2. Complex dielectric, modulus, and impedance data representations

In addition to the AC inputs such as voltage amplitude V_A and radial frequency ω, impedance spectroscopy also actively employs DC voltage modulation (which is sometimes referred to as "offset voltage" or "offset electrochemical potential") as an important tool to study electrochemical processes. Alternative terms, such as "dielectric spectroscopy" or "modulus spectroscopy," are often used to describe impedance analysis that is effectively conducted only with AC modulation in the absence of a DC offset voltage (Figure 1-4).

Dielectric analysis measures two fundamental characteristics of a material—permittivity ε and conductivity σ (or resistivity ρ)—as functions of time, temperature, and AC radial frequency ω. As was discussed above, permittivity and conductivity are two parameters characteristic of respective abilities of analyzed material to store electrical energy and transfer electric charge. Both of these parameters are related to molecular activity. For example, a "dielectric" is a material whose capacitive current (out of phase) exceeds its resistive (in phase) current. An "ideal dielectric" is an insulator with no free charges that is capable of storing electrical energy. The Debye Equation (Eq. 1-12) relates the relative permittivity ε to a concept of material polarization density P [C/m^2], or electrical dipole moment [C/m] per unit volume [m^3], and the applied electric field V:

$$P = (\varepsilon - 1)\varepsilon_0 V \tag{1-12}$$

Depending on the investigated material and the frequency of the applied electric field, determined polarization can be electronic and atomic (very small translational displacement of the electronic cloud in THz frequency range), orientational or dipolar (rotational moment experienced by permanently polar molecules in kHz-MHz frequency range), and ionic (displacement of ions with respect to each other in Hz-kHz frequency region).

The dielectric analysis typically presents the permittivity and conductivity material properties as a combined "complex permittivity" ε* parameter, which is analogous to the concept of complex impedance Z^* (Figure 1-4A). Just as complex impedance can be represented by its real and imaginary components, complex permittivity is a function of two parameters—"real" permittivity (often referred to as "permittivity" or "dielectric constant") ε′ and imaginary permittivity (or "loss factor") ε″ as:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1-13}$$

In dielectric material ε′ represents the alignment of dipoles, which is the energy storage component that is an inverse equivalent of Z_{IM}. ε″ represents the ionic conduction component that is an inverse equivalent of Z_{REAL}. Both real permittivity and loss factor can be calculated from sample resistance R, conductivity σ, resistivity ρ, and capacitance C measured in a fundamental experimental setup (Figure 1-1) as:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \text{ and } \varepsilon'' = \frac{d}{RA\omega\varepsilon_0} = \frac{\sigma}{\omega\varepsilon_0} = \frac{1}{\rho\omega\varepsilon_0} \tag{1-14}$$

Permittivity and conductivity values and their relative contributions to the measured voltage to current ratio (impedance) are often dependent on the material's temperature, external AC frequency, and magnitude of the applied voltage. In fact, real permittivity is often not quite appropriately referred to as the "dielectric constant," the parameter that should always be specified at a standard AC frequency (usually about 100 kHz) and temperature conditions (typically 25°C) and therefore is not exactly "constant." The concepts of "conductivity" and "resistivity" for a chosen material are also vague. These parameters have to be specified at standard temperature conditions and be carefully measured with full consideration of the impedance dependence on the applied electric field. In practice these rules are often not followed. For instance, conductivity of many solutions is often measured by hand-held meters operating at an arbitrary frequency around ~ 1kHz, which, as will be shown in Section 6-3, may or may not be appropriate conditions for many materials even when they belong to the same family (such as aqueous solutions). Alternatively, operating at much higher frequencies may result in the measurement being dominated by the out-of-phase capacitive impedance, which is a function of the sample's dielectric constant and not of its conductivity. For instance, saline (ρ = 100 ohm cm, ε = 80) is a conductor below 250MHz and a capacitor above 250MHz.

Dielectric spectroscopy, although using the same type of electrical information as impedance spectroscopy, is logically different in its analysis and approach to data representation. Dielectric response is based on a concept of "energy storage" and resulting "relaxation" per release of this energy by the system's individual components. Initially the concept of dielectric relaxation was introduced by Maxwell and expanded by Debye, who used it to describe the time required for dipolar molecules to reversibly orient themselves in the external AC electric field. In the experiments of Debye a step function excitation was applied to the system, and the system was allowed to "relax" to equilibrium after the excitation was removed. The time required for that process to take place was called "relaxation time" $\tau = 1/2\pi f_c$ that is inversely related to "critical relaxation frequency" f_c. Dielectric spectroscopy measures relaxation times by detecting frequency dependence of complex permittivity ε^* and determining f_c values from positions of the peaks in the $\varepsilon^* = f(f)$ plot as the input voltage signal is scanned over the experimental AC frequency range.

