

Electrochemical Applications

1/98

Advances in electrochemical applications of impedance spectroscopy
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Easy Living

Brazil possibly reminds you of Rio de Janeiro, Copacabana, a hot holiday, beautiful girls at the beach or the world's most famous carnival. At the moment, however, we think of the EIS'98 meeting in Brazil in August. Of course, Zahner will be there, together with the American partner BAS and we certainly make a scientific contribution to the congress. It is about a comparison between the "Logarithmic Hilbert Transform" and the "Linear Kramers-Kronig Rule" for validating electrochemical impedance spectra. All **EA** readers will be able to read about this topic in the next issue.

Test applications for the industry have to be easy to handle. This does not only mean that the user-interface has to be simple, but also that the hardware and software used for this application has to

be cost-efficient. If you study these applications you will often realise that fairly complex processes are running and a rather sophisticated hardware is doing the job. Until now there is no solution to this problem: Complex processes which should be investigated need complex hardware and software. But there is an important thing we can do to solve a part of this problem: Tools which make it easy to handle very complex applications can be created. Our latest software tool for the IM6, called **SCRIPT** is an example for this.

So have a good time in Rio, at home or elsewhere.
Your Zahner Team

SCRIPT

Define the testing procedure which fits your requirements

The IM6 system provides a multitude of functions to ease the standardization of measurement processes. For example, a measurement can be repeated as often as you like without having to set up parameters again and again each time. As parameter sets are automatically saved with each measurement file, you only have to load the desired parameter set needed - and you are ready to repeat the measurement. With this feature, simple, recurring measurement tasks can be handled also by inexperienced personnel.

Another step in this direction is performed by the "automatic series measurement" software (AS) of the IM6 system. Here, measurements of the same method are triggered by a third parameter. With AS, you are able to perform impedance measurements in dependence of time, potential, temperature, pH and others. The results are three-dimensional graphs or a series of single plots.

Many tasks in electrochemistry require the combinations of different sampling and analysis methods and with this the definition of a single complex process which can be used as a standard testing method. This is the reason for our developing a scripting language for the IM6 system, which on the

one hand allows to combine different methods with macro commands very quickly and easily, and on the other hand is able to define a process to the essential details.

The commands available in **SCRIPT** are divided into two groups:

1. **SCRIPT** keywords are macro commands with which you can call a complete, predefined method. This group of commands will certainly be used the most, because they require absolutely no knowledge of programming and nevertheless have access to very specific methods.
2. With andiBASIC commands, you can write your own sampling and analysis routines, you can react to external events or you can set very special parameters. The use of these commands, of course, requires a certain knowledge of the andiBASIC language.

Point 1 has been given highest priority regarding the development of **SCRIPT**. We tried to find an easy way for combining different methods in order to get a complex process which does not expect the knowledge of a programming language. With the keyword part of **SCRIPT**, each user, who set up and

saved the parameter set of each method, is able to access this library of single methods and combine them to a complex process by simply loading them in sequence.

In principle, scripts are edited with a common word processor. If the integrated text editor is used, editing, interpreting and testing will be done in an interactive way. You write down the desired keywords as uncoded text, call the interpreter and do a test run. The **SCRIPT** interpreter translates the keywords and helps to avoid syntax errors. Each script gets an icon which is implemented in the **SCRIPT** menu

page. This icon is used to start a script process. If the script is set up you can save it. **SCRIPT** automatically saves I/O parameters and system messages which occur in the course of a process as a protocol text file. This is helpful for testing scripts under development and gives information to the problem of failed measurement procedures.

To show the easy handling of this macro language, here an example. First an impedance and a CV measurement are carried out, then the measured data are loaded into the analyzing program to be analyzed and plotted.

SCRIPT_START	<i>Script start</i>
MEAS_OPEN_EIS(2,"8:\archive","eis1")	<i>Loads the predefined impedance parameter set "eis1" from the path "archive" of the harddisk</i>
MEAS_EIS	<i>Starts impedance measurement</i>
MEAS_SAVE_EIS(2,"8:\meas","testeis1",0)	<i>Saves the impedance data as file "testeis1"</i>
MEAS_OPEN_CV(2,"8:\archive","cv1")	<i>Loads the CV parameter set "cv1"</i>
MEAS_CV	<i>Starts cyclo-voltammogram measurement</i>
MEAS_SAVE_CV(2,"8:\meas","testcv1",0)	<i>Saves the CV data file</i>
CLRSIM	<i>Initializes the analysis software SIM</i>
ANA_OPEN_EIS(2,"8:\meas","testeis1")	<i>Loads the measurement file "testeis1" into the analysis software</i>
ANA_OPEN_MOD(2,"8:\mods","model1")	<i>Loads model file "model1"</i>
ANA_FITEIS(100,100000,10)	<i>Starts fit in the frequency range of 100 Hz to 100 kHz with a density of 10 points per decade</i>
ANA_PLOT_EIS(1)	<i>Plots impedance spectrum</i>
ANA_OPEN_CV(2,"8:\meas","testcv1")	<i>Loads CV measurement file "testcv1"</i>
ANA_PLOT_CV(1)	<i>Plots CV curve</i>
SCRIPT_END	<i>Script end</i>

