Electrochemical Applications

1/95

Advances in electrochemical applications of impedance spectroscopy
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Another Brick in the Wall

Do you also feel confused and paralyzed with all the information that flutters onto your desk, jumps from the fax, barks out of the phones, and "eye-catches" in a vast amount of magazines and other multimedia-channels ?

With Electrochemical Applications you hold a new magazine in hands. Another one of the above mentioned vast amount, another "brick in the wall"? No, we planned to make it different from most others: It will be short, informative and free. Issued quarterly the flood of information is not too hard to handle and you easily can take up all you are interested in.

From now on Electrochemical Applications will inform you about the latest news in the field of electrochemistry, especially of electrochemical impedance spectrum analysis and its wide spread applications. There will be scientific publications, application notes, praxis tips & tricks, introductions into new techniques, product news, interesting stories and of course we will answer **FAQs** ("frequently asked questions").

If you know about an interesting story, conclusion or application that fits the topic of Electrochemical Applications please write us or give us a call. If we think it is interesting enough to be published we will do it for free. Also if you have questions concerning impedance spectroscopy we will answer them - some of them in the chapter **FAQ**.

Of course form and contents of the first issues cannot yet be optimal. Give us your opinion about our idea of Electrochemical Applications as you hold it in hand right now. Please fill in the attached post card and return it to us. If you have some further suggestions, please write them down on a separate paper. We are eager to get your opinion.

We hope you like our new approach - either as a passive reader of Electrochemical Applications or with active contributions to one of the next numbers.

Successful applications ...
Dr. Hans-Joachim Schäfer

Surface Surfing

Impedance and Surface Layers

Corrosion inhibitors, coatings and passive layers of oxides, nitrides and more are in the focus of intensive efforts in corrosion preventing. They all are building protective layers on metals. One important tool to get more information about the structure and the mechanisms of protection and protection breakdown is the Electrochemical Impedance Spectroscopy EIS. The two-pole impedance, formed by the layers between metal and electrolyte, will often be described by a so called Constant Phase Element CPE, sometimes with an additional leakage resistance in parallel. But this popular model tells more about the phenomenology than the mechanism and is not adequate to the complex structure of such layers. They are typical objects characterized by the...

Impedance of Surface Layers with Conductance Gradients.

In cooperation with the Erlangen University our work group did some publications in this field. Under the above title we presented a poster at the Third International Symposium on Electrochemical Impedance Spectroscopy 1995 in May at Niewpoort, Belgium. The fundamental of this paper is a description of the layer dielectric not as homogeneous but with vertical gradients in permittivity and / or conductivity. For such dielectrica a general closed impedance formula cannot be given.

THALES software can treat them using iterative numeric integration methods. Under the above standing abstract and introduction a short look is given.

ABSTRACT

The interpretation of impedance spectra of electrochemical systems is extremely complicated, if impedances of double layers or surface layers

differ from those of ideal capacities. They may rather behave like loss capacities with nearly frequency independent phase angles deviating from -90°. This constant phase behavior may be caused by an inhomogeneous dielectric, e. g. by distributed coupling of the capacity of a fractal rough or porous surface with the electrolyte resistance. The frequency response cannot be described then by a singe RC element. Within the fractal theory concepts like 'true surface' and 'area capacitance' lose their unequivocal meaning due to an undefinable scaling factor. If, however, the inhomogeneity can be described by a profile of conductivity perpendicular to the surface, the impedance function is controlled by definite physical parameters again. Within a limited frequency range under certain conditions also some of these models prove nearly ideal constant phase behavior.

INTRODUCTION

When measuring impedance spectra of metal surface layers in electrolyte solvents, neither the component of the double layer nor that of the surface layer will correspond to the expression

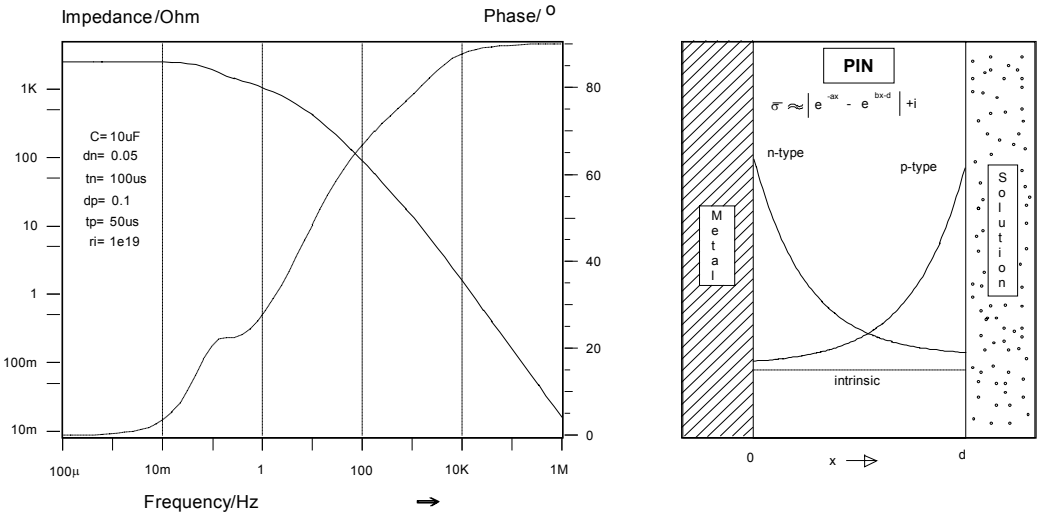
$Z_c=(j\omega C)^{-1}$ *(with Capacitance* $C = \varepsilon_0\varepsilon_r \bullet A/\delta$ *(1) and angular speed* $w = 2\pi f$*)*