Dispersion, or frequency dependence, according to the laws of relaxation, is the corresponding frequency domain expression of complex permittivity ε^* as a function of radial (or cycling) frequency ω. For example, as the applied frequency ω is increased, a steplike decrease in complex permittivity is observed due to the fact that polarized molecules that are fully aligned with each change in direction of the AC field at lower frequencies cannot follow the higher frequency field at each direction reversal (Figure 1-4B). As the high-frequency AC field changes direction faster, these molecules "relax" to nonaligned positions where they cannot store energy. Large nonpolar molecules typically lose their orientation with the field at low Hz frequencies and have relaxation times on the order of seconds. Smaller and more polar ionic species "relax" at kHz-MHz frequencies and show millisecond to microsecond relaxation times. The components of a sample typically have high permittivity (capacitance)

values at low frequencies where more different types of molecules can completely align with the field and store the maximum possible energy and are being effectively charged as dielectric dipoles. At high frequencies fewer dipoles store energy, and the total measured capacitance and permittivity of the system are low. Comparative analysis of dielectric dependencies of pure components presents an opportunity to identify and separate these species in complex mixed systems based on the AC frequency dependence of their dielectric response $\varepsilon^* = f(\omega)$.

The above frequency dependence of dielectric material properties, such as capacitance $C(\omega)$, permittivity $\varepsilon'(\omega)$, and conductivity $\sigma(\omega)$, can be expressed by Debye's "single relaxation" model [3, p. 65]. The Debye model is a popular representation used to illustrate bulk relaxation processes in ideal dielectrics, such as highly resistive polymers, where it is assumed that there is no conduction (or "loss") through the bulk material as the sample resistance R is infinitely high and conductivity $\sigma \rightarrow 0$ [3, 4]. This model is a classical representation of a simple dielectric or fully capacitive experimental system, where transition occurs from high-frequency permittivity ε_∞ (or capacitance C_2) to low-frequency permittivity ε_{LF} (or capacitance C_1) where $C_1 > C_2$ (Section 4-4). In the Debye model the response is ideally capacitive at both high and low frequency extremes, with the transition between the two regimes characterized by permittivity increment $\Delta\varepsilon = \varepsilon_{LF} - \varepsilon_\infty$. It is usually expressed for a medium permittivity ε as a function of the AC field's radial frequency ω, where τ is the characteristic "relaxation time" of the system. Expansion of Equation 1-13 leads to:

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + j\omega\tau} \text{ where } \varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \omega^2\tau^2} \text{ and } \varepsilon''(\omega) = \frac{\Delta\varepsilon\omega\tau}{1 + \omega^2\tau^2} \quad (1\text{-}15)$$

Complex permittivity of a more realistic "lossy" dielectric where non-zero parallel DC conductivity $\sigma(\omega)$ exists can be represented on the basis of a more complex Havriliak-Negami model. This model also accounts for non-idealities of both capacitive and resistive components accounting for the asymmetry and broadness of the dielectric dispersion curve and resulting frequency-dependent conductivity $\sigma(\omega)$ and permittivity $\varepsilon(\omega)$ contributions:

$$\varepsilon^*(\omega) = \left(\varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (j\omega\tau)^\alpha)^\beta}\right) - j\left(\frac{\sigma(\omega)}{\varepsilon_0\omega}\right)^N \quad (1\text{-}16)$$

Where: $\tau = 1/2\pi f_c$ = characteristic relaxation time, ω = radial frequency, N = parameter that defines the frequency dependence of the conductivity term (typically $N \rightarrow 1$ and equals the slope of the low-frequency increase in $\varepsilon^* = f(\omega)$ or $\varepsilon'' = f(\omega)$ plot due to the low-frequency conduction through the system, as shown in Figure 1-4B), α and β = shape parameters accounting for symmetric and asymmetric broadening of the relaxation peak.

In addition to the Debye model for dielectric bulk materials, other dielectric relaxations expressed according to Maxwell-Wagner or Schwartz "interfacial" mechanisms exist. For example, the Maxwell-Wagner "interfacial" polarization concept deals with processes at the interfaces between different components of an experimental system. Maxwell-Wagner polarization occurs

