Chapter 1
Introduction

1.1 Why Impedance?

Among the various electrochemical techniques, electrochemical impedance spectroscopy (EIS) holds a special place. The classical electrochemical techniques present measurements of currents, electrical charges or electrode potentials as functions of time (which can also be related to the electrode potential). In contrast, EIS presents the signal as a function of frequency at a constant potential. This often poses some problems in understanding what is happening because electrochemists try to think in terms of time, not frequency. On the other hand, in optical spectroscopy, nobody thinks that light consists of the sinusoidal oscillations of electric and magnetic vectors of various frequencies, phases, and amplitudes. In spectroscopy, we used to think in terms of the frequency domain (wave number, frequency, or some related functions as wavelength) and that what we observed was the Fourier transform of the optical signal.

The issues associated with understanding EIS also relate to the fact that it demands some knowledge of mathematics, Laplace and Fourier transforms, and complex numbers. The concept of complex calculus is especially difficult for students, although it can be avoided using a quite time-consuming approach with trigonometric functions. However, complex numbers simplify our calculations but create a barrier in understanding complex impedance. Nevertheless, these problems are quite trivial and may be easily overcome with a little effort.

The advantages of using EIS are numerous. First of all, it provides a lot of useful information that can be further analyzed. In practical applications of cyclic voltammetry, simple information about peak currents and potentials is measured. These parameters contain very little information about the whole process especially when hardware and software is able sampling the current-potential curve producing thousands of experimental points every fraction of mV. On the other hand, one can use voltammetry with convolution, which delivers information at each potential, although very few people know and use this technique in current research. EIS contains analyzable information at each frequency. This is clearly seen from the examples that follow.

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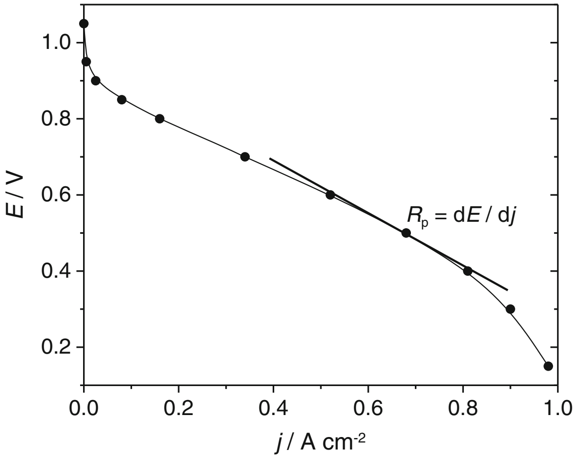

Fig. 1.1 Voltage (E)-current (j) curve for fuel cell. The slope is the polarization resistance (R_p)

Steady-state polarization measurements, that is measurement of the current at constant potential or potential at the constant current provide current-potential curves from which a slope, that is, a polarization resistance, $R_p = dE/dj$, can be determined. An example of such a curve for a fuel cell is displayed in Fig. 1.1.

However, taking the impedance at each potential produces series of data values at different frequencies. Examples of complex plane impedance plots that is imaginary versus real part at various frequencies for different fuel cells are presented in Fig. 1.2. The polarization resistance is the only point corresponding to zero frequency, as indicated in the plots. One may observe that the impedance plots, besides R_p, produce much more information that is not available in steady-state measurements. Impedance plots display complex curves that are rich in information. Such information is contained in every point, not only in one value of R_p. However, one must know how to find this information on the system being studied. This is a more complex problem and can be solved by the proper physicochemical modeling.

To characterize more complex electrochemical systems other studies of the system: including microscopic, surface morphology, structure, composition, and dc electrochemical characterization, should be carried out and understood thoroughly prior to EIS analysis. Studies may begin with EIS only for the electrical circuits and simple, well understood, systems. Beginning studies of complex systems with EIS is not recommended.

