Differential Impedance Analysis of Non-stationary Systems

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INTRODUCTION

The Differential Impedance Analysis has been approbated in the studies of a variety of different objects. It has been proven that the method is a powerful instrument for investigation of novel and complicated objects and that it can provide valuable results even in cases of noisy data of low quality (1 – 4). On the other hand, many interesting objects are non-stationary and evolve during the measurements. The previously developed technique of 4-Dimensional analysis, (4 – 7), can serve as an efficient tool for the study of such objects. The effective merge of these two methods is of interest for elucidation of processes taking place in batteries, fuel cells, corroding devices and other evolving systems.

FOUR –DIMENSIONAL ANALYS

The method of 4-Dimensional Analysis provides for correction of the biggest errors, arising during the measurements of evolving objects. It is based on the assumption for the continuum of the object's state and parameter's spaces. The requirements of this hypothesis are obeyed practically by all electrochemical objects. The method requires measurement of a number of impedance diagrams, containing one and the same scan of frequencies. Every measured data at a given frequency should additionally contain the time of measurement, defined as the instant of the central time of measurement. Thus, the experimental data form a set of 4-Dimensional arrays, containing frequency, real and imaginary components of the impedance and the time of measurement. The post-experimental analytical procedure previews the reconstruction of calculated Instantaneous Impedances. For every measured frequency two one-dimensional functions of iso-frequency dependencies (for the real and for the imaginary components) are constructed. Then, each iso-frequency dependence is modeled by an approximating formal model. On the basis of the continuity of the evolution, interpolation (and extrapolation) is performed. As a result, the reconstruction of the instantaneous impedances, related to a selected instant of the time (i.e. the beginning of each frequency scan), is performed. Thus a set of impedance diagrams, containing instantaneous impedances, virtually measured simultaneously, is obtained.

DIFFERENTIAL ANALYSIS METHOD

The Differential Analysis is based on the assumption for a continuum of the object's behavior with variation of the perturbing frequency. Thus the differentiation of the real and imaginary components with respect to the frequency is possible. As a result, the initial data can be enriched to a 5-dimensional array. The method is designed for investigation of stationary systems. It previews the selection of a simple operating model (an inertial system of first order) and consecutive fitting of this model to the local frequency behavior of the object in the entire frequency range. The resulting dependencies of the model parameters on the frequency are called temporal functions. They are significant for the object's structure and the described phenomena. In order to emphasize the nature of these phenomena, the data are converted to specific spectra by the technique of parametrical spectral transform. It performs a stratification of the data and serves for an efficient noise filtration and rejection. The Differential Analysis can recognize and locate the number of steps of the studied reaction as well as the presence of diffusion limitations, bounded diffusion or CPE element.

NON-STATIONARY DIFFERENTIAL IMPEDANCE ANALYSIS

The effective merge of the 4-Dimensional Analysis and the Differential Impedance Analysis, based on similar hypotheses, seems promising. As far as the 4-Dimentional analysis provides for the determination of instantaneous impedances, the application of Differential Analysis is straightforward. The common application of the two methods ensures elucidation of the fine processes taking place in evolving non-stationary systems.

EXPERIMENTAL RESULTS

The Non-stationary Differential Analysis was applied for the investigation of the processes taking place during the charge of the negative plate of classical Lead-Acid battery. The obtained spectra of the effective resistance and capacitance show the time evolution of the basic charge process connected with the formation of a new phase and with the parasitic gas evolution. At the final stage of the charge an additional process of second phase formation is discovered.

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