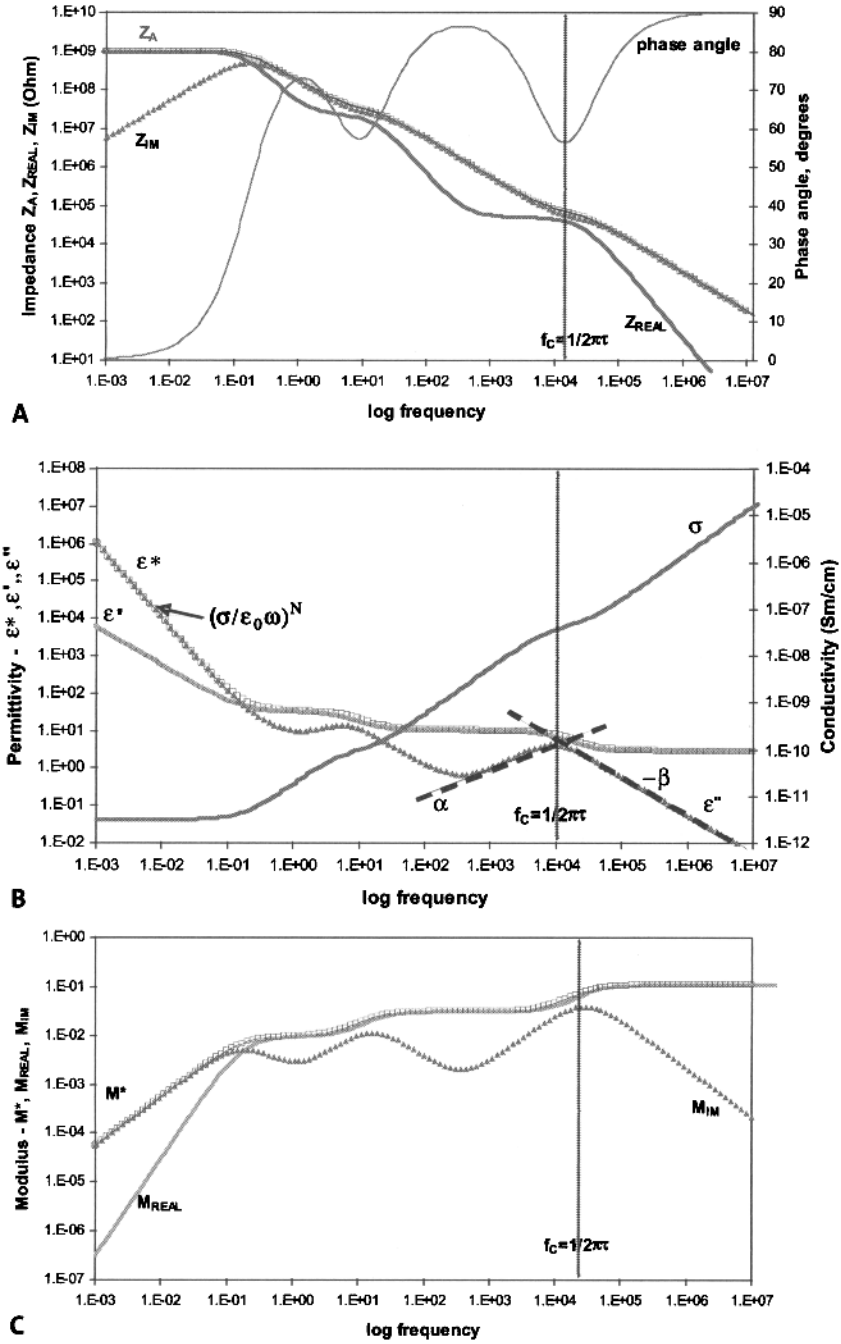

FIGURE 1-4 Representations of complex impedance data as function of AC frequency: A. impedance and phase angle; B. permittivity and conductivity; C. modulus

either at inner boundary layers separating two dielectric components of a sample or more often at an interface between the sample and an external ideal electrical conductor (electrode). In both cases this leads to a significant separation of charges over a considerable distance. This contribution of Maxwell-Wagner polarization to dielectric loss can be orders of magnitude larger than the molecular fluctuation's dielectric response described by the Debye mechanism. Maxwell-Wagner interfacial effects are prominent in electrochemical studies dealing with heterogeneous interfacial kinetics.

The Debye model is primarily describing a bulk material "dielectric" response. Traditional dielectric spectroscopy has found a significant use in the characterization of multicomponent resistive materials with mixed or particle-based conduction mechanisms, such as polymers, nonpolar organics (lubricants), and moderately resistive aqueous (cellular) colloids. However, there are relatively few practical cases of nearly ideal dielectric materials where more than one well-resolved dielectric relaxations can be identified at a constant temperature. The Maxwell-Wagner electrode-sample interface phenomenon and other interfacial effects (such as double layer charging and Faradaic kinetics) that result in apparent high interfacial capacitance masking settled capacitance changes in bulk material at frequencies below ~10 kHz are viewed as severe restricting factors in studies of dielectric materials. With the exception of extreme cases, such as ion-free insulating media with polarized particle conduction (such as electrorheological fluids) or subfreezing sample temperatures, the frequency range relatively free of the effects of interfacial polarization is often limited to high kHz-GHz. In such a limited frequency range at a constant temperature the appearance of several types of conducting species showing significant frequency dependence, not interfering with one another and present in a significant and balanced range of concentrations, is a rare occurrence. Hence, dielectric analysis often relies not on the AC frequency but on wide temperature modulation at a few selected AC frequencies as the primary interrogation mode to extract details of sample analytical information.

Another representation of the dielectric properties of analyzed media is complex modulus M* (Figure 1-4C). The modulus is the inverse of complex permittivity ε* and can also be expressed as a derivative of complex impedance Z*:

$$M^* = \frac{1}{\varepsilon^*} = M' - jM'' = j\omega\varepsilon_0 Z^* = -\omega\varepsilon_0 Z_{IM} + j\omega\varepsilon_0 Z_{REAL} \qquad (1\text{-}17)$$

Fundamentally, complex electrochemical impedance (Z*), modulus (M*), and permittivity (ε*) parameters are all determined by applying an AC potential at a variable frequency and measuring output current through the sample (Figure 1-1). In a broader sense dielectric, modulus, and impedance analysis represent the same operational principles and can be referred to as subsets of a universal broadband electrochemical impedance spectroscopy (UBEIS). This technique analyzes both resistive and capacitive components of the AC current signal response, containing the excitation frequency and its harmonics. This current signal output can be analyzed as a sum of sinusoidal functions (a Fourier series). Depending on applied AC frequency and voltage, the output

current can be supported by various conductive mechanisms through the analyzed system. These conductive mechanisms can be related to a single process, or be supported by a combination of various ionic, electronic, and particle conductors and their relative concentrations. The conduction process occurs both in bulk sample and at the interface between the sample and the electrodes, where a series of electron-exchanging reactions may take place. Critical relaxation frequencies can be determined from peak positions in complex impedance, modulus and permittivity plots.