EIS supplies a large amount of information, but it cannot provide all the answers. EIS is usually used for fine-tuning mechanisms and determining the kinetics of processes, resistances, and capacitances, and it allows for the determination of real surface areas in situ. It is a very sensitive technique but must be used with care; it is often abused in the literature.

EIS has numerous applications. It is used in the following types of studies:

1. Interfacial processes: redox reaction at electrodes, adsorption and electrosorption, kinetics of homogeneous reactions in solution combined with redox processes, forced mass transfer

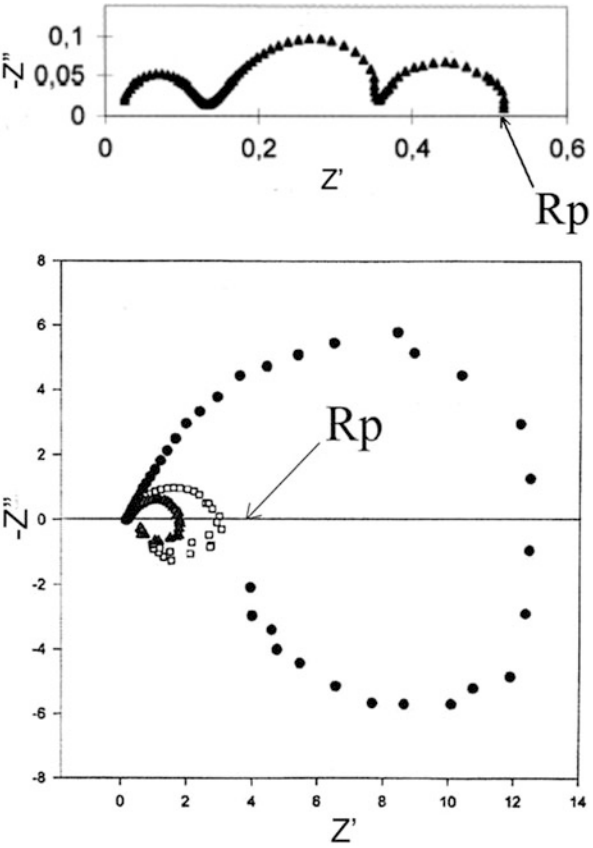

Fig. 1.2 Examples of complex plane impedance plots for fuel cells; *arrows*: polarization resistance also found in steady-state measurements; impedances are in Ω

2. Geometric effects: linear, spherical, cylindrical mass transfer, limited-volume electrodes, determination of solution resistance, porous electrodes
3. Applications in power sources (batteries, fuel cells, supercapacitors, membranes), corrosion, coatings and paints, electrocatalytic reactions (e.g., water electrolysis, Cl_2 evolution), conductive polymers, self-assembled monolayers, biological membranes, sensors, semiconductors, and others.

1.2 Short History of Impedance

EIS uses tools developed in electrical engineering for electrical circuit analysis [1–3]. The mathematical foundations of EIS were laid by Heaviside [4], who developed operational calculus and Laplace transform, introducing differentiation, s, and integration, $1/s$, operators. They made it possible to solve integrodifferential equations appearing in the solutions of electrical circuits (Sect. 2.8) by transforming them into a system of algebraic equations. Heaviside defined impedance,

Table 1.1 Eras in development of EIS [2]

Eras in development of electrochemical impedance spectroscopy
In the beginning (1880–1905)… (O. Heaviside and E. Warburg)
Age of double layer (1930–1965) (D.C. Grahame, R. Payne, J.O'M. Bockris, R. Parsons; C_{dl}/Hg, ac bridges)
Arrival of potentiostat (Hickling, Wenking) and the age of AC polarography (1965–1980) (D.E. Smith, J. H. Sluyters and M. Sluyters-Rehbach)
Age of electrical analogs (1948–present) (J.E.B. Randles, J.R. Macdonald, R. Buck). No unique EEC for a given system!
Age of material characterization (1970–present) (R.A. Huggins, J.R. Macdonald, W. Weppner)
Age of reaction mechanism analysis (1970–present). The real power of EIS! (A.N. Frumkin, R.D. Armstrong, I. Epelboin, M. Keddam, C. Gabrielli, D.D. Macdonald)
Explosion in applications (1985–present)

admittance, reactance, and operational impedance and explained the relation between Laplace and Fourier transforms by introducing a complex operator $s = \sigma + j\omega$. The main advantage of EIS is the fact that it is based on the linear time-invariant system theory, most commonly known as LTI system theory, and the validity of data may be verified using integral transforms (Kramers–Kronig transforms) that are independent of the physical processes involved.

