Hello everybody and welcome to the second issue of Electrochemical Applications. You had to wait for it some months longer than proposed - but now you get a double-sized issue. Being late with the publication has two main reasons. First: We had a lot of work getting the Electrochemical Information Line on-line. But now it is finished and it works. What you need and what you must do to join the EIL-community you can read below. The second reason for us being late is even more important ...

We are proud to announce here and now our new partnership with BAS Bioanalytical Systems Inc.

BAS is one of the biggest American manufacturers of analytical instruments with sales offices in UK, Australia, Japan and South Africa. The company manufactures a wide spectrum of high-quality analytical instruments for medicine, biology, chemistry, pharmacology and teaching. The IM6 meets very well this spectrum and therefore will be distributed in the above mentioned countries (except of Belgium) by BAS exclusively. With the BAS sales office in Belgium we have a loose co-operation for the moment. BAS also will be responsible for the service in these countries. This guarantees an even better, faster and more direct support for all the customers there. And it will open new markets for ZAHNER.

Correspondingly ZAHNER will sell BAS products in Germany from now on. These will be products mainly for electrochemical use such as DigiSim (electrochemical simulation software for PC), CGME (Controlled Growth Mercury Electrode), C-2 (Voltammetry Cell Stand), RDE-1 (Rotating Disk Electrode) and others.

The co-operation of BAS and ZAHNER is good news not only for the two companies and the overseas customers of ZAHNER. It also improves our continuity and our exposed position on the international market.

As you see there are many good news this time that the delay of this issue may excuse. But we also can present you a very interesting focal point in this issue: electrochemical noise. Zahner developed a revolutionary new technique for noise acquisition and analysis called CorrElNoise. In two articles of C. A. Schiller we give you an introduction into the fields of noise measurement and show you the problems coming up in practice. Beside this there is a practice report concerning chemical cleaning of corroded material. Interesting stuff enough, we think.

Hope you will enjoy it ...

Dr. Hans-Joachim Schäfer

Electrochemical Noise
Fundamentals and methods

The financial losses caused by the corrosion of metals - estimations state up to 4% of the production of the industrial countries - cause high interest in new methods of corrosion detection and prevention.

The initial redox processes of corrosion are correlated with the charge-transfer of the dissolution-deposition process of metal. Therefore one part of the main stream corrosion research is based on electrochemical methods studying typical systems consisting of the corroding material immersed in an electrolyte to initiate corrosion. The determination of the polarisation resistance $R_p$ quantifies the amount of corrosion. Among others, two methods are well established. The traditional method analysing steady state polarisation curves requires less expensive equipment but more time. The second method, the impedance spectroscopy, requires less time but adequate equipment. Even though both methods -
especially in combination - yield significant results, the new method of electrochemical noise measure-
ments became more and more popular during the last years.

Electrochemical noise measurements too are based on the fact that corrosion related redox-reactions are accompanied by charge transfer. The potential as the motive force of an electrochemical reaction is determined by the Nernstian equation. It is measured relative to a reference electrode. The Butler-Volmer-equation determines the actual current and finally the mass flow rate.

The steady state polarisation method as well as the impedance method rely on the determination of the exchange current. Commonly the so called polarisation resistance, which is inverse proportional to the exchange current, is used to characterise corrosion. The factor of proportionality is determined by natural constants and the temperature and does not depend on the electromotive force of the reaction. This important fact, if neglected, will cause misinterpretations of the measured potential noise.

The mass transfer caused by the corrosion is determined by the exchange current\(^1\). The inverse proportionality depends on the exchange current only. The thermal potential, i.e. that magnitude of the dimension “potential” with reciprocal proportionality to the rate of corrosion, will be determined by constants of nature and temperature only. A dependence on the motive force does not exist.

Measuring large potential differences, i.e. a high electromotive force, means that the corresponding reaction will be running by its own thermodynamic power. The corresponding redox-reaction, however, will usually be accompanied by concurrent or consecutive reactions. Thus the observed potential is a mixed potential of all reactions taking place. A characteristic potential may only be observed if one reaction will be kinetically favoured by its high rate. In the case of passivation protected systems the relative high electromotive force of the corrosion reaction will be suppressed by concurrent processes, as long as no significant corrosion is taking place.