The same data can be presented in modulus, dielectric, and impedance domains (Figure 1-4) and can be converted directly between the domains using expressions based on Maxwell equations. Although the data representing the electrochemical relaxation phenomenon fundamentally contain the same information and are independent of the chosen representation method, presenting the data sepa-rately as dielectric, impedance, and modulus plots often allows extracting additional useful information about the analyzed system. For instance, localized relaxations result in the peaks appearing at different frequencies in complex impedance or complex modulus vs. frequency plots, whereas long-range fundamental conductivity results in exact overlapping of the modulus and impedance peaks. Also, as will be shown later, these data representations have different resolving capabilities to present the results as a function of the applied experimental conditions.

Nevertheless, historically a differentiation exists between "dielectric" and "impedance" spectroscopies. Traditional dielectric analysis has been applied primarily to the analysis of bulk "dielectric" properties of polymers, plastics, composites, and nonaqueous fluids with very high bulk material resistance. The dielectric method is characterized by using higher AC voltage amplitudes, temperature modulation as an independent variable, lack of DC voltage perturbation, and often operating frequencies above 1 kHz or measurements at several selected discrete frequencies [2, p. 33].

Traditional impedance spectroscopy is preoccupied with investigating charge and material-exchange ("electrochemical") kinetic processes that occur at electrode-sample interfaces. This technique actively employs DC modulation just as most electrochemical techniques do, typically uses low AC voltage amplitudes to maintain linearity of signal response, and employs wide frequency ranges from MHz to μHz. Unlike dielectric spectroscopy, the analytical aspect of traditional impedance analysis is based not on bulk material investigations but rather on quantification of sample species through relevant interfacial impedance parameters. The majority of traditional EIS studies emphasize involved analysis of Faradaic and double-layer interfacial kinetics and the effects of DC potential modulation. As opposed to the dielectric spectroscopy experimental approach, traditional impedance analysis often attempts to minimize or keep constant the effects of bulk material impedance and related dielectric relaxations due to capacitance effects of energy-storage components in the system. That is typically achieved by operating in highly conductive samples (such as aqueous solutions with supporting electrolytes) with a total bulk solution resistance of just several ohms and negligible capacitive effects. The impedance response of the electrode-solution interface,

which is located in series with the bulk-solution impedance, can be easily determined at relatively low, typically Hertzian, AC frequencies. As demonstrated in Figure 1-4A, the impedance response of the conducting species and medium properties are qualitatively reflected in an integrative manner. Therefore the appearance of additional interfacial impedance at low frequencies results in an increase in the measured impedance to reflect a combined effect of both bulk and interfacial impedances. However, if the bulk impedance is kept very low by operating in highly conductive media, the total measured low-frequency impedance effectively becomes equal to the interfacial impedance.

The impedance output is fundamentally determined by the characteristics of an electrical current conducted through the system and is based on the concept that the obtained data represents the sample's "least impedance to the current." A significant portion of this book is dedicated to analysis of various possible parallel and sequential conducting mechanisms through the analyzed systems of interest. In any given experimental system there are always several competing paths for the current to travel through a sample. The current, however, chooses one or several closely matched predominant "paths of least resistance" between two electrical conductors (electrodes) under applied conditions such as AC frequency and voltage amplitude, DC voltage, electrode geometry and configuration, sample composition and concentration of main conducting species, temperature, pressure, convection, and external magnetic fields. Only the conduction through this predominant path of least resistance, or, to be more exact, the path of the least impedance, is measured by the EIS.

For example, for a sample represented by a parallel combination of a capacitor C and a resistor R (defined there as R/C), at high frequencies ω the impedance to current is the lowest through the capacitive component where impedance is inversely proportional to the frequency, as $Z^* \sim (\omega C)^{-1}$, and therefore is smaller than the impedance of the finite resistor R. At lower frequencies the opposite becomes true—the capacitive impedance component becomes large, and the current predominantly flows through the resistor; the total measured impedance reflects the resistance value as $Z^* \sim R$. The detected impedance output is determined by measuring the current passing through the least impeding segment of the circuit. The characteristic parameters of this ideal system can therefore be determined from the total impedance response $Z^* = f(\omega)$ as pure capacitance C at higher frequencies and pure resistance R at lower frequencies. Characteristic relaxation frequency f_c corresponds to a value where switching between the two conduction mechanisms occurs. The inverse of this frequency is characteristic "relaxation time" $\tau = 1/\omega_c$ for this circuit. For example, in aqueous conductive solution with permittivity of ~80 and bulk resistance ~ 1 ohm, it is easy to determine that at all frequencies under $f_c \sim 1$ GHz the current is conducted through a very small bulk solution resistor, and the capacitive characteristics are not contributing to the measured impedance signal. Similar results were shown for the above example illustrating current conduction through a saline solution.