An example of a **SCRIPT** application from the field of packing technology is described by Dr. Hollaender of the Fraunhofer Institute of Process Engineering and Packaging (FhIVV), Freising, Germany in the following contribution. The investigations focus on the quality of metallized foils and coatings of food containers. The **AC/DC/AC** methods developed by Dr. Hollaender run on an IM6 system with **SCRIPT**. This method results directly in the delamination in millimeters. For this purpose, an

impedance measurement (AC) is carried out first, then the sample is exposed to a cathodic loading (DC) and finally, another impedance spectrum (AC) is measured. The delamination is calculated automatically by comparing the two impedance spectra. A method which was rather complicated earlier, made room for a "push button" method which results in one single value, which is easy to interpret, by using **SCRIPT**. (HJS)

Implementation of EIS test routines into industrial application

Dr. J. Hollaender, FhIVV Freising, Germany

Aluminum and steel are base materials in metal packaging. Beside some chemical or physical surface treatments several steps of surface finishing are involved to enhance the interaction stability of the plain metal surfaces mainly by organic coatings, such as lacquers or laminates.

Since 1988 the Fraunhofer Institute of Process Engineering and Packaging (FhIVV) at Freising, Germany, and different industrial working groups of

the Industrial Association of Food Technology and Packaging (IVLV), Munich, Germany, forced the application of EIS-methods in material testing within research and development of the packaging industry.

Application fields are the metallic or metaloxidic surfaces, the surface treatments and the layer conversion or layer formation processes, the coated

metals with lacquers, primers, adhesives, laminated or coextruded films. The interest in surface properties ranges from surface reactivities, corrosion resistances, inhibition and passivation of the metal up to the interaction stability, porosity and adhesion of the coated systems.

EIS measurements are performed by using 3-pole and 2-pole techniques. Typical 3-pole measurements refer to edge-free testing of sample surfaces

fixed at the front sides of special twin-cells, or to container testing to get information on inside layers, material deformations, welding or seaming areas. In addition 3-pole measurements were used for special test routines on laminated material to get information on the delamination tendency (cut-edge test).

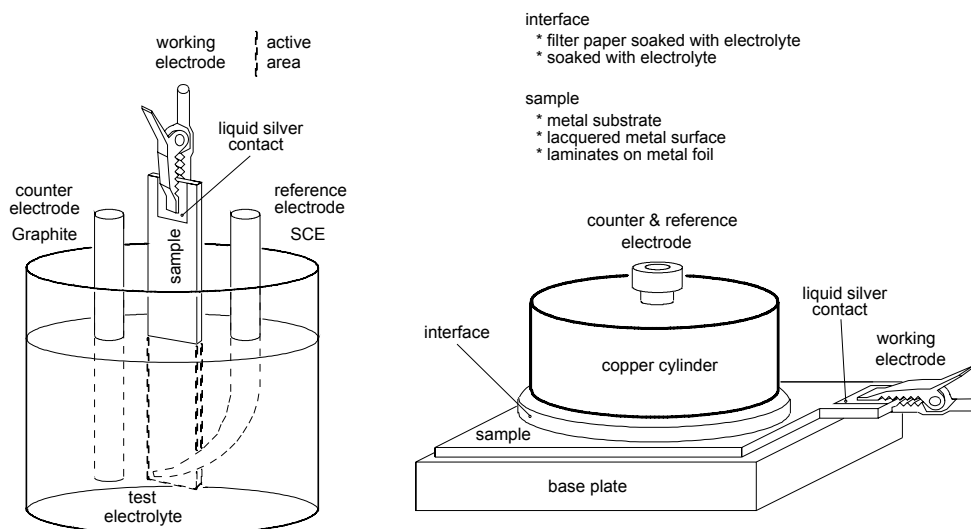


Fig. 1: Scheme of measurement arrangements for cut-edge delamination tests [1] (left hand part) and surface layer quality tests [2] (right hand part) of packaging materials.