Chemical applications of impedance spectroscopy began with the work of Nernst [5], followed by many others, including those applications to the distribution of relaxation time constants by Cole and Cole [6] and Davidson and Cole [7]. Warburg [8] developed the impedance of mass transfer (the so-called Warburg impedance), which allowed further applications of EIS to redox reactions.

The development of EIS is displayed schematically in Table 1.1. In the subsequent age of the double layer (1930–1965) [1, 2] the structure of a double layer in the absence and in the presence of adsorbed species was studied initially at a dropping mercury electrode and then at solid electrodes using ac bridges. The development of electronic potentiostats has revolutionized electrochemical and impedance measurements. With the presentation of the electrical analog circuit for electrochemical reactions by Dolin and Ershler [9] and Randles [10] the age of electrical analogs [2] began and continues up till now. Electrochemical systems are usually represented by analog circuits containing resistances, capacitances, and inductances, including some distributed elements such as, for example, the Warburg impedance and constant phase element. Commercial software allows for simple modeling of experimental impedance results. However, electrical analog circuits are analogs, not physicochemical models. Although in simple cases analog circuits can reflect chemistry of the model quite often they either cannot or can lead to the ambiguous circuits. In addition, several different electrical equivalent models can exactly approximate the experimental data because they are not unique. For example, two semicircles on the complex plane plots might be interpreted by a serial or a parallel connection of the circuit elements (see Sect. 9.1.2, Figs. 9.12 and 9.13). In certain cases although approximate electrical analog circuit can be found the physicochemical model may contain elements which cannot be represented by such elements (see Sect. 9.2.3 on porous electrodes). More discussion is provided in Chap. 14. However, the electrical equivalent circuits are often used in practice.

The age of mechanistic analysis [2] runs in parallel, where starting from chemical/electrochemical equations the impedances are built up, describing the system under study uniquely. These equations may, after some rearrangements, lead to proper electrical equivalent circuits (see, for example, the pioneering work of Epelboin, which was continued by Keddams, Gabrielli, Wiart, and other members of the Paris group [11], and that of D.D. Macdonald). This is the real power of EIS, but it is more difficult to implement. Presently, impedance is used in every area of electrochemistry to study, for example, interfaces, electrochemical reactions, and solid materials (on which more later).

1.3 Publications on Impedance

Electrochemical impedance spectroscopy is usually presented in electrochemistry handbooks [12–22], although such presentations are usually quite brief. There are few books on impedance in English [3, 23–26], one in Russian [27], one on differential impedance analysis [28], and many chapters on specific topics [29–72]. The first book [23] on the topic was edited by Macdonald and centered on solid materials; the second edition [24] by Macdonald and Barsoukov was enlarged by including other applications. Recently, three new books, by Orazem and Tribollet [3], by Yuan et al. [26] on proton exchange membrane fuel cells (PEM FC), and by Lvovich [25], have been published, while that by Stoynov et al. [27] was never translated into English. A third edition of the book by Macdonald and Barsoukov is in preparation. However, not all aspects of EIS are presented, and these books are not complete in the presentation of their applications. Plenty of review articles on different aspects of impedance and its applications have been published; however, they are very specific and can usually be used only by readers who already know the basics of this technique. A Scopus search for “electrochemical impedance spectroscopy” to the end of 2012 comes up with 18,000 papers, most of them since 1996.