If homogeneous corrosion affects the whole electrode surface, the course of the measured potential will indicate this when settling to the characteristic potential of the corresponding reaction. As homogeneous corrosion does occur rarely, the potential course usually is not very significant for corrosion characterisation. Typical corroding systems may be described by inhomogeneous corrosion attacks, e.g. pitting. Inhomogeneous corrosion is typically showing potential fluctuations with time. The reason is the fluctuating relative contribution of concurrent processes to the resulting mixed potential. The corrosion current and thus the mass transfer cannot be observed directly as the corresponding reactions take place within finite surface elements. Balancing currents are flowing in the vicinity of the metal surface and do not require bypasses like connecting cables. Nevertheless exchange currents caused by corrosion may be estimated indirectly, compared with the situation, when no corrosion is taking place. The main principle is as follows:

Considering a system of two electrodes of identical material with symmetric geometry, no significant current flow across an external bypass will occur, if both electrodes will act in an identical way. In this case the electromotive forces of both electrodes will compensate each other exactly. This is true in the case of absolute homogeneous corrosion too. But if corrosion attack takes place locally, a small difference between the mixed potentials of both elec-

\(^1\) Exchange current in this context means the anodic partial current where the net current adds to zero.

Current fluctuations in time of a symmetric system caused by statistically distributed corrosion processes.
trodes as a fluctuation in time can be recognised. This is what we call *electrochemical potential noise*.

A shortcut across both electrodes will enable a small current flow caused from the differences in the electromotive forces. This is what we call *electrochemical current noise*. As a first estimation this current noise will be correlated to the corrosion reaction mass flow: According to increasing corrosion rates, their differences in location and time as fluctuations will increase too - causing higher current noise.

These facts are the fundamentals of corrosion monitoring via electrochemical noise measurement.

As mentioned above, different opinions can be found about the role of the potential noise. Some people believe, that this magnitude should be placed in the numerator of some polarisation resistance estimation according to

\[
\text{resistance} = \frac{\text{rms noise potential}}{\text{rms noise current}}.
\]

This should cause an inverse proportionality between potential noise intensity and corrosion rate - which is in contradiction to both observation and the above mentioned facts about the electromotive force of mixed potential processes.

Therefore corrosion examination based on electrochemical noise should record both current and potential noise in order to increase the significance.

If there are any, where are the advantages of noise methods compared with more traditional electrochemical techniques? Impedance spectroscopy, for instance, is based on the assumption of steady state of the examined electrochemical system. The same premise is valid for polarisation curve measurements and related methods.

### Measurements on stainless steel ST1.4571 in 6%NaCl / pH2

- **Polarisation curve in the vicinity of the rest potential** (T=75°C)
- **Impedance spectrum at rest potential** (T=85°C)

Continuous measuring techniques are severely disturbed by discrete corrosion events

Applying traditional techniques on systems with inhomogeneous corrosion attack, impedance spectra and polarisation curves for instance will be heavily distorted - they become "noisy". In contrast noise measurements are quantifying these discrete events, which are disturbing the continuous methods: That is the gap that can be filled with electrochemical noise investigations.

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*A revolutionary new method called CorrElNoise will help to make a serious analysis technique out of common electrochemical noise measurements. In the next article you will learn a little bit more about this unique Zahner method. So sit back, turn the page and read more about a little revolution ...*
The revolution in measurement and analysis of electrochemical noise

Recently electrochemical noise (ECN) investigations became popular among material scientists and chemists. They see the advantage of this new method to get experimental results, even in those cases, where traditional methods fail. The reason is, that ECN methods are quantifying exactly that events, which are disturbing the continuous measuring techniques. The acquisition of noise signals is not as simple as it seems. In order to understand the problems occurring with ECN, a short characterisation of ECN signals is necessary. This overview is limited to noise caused by inhomogeneous corrosion attack.