These examples represent a circuit composed of ideal capacitive and resistive electrical components. The path of least impedance through a real-life sample placed between two conducting metal electrodes can be represented

by a combination of chemical and mechanical elements that can only to some degree be approximated by these ideal electrical elements. These conducting venues through the sample may be the most plentiful and mobile electrons, ions, and particles; double-layer capacitive charging effects, specific adsorption, charge transfer "resistance" to tunneling electrons crossing the interface between the sample and the electrodes, and transport of discharging species to the surface of the electrode through diffusion layer concentration gradients at the electrode/sample interfaces. To interpret the EIS results, scientists and engineers have to intelligently devise the experiment to extract the needed analytical information from the experimentally obtained impedance. This interpretation includes initial development of the relationships between the electrical parameters representing the path of least impedance to the current and the "real life" investigated chemical and mechanical components that result in the measured impedance response. Through these relationships it may be possible to analyze the actual chemical, physical, and mechanical processes inside the analyzed system.

To the great benefit of analytical chemists concerned with the accurate analysis of concentrations of analytes and material scientists preoccupied with sample properties, the mechanisms of transporting current are largely determined by limited types of species that are present in the analyzed sample at significant levels. In that respect UBEIS is indeed a "spectroscopy," where a combination of carefully conducted experiments, some degree of initial preconceived knowledge of the analyzed sample, selection of experimental conditions, and careful interpretation of results are required to determine the sample composition and the mechanisms responsible for the impedance response, quantify them, and develop a mechanical model of the entire system's physical and chemical response to applied external electric field.

With that in mind, one cannot always determine "all" species present in the experimental system, as not "all" species may participate in the conduction through the path of least impedance, even if their response is dependent on the controlled experimental parameters, such as AC frequency. As with many other spectroscopy methods, UBEIS has the advantage of often being able to separate and identify several types of species inside an experimental sample, as various species may create a path of least impedance through the sample at different (and variable) experimental conditions. However, many potential analytes may still not be detectable, as they do not conduct current or are present in such low concentrations that their contribution to the overall conduction process may be negligible. However, they may have a disproportionably strong activity at the electrode interface. The same general limitations are present in optical and other "spectroscopies" based on "detection of the most prominent contributors" principle. It is the task of good experimental scientists to develop experimental designs that would provide the necessary information about the task at hand.

As will be further discussed, current traveling through a sample has to overcome successive impedances of two fundamentally different regions. One of them is the "bulk" of the sample, and the other is the "interface" where the sample meets the current conducting electrodes. Electrochemistry in general and the UBEIS in particular are often used to analyze both bulk sample

conduction mechanisms and interfacial processes, where electron transfer, mass transport, and adsorption are often present. EIS analysis has often treated the bulk and interfacial processes separately [2, p. 28]. The analysis is achieved on the basis of selective responses of bulk and interfacial processes to sampling AC frequencies. The peaks appearing in the impedance spectrum can be described according to the theory of dielectric/impedance relaxations. Again, as in the case of any other spectroscopy method, the subject of the UBEIS analysis is the detection and interpretation of these peaks.

1.3. Electrochemical experiment: charge and material transport

In the basic electrochemical experiment there are at least two electrodes bounding a sample (such as electrolyte solution) with external potential (voltage) V difference applied between the two (Figure 1-5). Under the influence of the electric field the current I passes through a complete circuit, transported by electrons in the metal conductors, the electrodes, and ionic migration in the electrolyte. The electrons are free to move in the conduction bands inside the metal. A current that seems to flow quickly is not due to a "very fast" speed of the electrons in metal conductors (which is, in fact, rather slow at ~ 0.3 mm/sec), but because there are different electrons entering and leaving a conductor. In principle, when an electron is supplied to a wire end, "another" electron is coming out of the other end.

Ionic liquid (electrolyte), such as water with added ionic salts, is one of the common samples investigated by EIS. An average ion electrophoretic migration velocity in aqueous solution is ~ 10 mm/sec. As was shown above, the resistance to ionic migration current in the aqueous bulk solution within the frequency range of a typical impedance measurement can be simplified by a

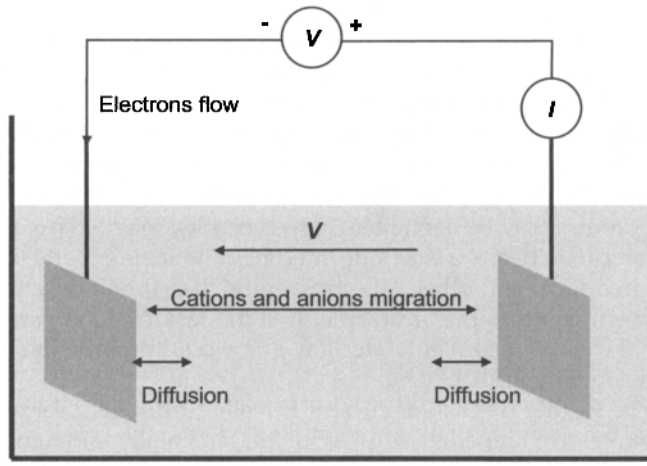

FIGURE 1-5 The basic electrochemical experiment with material transport directions

small "solution resistance" component R_{SOL} (Figure 1-6). Current in the bulk solution is transported predominantly by migration, which is dependent on the applied external voltage V (often referred to in the electrochemical literature as "electrochemical potential difference $\Delta\phi$"). For migration processes involving electroactive species of type i, the Kohlrausch equation applies as does the familiar Ohm's Law equation, and for flux of charged species J_i [mol / sec] under the influence of electrochemical potential gradient $\Delta\phi/\Delta x$:

$$J_i = \frac{\Delta V(x)}{\Delta x} AF \sum z_i u_i C^*_i = \frac{\Delta\phi(x)}{\Delta x} A \sum \sigma_i \qquad (1\text{-}18)$$

Where: A = surface area of electrode, z_i = full charge of electroactive species of type i, F = Faradaic constant (96500 C/mol) representing free charge of 1 mol of elementary charges, C^*_i = concentration (mol/cm^3) of ions in solution participating in migration, u_i = the mobility constant, and $\sigma_i = F \sum z_i u_i C^*$ = bulk solution conductivity of this type of ions [Sm/cm].

