

## ***New Frontiers***

**H**ello 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 ***CorreINoise***. 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.

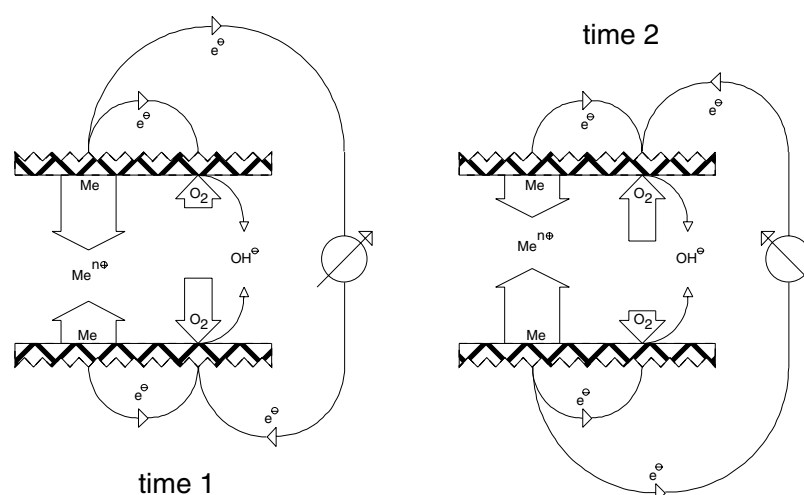
Hope you will enjoy it ...  
Dr. Hans-Joachim Schäfer

## ***Electrochemical Noise Fundamentals and methods***

**T**he 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* measurements became more and more popular during the last years.



Current fluctuations in time of a symmetric system caused by statistically distributed corrosion processes

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<sup>1</sup>. 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 electrodes as a fluctuation in time can be recognised. This is what we call *electrochemical potential noise*.

<sup>1</sup> Exchange current in this context means the anodic partial current where the net current adds to zero.

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

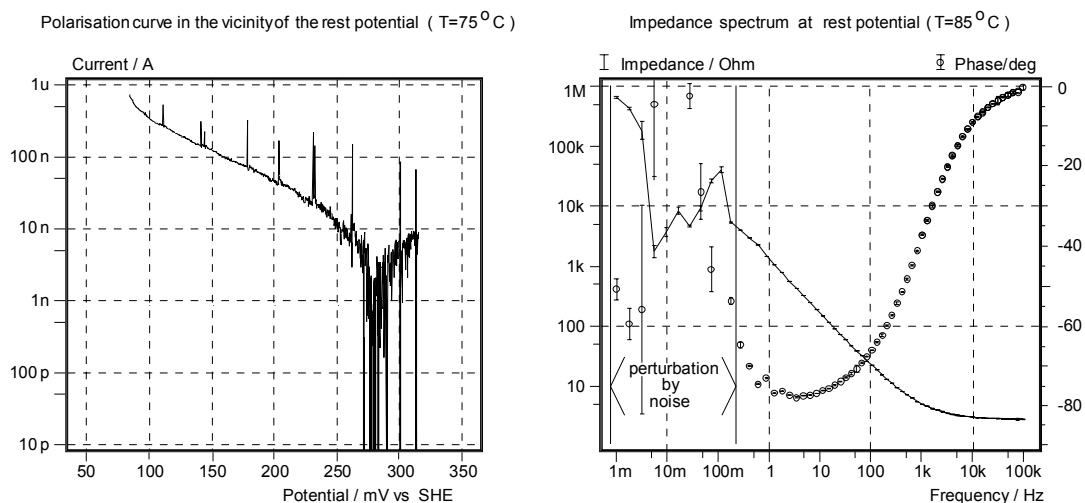
$resistance \approx rms\ noise\ potential / rms\ noise\ current.$