Both potential and current noise from such sources span a relative wide dynamic amplitude range. Materials like aluminium, magnesium and related light metal alloys are corrosion protected by passive layers, while the electromotive force for the corrosion reaction is very high. As a result of this fact, potential noise amplitude of such materials may exceed several mV, if corrosion takes place. Also peak current densities up to several mA/cm\(^2\) may occur. These amplitudes are high enough to be detected by any low noise electrochemical equipment such as the IM6.

On other materials of interest, for instance on high quality steel, the noise amplitudes are much lower. To amplify these low level signals special amplifiers are needed. For the IM6, a standard noise probe such as the CorrElNoise probe will extend the low level ranges by two decades.

Another important aspect deals with the frequency band that is of interest for corrosion event noise. Basic research found, that the main noise sources are active in the range of mHz up to several Hz. Looking at the signal course in time, this means, that slow "drift" can be observed as well as transients in the range of second. Although sometimes spectral components around and beyond 50/60 Hz will occur, it makes no sense to analyse these frequencies, because in every lab or industrial environment "electrosmog" caused by line frequency is dominating the electromagnetic pollution. These frequencies must be suppressed with high efficiency. It seems to be a good compromise to investigate the frequency band from mHz up to about 10 Hz. This allows effective line frequency suppression without significant loss of information.

Regarding analysis, it is of great value to measure both current and potential noise. But the measurement requirements are in contradiction to each other: Current noise needs virtual short cut condition, potential noise must be measured with a virtual open circuit, that means with high impedance load. If you have to get both informations at the same time, with standard methods you have to investigate two identical systems, one under open circuit, the other under short cut condition. A useful technical arrangement (Abb.) for that purpose consists of one couple of identical electrodes, which serves as noise current source under shortcut conditions. An additional electrode (optionally out of the same material) acts as reference electrode. In reference to the short cut couple it builds the second system and serves as potential noise source under open circuit condition.

This arrangement is often used in monitoring applications. It can be performed with the IM6 as well as with some other equipment. But there is an important disadvantage: The measured current- and po-
tential noise does not come from the same electrochemical system. Even under the assumption that regarding corrosion both systems behave identical, nevertheless current and potential are uncorrelated. This means, that only the scalar rms-values can be related, whereas vector operations like power calculation do not make sense.

The question for us was: Is it possible to overcome this unpleasant situation? Regarding the fact, that corrosion relevant noise is observed mainly in the low frequency range, there is a solution for the problem. If in a first approximation the noise source may be described as a low frequency noise oscillator in series with a distinct source resistance, it must be possible to sample both current and potential signals by fast switching between the two modes open circuit and short cut. If the switching respective sampling frequency is high compared with the highest noise frequency of interest, this technique works without loss of information.

Zahner developed such a method and named it CorrElNoise, which stands for the measurement of correlated electrochemical current- and potential noise coming from the same source. An international patent for it is claimed. The method is available as an addition to the IM6 and enables the user to record current-, potential- and power noise in the frequency range from DC up to about 5 Hz. In addition to the unique advantage of getting correlated signals from one system, CorrElNoise profits from the chopper principle. This means, that electronic offset- and drift problems as well as line frequency interferences are automatically suppressed to a minimum.

All three methods have their specific advantages and disadvantages: Using the normal potentiostat seems to be the most flexible technique but it is not very sensitive. The standard three-electrode probe amplifiers have a high gain and are able to suppress systematic DC-potential offsets coming from asymmetric objects. In contrast CorrElNoise needs a spatial and electrical symmetric arrangement of the electrodes but is the only method to get correlated potential and current information.

**Principle of the CorrElNoise technique**

We must keep in mind that noise experiments normally have a very long acquisition time. There is a lot of data being pushed out of these experiments. How can we handle this flood of information?

Under certain conditions we need to record the original information, that means the true course of current- and voltage vs. time. In this case the time resolution should be high enough to get a good representation of pulse shapes. This will sum up to approximately 50 Mbytes in a day at a rate of 100 Samples/s. It is obvious, that such a "real time acquisition mode" must be the exception. A powerful online data reduction is necessary for applications like long-term corrosion monitoring. In the case of the IM6 this is done by Zoom-FFT frequency analysis and further compression. At the end this process leads to 60 representative frequency samples with approximately logarithmic distribution on the three decades of the observed frequency band.