Other types of samples can be subjected to electrochemical analysis, such as aqueous and non-aqueous solutions of ~ 1 μm-sized colloidal particles, where a charged double layer of "counterions" surround each particle and the particles can be regarded as "macro-ions." The colloidal particles will migrate and contribute to the solution conductivity. Solid ionic electrolytes and composite materials are also a possibility. There are also mixed conductors with both ionic and electronic conductance, such as many polymers. Lastly, semiconductors possess "forbidden gaps" that prevent electrons from entering conduction bands, resulting in low conductivity. The conduction can be significantly and selectively enhanced by adding impurities and creating local energy centers.

At the electrode-electrolyte interface separating the electrodes from the sample, there is a charge carrier shift—a transition between electronic and ionic conduction. The transfer of electric charge across the solution/electrode interface is accompanied by an electrochemical reaction at each electrode, a phenomenon known as electrolysis. Electrochemical discharge of the species at the interface is determined by their electrochemical properties, such as their ability to release or accept an electron at a voltage (or electrochemical potential) of this "electrochemically polarized" electrode. The electrode potential is essentially a measure of an excess of electrons at the electrode, which is charged negatively, or a lack of electrons on a positively charged electrode. In electrical terms, the impedance of the system to combined current generated by the discharge processes occurring in a nanometer thick "Helmholtz" interfacial layer of the sample immediately adjacent to the electrode can be represented by the so-called "charge transfer" resistance R_{CT} (Figure 1-6).

As a result of electrolysis reactions, depletion or accumulation of matter and charge may occur next to the electrodes. This reaction consumes or releases additional ions or neutral species from or into the bulk solution, resulting in a concentration gradient when concentration of the species in the bulk solution is different from that in the vicinity of the electrodes. However, all species always attempt to maintain equal concentration distribution inside any sample volume. For instance, when the local concentration gradient is

created in the vicinity of the electrodes as a result of the species' consumption over the course of the electrochemical reaction, the more abundant solution species always attempt to replenish continuously depleting species at the interface by moving or "diffusing" to the electrode surface. Alternatively, the release of new species as a result of completion of the electrochemical reaction leads to their diffusion away from the electrode into the bulk solution where their concentration is lower than that at the electrode-solution interface. This concentration gradient results in a diffusion mass transport process occurring in a thick "diffusion layer" that can be measured by electrochemical impedance and is represented by a complex diffusion impedance element Z_{DIFF}.

Many species that are also deposited at the interface do not participate in electrolysis at the electrode potential. The charges of these species are countered by electronic charges of the opposite sign on the electrode's interface, producing a "double layer capacitance" with a value C_{DL}. In conductive solution an electric double layer is formed at the electrode as soon as the electrode is wetted. It may be useful to remember that at all interfaces (such as transition areas between the electrode and solution, tissue, or gel, between the solution and the surface of a colloidal particle, or inside the sample) there will be a nonuniform distribution of charges and a resulting electrochemical potential gradient. The capacitive element is created by species that are different from the species that are discharging and diffusing to the electrode, producing a parallel ("energy storage") electrical pathway. Therefore the double layer capacitance is placed in parallel with charge transfer resistance and diffusion pathway

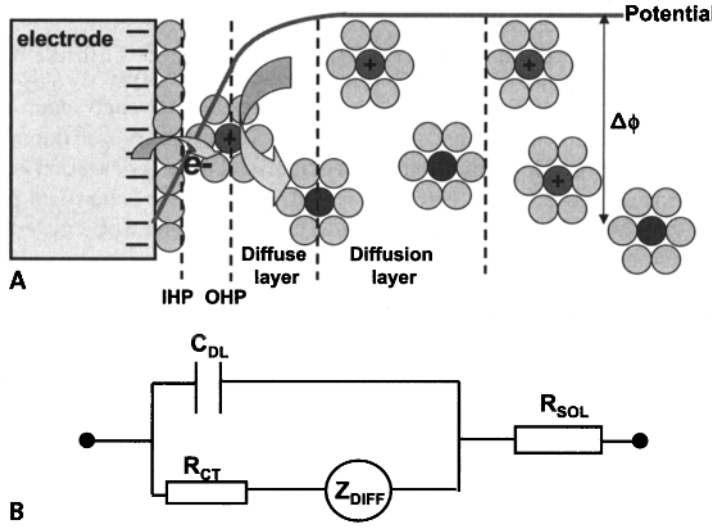

FIGURE 1-6 A. Interfacial electrochemical reaction with diffusion and double layer components; B. Representative electrical circuit

(Figure 1-6). Maxwell-Wagner, Helmholtz, Gouy-Chapman, Stern, and Grahame theories have been used to describe the interfacial and double layer dynamics [9].