0

applicable to an ideal clutch capacitor of the surface A, thickness (electrode distance) δ *and permittivity* $\varepsilon = \varepsilon_0\varepsilon_r$ *at any frequency. This would require a homogeneous dielectric medium between two planar, smooth and parallel equi-potential surfaces, not allowing gradients in relative permittivity* ε_r *or any texture of the surface. Even doublelayers of ideally polarizable electrodes will obviously not meet all these requirements. Questions on this context have recently been discussed by T. PAJKOSSY [1].*

The paper shows impedance behavior results of different models for the layers, dependent on different shapes of the characterizing gradients. For instance, gradient profiles are demonstrated, which are showing almost perfect constant phase behavior and others, showing the typical spectra of technical coatings (see the following graphs for example, a simulation under IM6-THALES software).

If you are interested in the complete paper a reprint may be requested from ZAHNER-elektrik. In German the matter is discussed in "Impedanz von Deckschichten mit Leitfähigkeitsgradient", published in 'Dechema Monografien...'.
CAS




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6 'Parameter count n'
pin-Schichtelement, pin layer element
Kapazität          C/F      ,capacity          C/F      ,1 e-39 , 1 e3
rel. Eindringtiefe dn       ,rel.penetr. depth dn       ,0      , 1
Zeitkonstante      tn/s     ,time constant     tn/s     ,1 e-12  , 1 e12
rel. Eindringtiefe dp       ,rel. penetr. depth dp      ,0      , 1
Zeitkonstante      tp/s     ,time constant     tp/s     ,1 e-12 , 1 e12
intr. Widerstand   ri/Ohm   ,intr. Resistor    ri/Ohm   ,1 e-12 , 1 e39
formula: local C,de,te,dh,th,ri,dx,x,ge,gh,gi,Z&,G& : dx=de/2 : ge=C/te : gh=C/th : gi=1/ri : x=dx/2
while x<1
    g=abs(ge*exp(-x/de)-gh*exp((x-1)/dh))+gi : x=x+dx : G&=cmplx(g/dx,C/T/dx) : Z&=Z&+1/G&
wend : fnendZ&
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The Evolution of a Revolution

From IM5 to IM6 ...

In more than 8 years the IM5d impedance spectrum analyzer made its way and became one of the most precise, most reliable, most versatile, most user-friendly and most compact electrochemical high-end measurement systems in the world. Now it has got a successor: the IM6.

The Zahner impedance spectrum analyzers are developed by C.A. Schiller - electrochemist and president of ZAHNER-elektrik GmbH & Co. KG. He did it on the base of his own experience in the field of impedance spectroscopy applications at the university of Erlangen, Germany and in close cooperation with many well-known electrochemists in the world. Therefore from the beginning the IM5d fitted the needs of electrochemical-impedance-spectroscopy-users very well and found a lot of friends in both industry and universities all over the world.

Since the first IM5d system was installed in 1985, soft- and hardware was developed continuously to be always state-of-the-art. This is the reason why the IM5d soon was well-known as one of the most modern impedance spectrum analyzers you can buy.

The latest step of development was a very big one as on one hand the analogue hardware such as frequency generator, frequency analyzer, potentiostat, U/I-amplifiers and parallel-A/D-converter etc. was upgraded and on the other hand a completely new software package with many new features and an easy-to-use graphic-based user-interface was installed.

With all these new features time had come to change the baby´s name: The IM6 is the direct successor of the IM5d and works on the same, patented acquisition- and analysis-concept. It also is an open system that can be extended on the software- and the hardware-side to integrate other quantities such as temperature or pH into the impedance-measurements or to control an oven. In the one year it is on market the IM6 proved to be a worthy successor.