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



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. CAS

***A revolutionary new method called CorrEINoise 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 ...***

## ***CorrEINoise***

### ***The revolution in measurement and analysis of electrochemical noise***

**R**ecently 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.

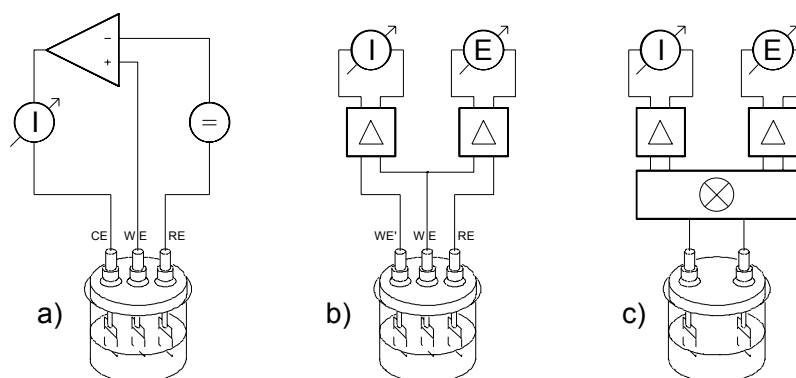
Both potential and current noise from such sources span a relative wide dynamic amplitude range. Materials like aluminium, magnesium and related light metal alloys are corrosion protected by passive layers, while the electromotive force for the corrosion reaction is very high. As a result of this fact, potential noise amplitude of such materials may exceed several mV, if corrosion takes place. Also peak current densities up to several mA/cm<sup>2</sup> 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 *CorrEINoise* 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.



Principle methods to measure electrochemical noise (schematic)

- current noise under potentiostatic control
- uncorrelated 3-electrode setup (standard setup)
- CorrEINoise* technique

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 potential 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.

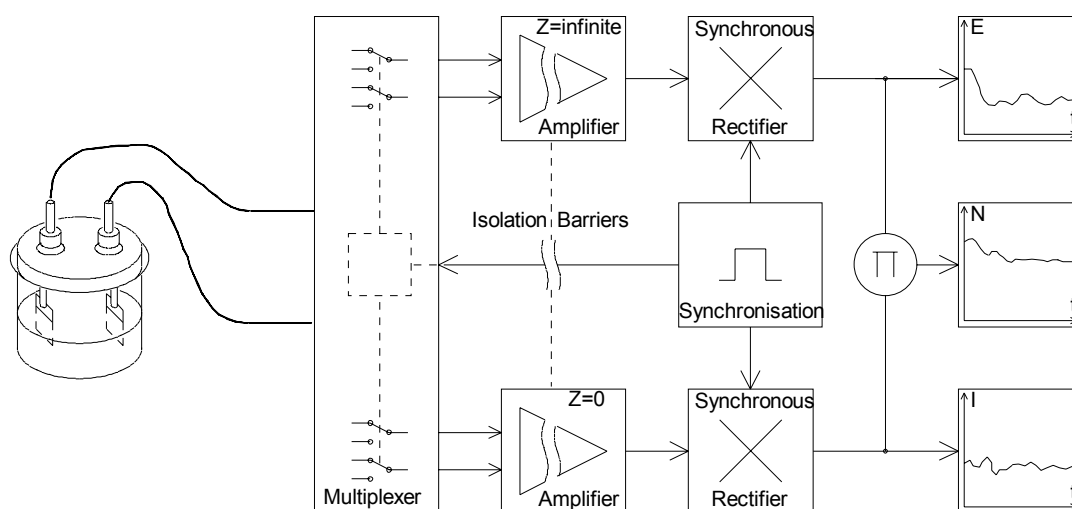
The question for us was: Is it possible to overcome this unpleasant situation? Regarding the fact, that corrosion relevant noise is observed mainly in the low frequency range, there is a solution for the problem. If in a first approximation the noise source may be described as a low frequency noise oscillator 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 **CorrEINoise**, 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, *CorrEINoise* 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 *CorrEINoise* 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 CorrEINoise 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.

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