In addition to the double layer electrochemical reactions and diffusion effects, specific adsorption (or chemisorption) effects can be present in some systems. Adsorption is a process where species are chemically bound to the metal surface of an electrode due to their chemical affinity and not to coulombic forces based on charge difference or polarity. Adsorption and electrochemical reactions take place on the electrode surface as a function of applied DC electrochemical potential and are determined by specific electrochemical properties of participating species. For the overall analyzed system, the voltage difference between two electrodes and the resulting current can be measured with an ordinary voltmeter and amperemeter (Figure 1-5).

Unlike heterogeneous electrochemical reactions that typically occur at the interface, the overall mass transport in the bulk of a sample is a homogeneous phase phenomenon that has to be carefully controlled. Ohm's Law is completely valid under the assumption of a homogeneous and isotropic bulk sample medium when the current direction and the field coincide and other effects, primarily related to electrochemical interfacial reactions (such as diffusion, electrolysis, etc.) are absent. In a bulk solution with free ions the electroneutrality condition $\sum z_i C^*_i = 0$ applies, and the sum of charges is zero. Electroneutrality does not prevail, however, at the interfacial boundaries where space charge regions. The hypothesis often made is that of a dilute solution for which the flux of a species i can be separated into a flux due to diffusion and a flux due to migration in an electric field. At the electrochemical interfacial region the current is transported by both migration and diffusion; the latter is driven by the concentration gradient at applied DC potential. In some situations an external mixing, or "convection," is added, moving the sample with a flow rate of v. Overall current equation, which includes diffusion (first term), migration (second term), and convection (third term), can be expressed as the Nernst-Planck equation [2, p. 45, 6]:

$$\begin{aligned} I &= -R_G TF\sum(z_i \Delta C^*_i u_i) - F^2\sum(z_i^2 C^*_i u_i \Delta\phi) + Fv\sum(z_i C^*_i) \\ &= -F\sum(z_i \Delta C^*_i D_i) - F\sum(z_i \sigma_i \Delta\phi) + Fv\sum(z_i C^*_i) \end{aligned} \tag{1-19}$$

Where: the mobility constant u_i is related to the diffusion coefficient D_i and gas constant R_G through the Nernst-Einstein equation $u_i = D_i / R_G T$ and conductivity is $\sigma_i = F\sum z_i C^*_i u_i$.

In principle, the mobility can be viewed as a balance between a drag force $F_{DRAG} = 6\pi\eta v_i a_p$ on a particle of size a_p in a sample of viscosity η, which is moving under the influence of an electric field $F_{EL} = z_i e_0 \Delta\phi$. Assuming that the transport properties (D_i, u_i) are uniform in the solution bulk and hence are independent of C^*_i, the concentration change of species type i in the absence of a chemical reaction becomes:

$$\frac{\partial C^*_i}{\partial t} = D_i \nabla^2 C^*_i + z_i F u_i \nabla(C^*_i \Delta\phi) - v\nabla C^*_i \tag{1-20}$$

Practical electrochemistry always attempts to analyze a complicated system by minimizing the effects of some of its components until a limited number of unknowns can be solved. The aim of the electrochemist is to be able to study each elementary phenomenon in isolation from the others. Hence, a technique capable of extracting the data and allowing these phenomena to be separated should be employed. Mobility dominates the conduction mechanism when the electrolyte has mobile ionic species on reversible electrodes or at high frequencies where only the bulk solution resistance is visible in the impedance spectrum and polarization at the electrodes does not develop. If the electroneutrality of the solution is assured through the presence of major ionic species (or so called "supporting electrolytes") that are not taking part in or consumed by the electrochemical reaction and therefore are not participating in concentration-driven diffusion, a small migration impedance term essentially does not change with applied electrochemical potential. The constant migration term therefore can be relatively easily identified and subtracted. Concentration calculations in the presence of convection are difficult unless very particular hydrodynamic conditions are fulfilled. The well-known example of the rotating disc electrode introduces a steady convection and a constant concentration gradient at the electrode-solution interface. However, in the majority of situations, analyzed media are stagnant or move at constant speeds, and the contribution of convection becomes negligible or easily identifiable. This happens when Schmidt's number, η/D_i, is sufficiently high (several thousands). If the effects of constant mobility and convection can be identified and subtracted from the overall impedance response, the remaining diffusion process results in a concentration gradient located in a so-called "Nernst" or "diffusion" layer of thickness L_D, within which the liquid is nearly motionless (v = 0). For such conditions the transport Equation 1-20 can then be reduced with good accuracy to the Fick's diffusion equation:

$$\frac{\partial C^*_i}{\partial t} = D_i \nabla^2 C^*_i \tag{1-21}$$

Diffusion coefficient in aqueous solution can be expressed as [3]:

$$D = \frac{7.4 \times 10^{-8} \sqrt{yM}}{\eta V_M^{0.6}} T \tag{1-22}$$

Where: y = the association parameter accounting for hydrogen bonds (for water it is 2.6), M = solvent's molecular weight, T = temperature (K), η = solvent's viscosity (cP), and V_M = molar volume (mL/mol), typically ~ 200 cm^2/mol. Typical values of diffusion coefficients in aqueous solutions are on the order of 10^{-7} cm^2/sec (large molecules) to 10^{-5} cm^2/sec (small molecules) at room temperatures and atmospheric pressure.