2-pole measurements have been developed for direct surface testing. The surface properties are measured by a round copper block, which resembles both the counter and the reference electrode. The electrolyte phase is reduced to a filter paper soaked with electrolyte (e.g. test electrolyte 0,2 m phosphate buffer) between sample surface and copper electrode.

Testing methods in the field of packaging do not restrict to single status measurements only. An important tool of information is the application of combination methods, where the sample (sample surface) is treated by chemical and/or physical action between two status measurements. Treatments may involve e.g. the interaction with chemical energy (aggressive media), temperature or deformation energy.

A special test method is characterized by the application of electrochemical energy, e.g. a cathodic treatment of 2000 mV (DC). This AC/DC/AC test aims to the cathodic induced delamination of organic layers on metal surfaces, which informs about the adhesion properties of the coating. This test procedure is used in combination with other stress operations on the sample (sample surface). Ideal systems are lacquered surfaces exhibiting some defects or residual porosity, pore-free lamina-

tions like multilayer materials are tested via the cut-edge method. Especially the influence of migrating substances (e.g. aroma components of food stuffs) on the delamination tendency of flexible packages containing metal foil or metallizations can be worked out.

Simple status analysis can be used for rapid estimations of quality levels, e.g. in beverage container testing. The test routine is restricted to a frequency range between 1000 and 1 Hz, which runs only seconds. Information on the individual container coating is given by the impedance value at 1000 Hz (capacity), the phase angle at 1 Hz is used as an indication of the coating porosity. Statistical evaluation is made by summation frequency diagrams which inform about the quality criteria of the tested can collective.

Other testing procedures refer to simple capacitive measurements of layer thickness and lateral thickness distributions of organic layers even in very low amounts (e.g. primers). Extensions are made to more complex layer combination analysis. Recent applications are set up for the analysis of the thermal activation of adhesion mediators at sealing layers.

The 2-pole technique exhibits some advantage for the direct testing of metal surfaces (e.g. aluminum foil) because of the low ohmic electrolyte resistance,

which enables additional information on different surface states depending on the outmost oxide/hydroxide/hydrate layer properties.

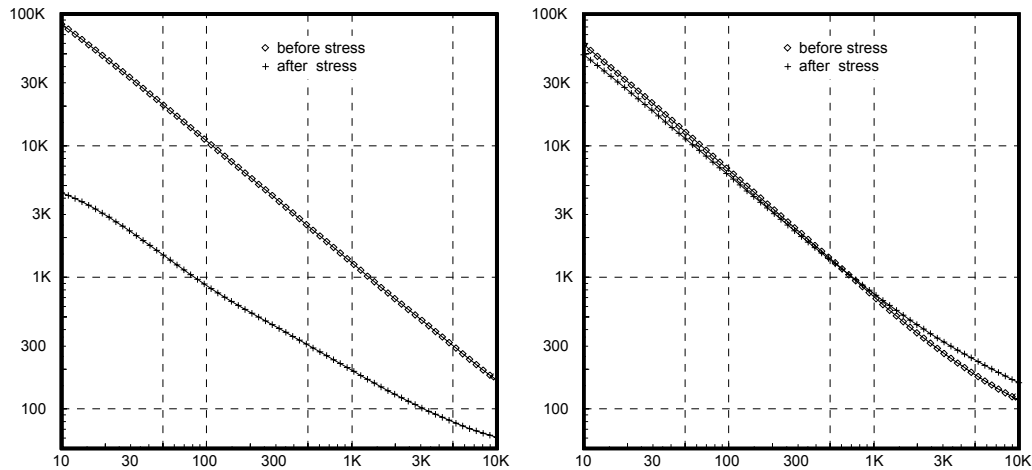


Fig.2: Typical impedance spectra of delamination tests at two different laminates for food packaging. The not tempered sample of the left hand graph shows a much higher delamination tendency than the tempered sample of the right hand graph.

Ohmic resistances and capacitive parameters are used for the evaluation of the impedance spectra. Deviations from the ideal capacity are expressed by the „non ideal“ constant phase element (CPE) in capacity and „slope“ or in a phase angle relation. A more sophisticated equivalent circuit defines the „defect“ part (ohmic) of a layer beside an „affected“ (CPE) and an „intact“ part (ideal capacity), which contact the metal surface (RC-element).

The crucial step in the implementation of EIS methods to the industrial praxis was accomplished in cooperation with Zahner-elektrik by the development of a low-priced equipment for the routine testing. Furthermore, the testing is performed by automatically running sequences (SCRIPT) of EIS measurements (AC) mostly in combination with electrochemical sample treatments (DC). The relevant parameters of each test routine are calculated.

From the comparison of different status measurements the test result is estimated and documented (see figures).

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