It was found, that several corroding systems are showing a characteristic intensity distribution in the frequency domain. This is the reason, why optional weighting of the broadband noise often may increase the significance of the corrosion indication. A further possibility is the characterisation of the time courses by online cross correlation with reference shapes. The reference signals must have the shapes, which are expected when corrosion is present. At least it is possible to define different criteria like maximum rms. value violation, maximum intensity violation at certain frequencies or the detection of the characteristic signal shapes. Each parameter can serve as trigger for corrosion alert.
The most severe problems in practical applications of noise methods are caused by additional noise sources that are not related to corrosion. These are, for instance, electromagnetic interference, thermal and concentration fluctuations, convection related potential differences and more. Concerning this difficulties, some people doubt of the principal applicability of noise methods. The choice of an adequate acquisition technique in combination with sophisticated analysis methods will help to overcome these doubts. CAS

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**Cleaning Corroded Material**

Recommended Practice for Cleaning Corroded Specimens by I. H. Plonski
Institute of Atomic Physics, IFTM, Bucharest, Romania

This recommended practice gives a new cleaning media and procedure for removing without any significant corrosion damage of the basal metal, corrosion products formed on iron and low alloyed steels under oxidising conditions. Emphasis is placed on a procedure suitable for removing slurry, sludge and deposits from corroded specimens cut from heat transfer components of conventional and nuclear power plants in order to evaluate the quantity of corrosion deposits before chemical cleaning.

1. Agents for chemical cleaning of corroded specimens

The recommended agent is a complexing solution containing 0.1 to 0.2 M citric acid, 0.01 to 0.03 M ferrous citrate as catalyst, and a corrosion inhibitor, optionally adjusted during cleaning with hydrochloric acid at pH 2.2 to 2.6.

The 0.1 litre agent can be prepared, before use, as follows:
* Boil for 1 hour 0.1 litre demineralized or distilled water, in a distillation flask provided with a vertical refrigerator, in order to eliminate the dissolved oxygen.
* Dissolve, at 100°C, 2.1 to 4.2 g citric acid (C₆H₈O₇•H₂O).
* Dissolve 0.264 to 0.792 g Fe(II) citrate. If Fe(II) citrate is not available, it can be prepared in situ: Add 0.21 to 0.63 g citric acid and 0.056 to 0.168 g metallic iron, respectively, and boil to the complete solution.
* Add 0.4 to 0.6 pelicular acid corrosion inhibitor, such as SOMAFER™ GV-P9.

2. Procedure of chemical cleaning of corroded samples

* Cut specimens from corroded carbon steel or low alloyed steel components. Optionally scrub gently with a soft bristle brush to remove the loosely attached corrosion products.
* Immerse the specimens in the distillation flask containing the agent and continue the boiling.
* During the treatment adjust the agent to pH 2.2 to 2.6 by adding small portions of hydrochloric acid.

The pH value should not exceed 3.0 due to the risk of approaching the solubility product of the main dissolution product Fe(II) citrate (0.4 to 0.8 g l⁻¹) which decreases with the pH increase.

* Continue the boiling up to the complete removal of any layer of corrosion products.
* Rinse the samples with distilled water and dry with nitrogen gas or by immersion in acetone.

* When evaluation of the quantity of sludge and deposits is necessary, weigh the mechanically detached corrosion products and the samples before and after the chemical cleaning and calculate the weight loss per area surface unit. In order to make correction for the metal dissolution, a clean sample must be exposed simultaneously with the corroded ones, in close contact with one of the corroded specimens, in order to ensure the galvanic coupling conditions and the presence of ferric ions resulted from the dissolution of magnetite, gamma ferric oxyhydroxide, and hematite, which enhance the iron corrosion.