When the above conditions of convection and migration are realized, the resulting current is limited only by the diffusion-driven transport of the electroactive species to the electrode-solution interface. At the interface charge transfer reactions take place that can be studied as a function of the electrochemical potential (Figure 1-6). That experimental situation contains the fundamental

premise of the traditional impedance analysis—make mass-transport impedance in the vicinity of the electrode interface exclusively diffusion-limited and investigate the interfacial kinetic phenomena composed of the diffusion (Z_{DIFF}) and electrochemical (R_{CT}) reaction (such as discharge or electrolysis) impedances that can be combined in so-called "Faradaic impedance." The premise of the traditional dielectric analysis is largely different. It attempts to avoid the influence of all interfacial effects by operating at higher AC frequencies where there is no time to develop double layers and electrolysis reactions and to study exclusively migration-driven conduction and bulk sample dielectric relaxation effects under the influence of voltage difference between two bounding electrodes. The combined data are often presented as "equivalent circuits" composed of a combination of series and parallel resistances, capacitances, and inductors, representing combined impedance to the current passage though the bulk solution (at high frequencies) and through the interfacial region (at low frequencies) as shown in Figure 1-6.

1.4. Fundamental ambiguity of impedance spectroscopy analysis

EIS involves a significant body of research that has been the subject of many controversies. Impedance analysis is based on detection and interpretation of the meaning of processes that occur in response to external voltage perturbation applied at some predetermined AC frequencies. As a response to this external perturbation, the current response indicative of the physical/mechanical structure and chemical composition of the analyzed system or sample is recorded.

EIS was historically applied to two very large groups of systems—those with a significant interfacial electrochemical electron and mass-transport phenomena (such as electrically conductive ionic fluids) and those with predominantly bulk media relaxation phenomena (highly resistive materials, such as polymers, ceramics, and organic colloids). For traditional impedance analysis focused on an understanding of Faradaic processes, mass transport can be made diffusion-related while the migration dependence in the bulk solution can be controlled by adding supporting electrolyte and convection effects can be made constant or absent. For traditional dielectric spectroscopy, material relaxations (or energy storage and release effects) and migration-driven conduction are often studied using temperature modulation, while the low-frequency electrochemical interfacial polarization processes become of secondary importance. This "interfacial polarization" effects are often not studied by dielectric scientists, just as solution effects are often not studied in the traditional impedance literature. The above discussion of experimental strategies offers seemingly uncomplicated concepts of the UBEIS implementation, at least in the laboratory environment.

The experimental approaches and interpretation strategies for investigators working in the traditional impedance and dielectric analysis areas have drifted apart significantly over the years, often leading to misconceptions about assignments of frequency relaxation ranges and broader data interpretation. A combination of these two techniques in a universal broadband EIS

(UBEIS) measurement presents interpretation challenges, as both solution and interfacial effects come to play. For example, the same critical frequency of 100Hz can be assigned to a double layer charging in an aqueous system and to a bulk solution capacitive dispersion when a highly resistive material with a bulk resistance of 1 Mohm is analyzed. One of the intentions of this book is to bring these two types of analysis together and to attempt to reconcile possible interpretation contradictions in examples of several practical common systems. Therefore, it is important to first consider the analyzed sample and to look at its fundamental bulk material properties and geometrical dimensions, as the current passes through the bulk first before reaching the interface. The second step includes electrochemical analysis of possible interfacial kinetic processes (Section 8-7).

An even larger problem in impedance analysis is related to the fact that narrowly defined experimental conditions, such as limiting the measured impedance response by diffusion mass transport or rejection of the interfacial effects, cannot be imposed or controlled in many real-life applications. Very frequently an unknown system or phenomenon has to be characterized, and the ensuing complexity of analysis with many potential unknowns has to be faced. Therefore, a preliminary concept for the investigated system often has to be developed even before the system is analyzed.

While UBEIS is a powerful and versatile method applicable to many areas of science and technology, it is completely inapplicable to blind analysis of systems about which the investigator has no preliminary knowledge. At least in very general terms one almost has to have a significant amount of advance knowledge about the analyzed subject. A series of basic questions about the system has to be answered. Is the system a solution, solid, or gas? Is it aqueous or nonaqueous? Is the analyzed medium composed of ions or conductive or polarizable particles, or is it a semiconductor? Are there any electrochemically active components in the system that may be able to discharge and/or adsorb on the metal electrodes? Interpretation of the data depends greatly on initial understanding of basic components of the system and their projected response to the applied AC and DC electric fields. In response to these questions, it is highly recommended that the scientist develop a series of preliminary expectations and assumptions about the chemical, the physical and mechanical characteristics of the analyzed system, and the anticipated general type of the experimental setup, expected impedance data, and possible interpretation strategy. Intelligent characterization of a studied system is typically based on iterative comparison of the obtained experimental impedance data with these expectations. The expectations are typically based on previously published examples of electrochemical, physical, mechanical, and chemical analysis for similar types of systems, both in application-driven and laboratory experimentation environments. In this manuscript multiple examples of impedance data and analysis in the systems that investigators meet in practical applications or research laboratories are presented as a starting reference point.

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