

FEATURE ARTICLE

Challenge for electrochemical impedance spectroscopy in the dynamic world

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Electrochemical impedance spectroscopy is a powerful method which provides separation and analysis of individual constituents of the electrochemical response originated from different objects (processes and structures) in an electrochemical system. The impedance spectrometer, after having been a separate instrument which was used by specially trained people, transformed into computer programs supplied with modern potentiostats and thus became available to any researcher who uses electrochemical methods. Complexity of theory of impedance spectroscopy has become hidden behind simple user interfaces and powerful software for impedance spectra analysis. This is of great help for efficient use of impedance spectroscopy but also a catch for those users who misunderstand its concepts. In order to minimize risk of obtaining artifacts instead of meaningful data, several restrictions are applied as prerequisite on impedance spectrum acquisition and the strongest restriction contains in the requirement of stationarity of the object under investigation.

The two kinds of restrictions related to the stationarity prerequisite in electrochemical impedance spectroscopy have to be taken into account. First, very many objects which require frequency response analysis are in fact non-stationary objects. Electrochemical reactions of dissolved substances often strictly comply with the prerequisite, but stationarity is less characteristic to reactions of solid reagents. Second, even in the perfect stationary state, the frequency response not necessarily contains the anticipated information which motivated the use of impedance spectroscopy. The characteristic examples of the latter case are the electrochemically irreversible surface-limited reactions which lack back current at the potential of voltammetric peak of the forward reaction. Attaining the stationary state at the peak potential would result in completion of the forward reaction, so neither forward nor back reaction contributes to the impedance spectrum. Though impedance spectrum in such a stationary state may

be obtained accurately, parameters derived from impedance spectrum turn to be unrelated to the completed reaction.

The most lacking in informative frequency response characterization are various electroactive materials, i.e., materials in which capacitive charging is strongly interrelated with Faradaic current. Especially important among the latter are supercapacitors with capacitances originated from “pseudocapacitance”, i.e., capacitance other than double-layer capacitance. A typical example of pseudocapacitance, identical to physical capacitance of a capacitor in frequency response analysis, is the adsorption capacitance in systems which comply with Frumkin–Melik-Gaikazyan and similar equivalent electric circuits that exhibit capacitance in the Faradaic branch of the circuit. Unfortunately, due to the reasons mentioned above, adequate frequency response analysis by stationary impedance spectroscopy is often not possible for systems which are regarded as pseudocapacitive supercapacitors and this has led to a rather strange situation. While impedance spectroscopists strive in strict physical terms for high accuracy in separation of capacitive and dissipative element contributions to electrochemical response, the other substantial part of electrochemical community derive capacitances just from the current in chronopotentiometry and cyclic voltammetry, postulating capacitive origin of the current. The motive for use of such a fictional capacitance in supercapacitor characterization is the need in comparing different materials by efficiency of charge storage. A bitter irony of the practically motivated but physically ungrounded derivation of capacitance from direct current comes from the fact that the current which is arbitrarily assumed to be “charging” current not necessarily characterizes capacitive energy storage. The assumed “charging” current may refer partly to energy dissipation, as dissipative elements (resistors and dissipative contributions of constant phase and Warburg elements) are typically present in equivalent

electric circuits of electroactive systems. Impedance spectroscopy could have helped to resolve problems of this kind, if it worked reliably on any kind of electroactive system.

Perfect and informative stationary states are rarely observable in general in the real dynamic world, but the deviations from stationarity do not exclude in principle frequency response acquisition and analysis. Frequency response analyzers are widely used in engineering on real non-stationary objects. Moderate non-stationarity, typical to variable electrochemical systems, just applies a restriction on a minimal frequency which can be presented reliably in impedance spectrum. The higher the temporal resolution of a dynamic system evolution examination by frequency response, the shorter the range of frequencies available for frequency response analysis. The cost of the temporal resolution introduction into impedance spectroscopy is the truncation of low-frequency part of the spectrum and the corresponding loss of information about slow processes, mostly the loss of characteristics of mass transport. When impedance spectrum is truncated, distinguishability of spatially restricted and unrestricted diffusion is the first sacrifice; however, charge transfer resistances, series resistance of electrolyte solution, double-layer capacitance, and capacitances of Faradaic origin are effective at higher frequencies, and their derivation is typically least affected by short-ening of the measurement time interval.

Dynamic impedance spectroscopies based on different fast algorithms of frequency response acquisition and analysis have been developed by several groups throughout the world since the beginning of the century. Truncation of low frequencies in dynamic impedance spectroscopies is rewarded by acquisition of series of gradually varying spectra and their further analysis on time and potential scales. The typical number of impedance spectra recorded, e.g., in potentiodynamic electrochemical impedance spectroscopy, is 500 spectra per volt of potential scan. Concerted frequency response analysis on such massive sets gives potentiodynamic profiles or kinetic curves of charge transfer resistance, double-layer capacitance, and other variables that represent contribution of constituents of frequency response as functions of potential or time.

Effective applications of various versions of dynamic impedance spectroscopy, however, have not led yet to a widespread dissemination of the approach. The main obstacle is probably the short-project way of development in the modern science. A new complex method elaboration to the stage of commercial availability requires combining efforts of experts in electrochemistry, electronics, software engineering, and marketing and this exceeds resources of a single research team in a limited time interval. Not only objects of electrochemistry but also research teams are dynamic. A super-additive breakthrough configuration of a team can be maintained for a period of one or two projects which is not sufficient for solving the whole complex of scientific and applied tasks in the elaboration of a fundamentally new approach. However, the experience of two decades of experimental testing of the concept of dynamic, in particular potentiodynamic, electrochemical impedance spectroscopy suggests the outline of the future generation of electrochemical impedance spectroscopy and electrochemical methods in general.

The variable resolution on time and electrode potential scales of dynamic electrochemical impedance spectroscopy and also the possibility of simultaneous monitoring of current and frequency response variation remove the boundaries between dc, single-frequency ac methods and impedance spectroscopy. The future instrument for electrochemical investigations has to unite ac and dc methods in a universal electrochemical response analyzer incorporating dynamic frequency response analysis of variable electrochemical systems. Classical electrochemical methods will be supported in such an instrument by particular options in the general settings of resolution and path of the composite electrochemical response examination. The active and competent role of researchers will be still essential for setting the adequate and optimal path of acquisition and analysis of the multidimensional data, while computer will execute automatically the methodical routine part of the electrochemical examination.