3. Remarks

The rate of removal of corrosion products such as magnetite, gamma ferric oxyhydroxide, and hematite grown in water on carbon steels and low alloyed steels is 30 to 40 mg cm⁻² h⁻¹; 100 ml agent removes approximately 1.2 g iron oxides. The general corrosion rate of base metal is less than 1.5 mg cm⁻² h⁻¹. No pits are visible by light microscopy. The hydrochloric acid can be replaced by fresh agent when chloride ions are prohibitive.

IHP
It is done and it works! The "Electrochemical Information Line" (EIL) is set up and since June online - 24 hours a day. It already helped a great number of customers to get their software updates right on the spot, to send us IM6 data asking for hints how to analyse it, to up- and download scientific manuscripts and... and... Interested? So how can you become member of the EIL family and what do you need to participate in our new online-service?

What you need  To communicate with a BBS (Bulletin Board System) such as EIL you need a few components that you probably still own. First of all you need a computer. It is not essential to use an MS-DOS-PC - a Mac or an Atari will do it as well. Then you need a telephone line. Both, computer and telephone line surely still are available in your lab, office or home.

What you need else is a modem - the link between the computer and the telephone line. A modem encodes the data it receives from the computer and sends it through the telephone line to the modem on the other end of the line and vice versa. A major aspect when buying a modem is the maximum speed at which it can communicate through the telephone line. The speed is measured in "bits per second" ("baud"). A standard modem today works at 14.400 or 28.800 baud. The EIL works with a 14.400-baud-modem, that means that at maximum 14.400 bits per second that is about 85 Kbytes per minute can be sent through the phone-line. Further more it should support the „Hyes“ command set.

Software  Of course you need a software that is able to control your modem and display the dialogs. Many modems are shipped with a quite good terminal program that will work fine with the EIL. Windows 3.1 comes with a terminal program called "Terminal", Windows95 with "Hyperterm".

The handling of these programs is rather simple. You have to define the data-protocol „8N1“ (8 data bits + 1 stop bit). All other parameters are not of interest for EIL but they may be important for your computer. These are e.g. the COM connected to your modem, the baud rate between computer and modem or the flow-control protocol (RTS/CTS and/or XON/XOFF). If you are not sure about the correct settings please refer to the manuals of your modem and your terminal software.

How to log in  Before you have access to the EIL system we have to enter your name and your personal password. So if you are interested in participating in the EIL please give us a phone call, a fax or a post card with your name, address and phone number. As soon as you are registered you will get a note with your password from us. Now you have full access to all services of EIL.

Logging in to the EIL is simple. You dial the phone number of EIL with your terminal software - that's all to go into communication with the BBS. The EIL phone number is: (49) 9261-52004

EIL now asks you for your name (first and surname!) and your password. You exactly have to input the data you got from us. If all inputs are correct, EIL will come up with the FILE AREA menu page. An online help system is available pressing the question mark („?“). EIL is divided into two main areas:

FILE Area  The FILE AREA is subdivided into four sub-areas: The first one is reserved for “Uploads” from users to EIL. The second one contains “Software” for IM6 and AMOS/ANDI systems you can download for the use on your Zahnner system. All downloads are for free.

To avoid trouble please contact us before you install a new system boot or user software!!! Not all programs are good to run on every IM6- or AMOS/ANDI system configuration!!!

In the sub-area “Papers” you will find scientific articles - e.g. those of Electrochemical Applications. In addition we will place here all lectures and posters we present on scientific meetings. But most important: we invite you to send us your manuscripts (preferably on disk) to make them public via EIL. Of course you also can push them via modem to the “Upload“ sub-area. We will have a look at new manuscripts and if we think they are OK for EIL we will transfer them to the “Papers“ area.

MESSAGE Area  In the MESSAGE AREA you can write down short messages (e-mail) for a certain user or for public access and you can answer messages directly.

Up- and Download  The up- and download procedure is quite simple: Press the u-key when you are in the FILE AREA of EIL to initiate an upload. The BBS then will wait for data. All following operations may vary with the terminal software you use. In any case you have to define a protocol for data transmission. If your software supports it, use the Z-Modem protocol. It is very reliable. Now select the file you want to send from a standard file selector box. The file will be stored with the same filename in the upload area of the EIL-harddisk.

