

# Impedance Spectroscopy

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

**Keywords**—*Impedance, Immittance, Complex dielectric constant, Complex modulus.*

## INTRODUCTION: SHORT HISTORY OF IMPEDANCE SPECTROSCOPY

Since impedance spectroscopy (IS) deals directly with complex quantities, its history really begins with the introduction of impedance into electrical engineering by Oliver Heaviside in the 1880s. His work was soon extended by A.E. Kennelly and C.P. Steinmetz to include vector diagrams and complex representation. It was not long before workers in the field began to make use of the Argand diagram of mathematics by plotting immittance response in the complex plane, with frequency an implicit variable. Electrical engineering examples were the circle diagram introduced by C.W. Carter (5) and the Smith-Chart impedance diagram of P.H. Smith (20). These approaches were soon followed in the dielectric response field by the introduction in 1941 of the Cole-Cole plot: a plot of  $\epsilon''$  on the  $y$  (or imaginary) axis vs.  $\epsilon'$  on the  $x$  (or real) axis. Such complex plane plots are now widely used for two-dimensional representation of the response of all four immittance types. Finally, three-dimensional perspective plots that involve a log-frequency axis were introduced to the IS area by the author and his colleagues in 1981 (10); these plots allow complete response at a given immittance level to be shown in a single diagram.

Because IS analysis generally makes considerable use of equivalent circuits to rep-

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resent experimental frequency response, the whole history of lumped-constant circuit analysis, which particularly flowered in the first third of the century, is immediately relevant to IS. Since then, much work has been devoted to the development of theoretical physicochemical response models and to the definition and analysis of various distributed circuit elements for use in IS-equivalent circuits along with ideal, lumped elements like resistance and capacitance. The preferred analysis method for fitting of IS data to either equivalent circuits or to a mathematical model is complex nonlinear least squares fitting (CNLS), introduced to the field in 1977 by Macdonald and Garber (8). In this procedure, all the parameters of a fitting model are simultaneously adjusted to yield an optimum fit to the data.

Early experimental work in the IS field is discussed in the 1987 book on IS (11) listed in the bibliography. Here it will suffice to mention the work of Grahame on electrolyte double-layer response, the technique of AC polarography pioneered by D.E. Smith (19), and the electrolyte studies of Randles and Somerton (15), Sluyters and Oomen (17), Buck and Krull (4), J.E. Bauerle (3), and the reviews of (1,2,18). Since the late 1960s, IS has developed rapidly, in large part because of the availability of new, accurate, and rapid measuring equipment. Modern developments are discussed in (6).

### **CATEGORIES OF IMPEDANCE SPECTROSCOPY: DEFINITIONS AND DISTINCTIONS**

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

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

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