Not only that the IM6 kept the versatile concept. It provides even widely enhanced technical specifications such as a frequency range from 10 μHz up to 8 MHz for the complete system and an impedance range from 10 mΩ up to 1 GΩ. Please note that there is a difference between the frequency range of a complete system with all its components and the frequency range of only one single component. Some other systems come with frequency generators covering a range up to over 30 MHz whereas the potentiostat - and therefore the complete system - only works at up to 1MHz.

Beside this the IM6 has got a completely new and even more user-friendly software. You only have to click icons and input your measurement specifications - and go. There are many new and very useful functions in the standard software and a new optional plug-in for the acquisition and analysis of electrochemical noise is available.

The IM6 comes in a compact 19" desktop or rack-mount unit as a complete system with plug & play handling: plug in your cell connections and play ...

The IM6 works with a standard PC and supports nearly all file formats needed to analyze the data with other software such as table calculation, data base or specific EIS programs. HJS

And here our special offer: TEST the IM6 system for 4 weeks FREE* ! You will see the difference and learn a lot about modern measurement techniques.

*Only freight is to be paid by tester

Join the "Electrochemical Communication Line"

BBS for electrochemists is coming

Especially for electrochemical information interchange and an even closer and faster support of our customers ZAHNER will set up a new mailbox system. With a standard modem and a PC you can communicate directly with other electrochemists and of course all at ZAHNER.

In the last years new communication media came up and some of them established to be a standard in certain fields. Multimedia is one catchword, BBS ("Bulletin Board System") or mailbox is another one. Nearly one out of two PC-users owns a modem to let his computer talk to other computers in all parts of the world via analogue or digital telephone lines.
This communication form is used in very different fields: You can directly order from a mail-order firm, you can transact your banking business, you can meet online a worldwide conference, you can download computer programs or transfer documents or measurement data. Do all this sitting at home in your easy chair or in the office, in the lab or elsewhere a computer, a modem and a telephone line is available. With modern communication technique data tele-transfer is possible even in the car or in the field without problems.
There are mainly two paths on which you can bring your data on the way. Accessible for nearly all users is the analogue telephone line. With a standard modem and a PC you can communicate at moderate speed (up to 28.800 baud) and the low cost of a telephone call. Faster are the digital telephone lines, e.g. in Germany the ISDN-net. You need a special installation, a special modem and an entry to one of the data-nets such as Internet, CompuServe or the new Microsoft network.
We decided to make the first step with the common analogue telephone line to reach as many prospective subscribers as possible. The cost for participation is minimized: A PC, a modem and a telephone line is all you need. For all those who do not own a modem we make a special offer for a 14,400 or 28,800 baud modem. Please contact us.
There are different intentions for us to set up a BBS especially for electrochemists. The first is that there is no generally accessible BBS forum for this group of people in Germany yet. The BBS shall offer a public information- and discussion-board and enable an even closer communication between electrochemists. The second intention is to give all IM5/6 users the possibility to discuss measured data with other specialists and with us at Zahner. Beside this IM5/6 users will be able to download new software-updates at any time very easily.
The use of the ***Electrochemical Information Line*** is free for everybody. We hope that the acceptance is high enough to justify cost and manpower we invest. Please give us a note on the attached postcard if you are interested to join the ***EIL***. As soon as the system is working, we will inform you and look forward to... HJS

...welcome *y o u* **as a member of the new *Electrochemical Information Line.***

Frequently Asked QuestionS

"What influence have connection cords between cell and impedance analyzer onto measurement ?"

One of the most critical elements of an impedance measurement setup are the cell and the connection cords between cell and measurement system. By reason of its impedance (capacitance, inductance and resistance) the cords work as a low-pass filter that will damp high frequencies and cause a small phase shift. Beside this the cables are antennas that can pick up every electromagnetic field such as the 50/60 Hz power line frequency.
So what can you do ? You should use relatively thick cables (more than 3 mm in diameter) as short as possible if you examine low impedance objects. The connectors should be high quality and of BNC- or Lemosa-type. You should not lay the cables in parallel with a line or another high voltage or high frequency cord.
To discuss this important question in detail we decided to publish an article in the next number of Electrochemical Applications.
HJS

"Can you export a graphic created with the IM6 to PC programs ?"

Yes, you easily can export IM6 graphics to any MS-DOS® or Windows® software that is able to import HPGL-files. HPGL ("Hewlett Packard Graphic Language") is a standard file format today that is supported by the IM6 software and nearly every good graphic and word processing program on the market. Examples are Corel Draw, Designer, Word for Windows and many others.
The handling is quite easy: In every page of the ***Thales*** software you can create a graphic that you can print out. In the printer-menu you select the option *HPGL file* that will store the complete graphics as in the HPGL file format on disk. In the PC program you only have to select *Import* in the *File* menu and chose the HPGL-extension *hgl*. The file selector will show you all HPGL-files and you can select one to be loaded.

HJS

Editorial
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