Pressing the d-key you initiate a download - this is a transfer of a file from EIL to your computer. You simply have to type in the name of the file you want to be downloaded and the file will be soaked to your harddisk. In what path you will find it, is defined in your terminal software.

Safer bits  The fear to “infect” your computer with a virus is an actual problem. There are different sources from which a computer can be "infected". One of these sources can be bulletin board sys-
tems. Therefore we should talk about the virus problem and what we will do to keep \textit{EIL} clean.

\textit{EIL} handles mainly three types of files: IM6-files (programs and data), PC-software (e.g. PC-term driver) and PC-data-files (e.g. documents or ASCII-files). For the IM6 platform we guarantee that \textbf{NO VIRUS EXISTS}. Therefore it is not possible to "infect" your IM6 system in any way.

On the PC mainly executable files (.exe, .bat, .com) and the boot sector of disks and harddisks may be infected. We will do two different things to give such link- or boot-sector-viruses no chance: We will scan the \textit{EIL}-harddisk at least one time a week with a professional virus scanner software. The \textit{EIL} hard-

disk then is clean and should be no danger for other computers. But we also beg all of you who will upload PC-files to \textit{EIL} to scan the files very carefully for viruses. This will prevent trouble with other \textit{EIL} users.

The chance to catch a virus is no argument for not using a BBS. Even more \textit{EIL} is more save than other bulletin board systems for it handles mainly IM6 files that cannot transport any kind of PC virus. And please remember: On the IM6 system no virus exists!

\textbf{HJS}

\section*{Frequently Asked Questions}

\textit{``When I'm examining objects dominated by double layer capacities, my cyclic voltammograms (CV) sometimes show strange effects. What is the reason for these effects?''}

Seeming simple, capacitances are not at all easy objects for an electrochemical measuring system. One reason for problems may be the instability of the feedback loop of the potentiostat used. The capacity adds phase shift to the loop. So undetected parasitic oscillations of the potentiostat may produce irregular results such as "starry skies" or severe current offsets.

Another problem arises with the measuring method itself used by certain equipment. In the era of computers it seems easy to change from the traditional analogue scan technique to its digital approximation by a small steps staircase technique. This task can be done by a software controlled D/A-converter. The advantage of such a technique is the possibility to easily produce arbitrary waveforms, for instance stable slow signals (slow rate down to zero). The measurement itself too can be performed with the computer using A/D-converters. This is the base for flexible and user-friendly CV equipment - but the staircase-sweep-approximation idea is too simple to be good! Signals, created by a DA-converter remain discrete. Even if one tries to increase the resolution dramatically, it will stay finite. On the other hand the theories of CV techniques claim steady sweep signals. Regarding capacitive objects will help to focus on this important difference.

If one applies a voltage signal \(U(t)\) to a capacitor, the current \(I(t) = \frac{dU}{dt}\) will flow. A constant slew rate results in a constant current. Discrete steps will cause current pulses with \(\delta\)-pulse shape - that means in theory infinite height for an infinite short time interval but with a well defined integral charge of \(Q = C \cdot \delta U\). In practice the \(\delta\)-pulse will be distorted to a short pulse of high amplitude. Its shape is determined by the pulse response of the potentiostat and parasitic effects. If the measurement technique samples the response signal after a short time delay relative to the step, the result must be wrong! The only way to get a correct current result is to measure the charge by integrating the total step interval and calculate the mean current. This calculated current value is identical with the one measured with the continuous method.

How can you find out, if your equipment uses this "clean" integrating CV technique? Take the enclosed aluminium electrolyte capacitor and perform a test measurement. Choose, for instance, a triangle scan of \(\pm 1\text{V}\) at \(\pm 100\text{mV/s}\) slewrate. The approximate capacitance value of \(1\mu\text{F}\) should cause a square wave of \(\pm 0.1\mu\text{A}\) current to flow. Consider the capacity tolerance of \(-5\%/+25\%\). Check the correct capacity using an impedance measurement at low frequency (e.g. \(1\text{Hz}\)): Now the measured current should fit the calculated current exactly.

If not, call the service-hotline of your equipment's manufacturer!

\textbf{CAS}