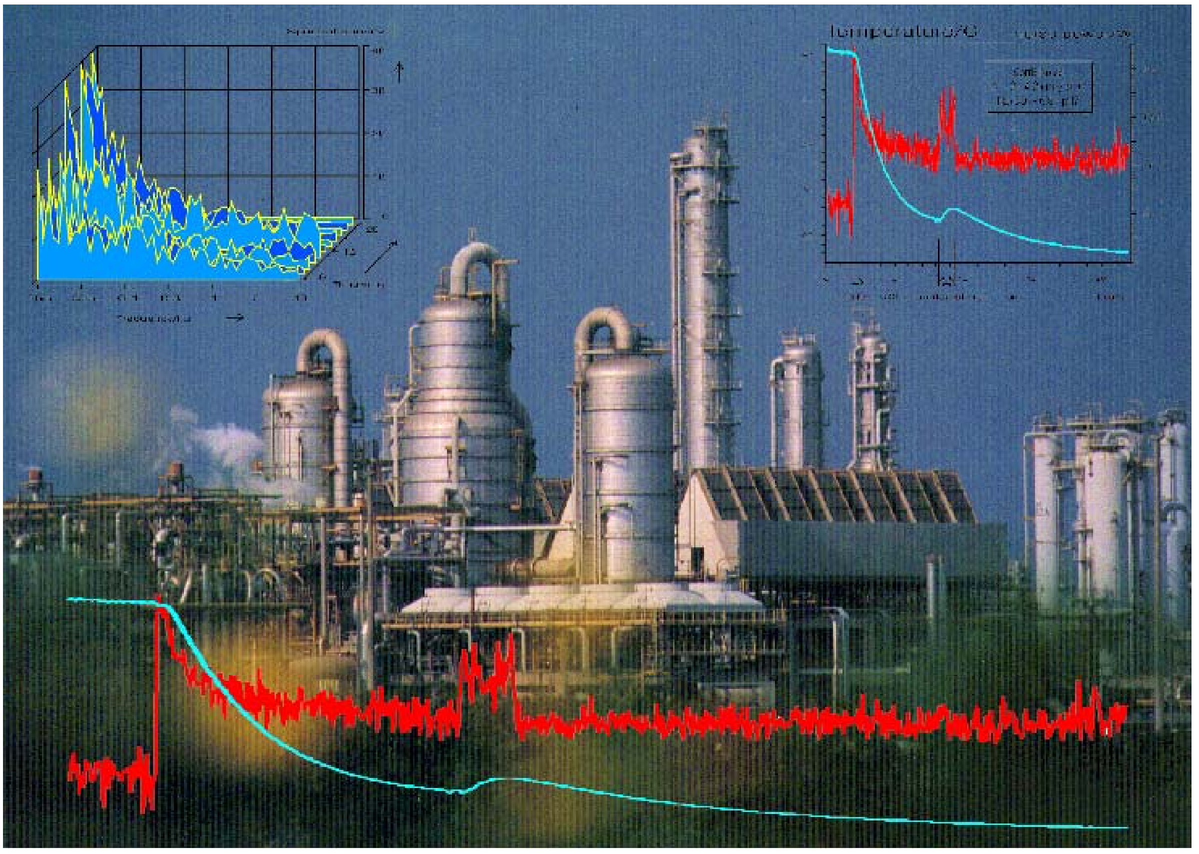
Electrochemical Noise

NOISE

Add-on module for IM5/6 impedance spectrum analyzers



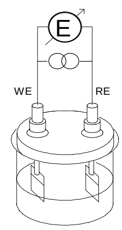
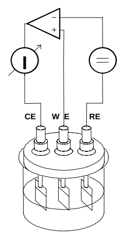
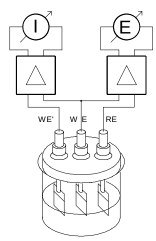
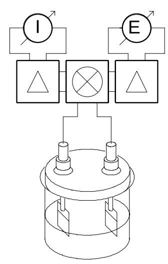
for CORROSION MONITORING ...

ZAHNER

MESSTECHNIK

The financial losses caused by the corrosion of metals - according to the latest estimates up to 4% of the production of the industrial countries - cause high interest in new methods of corrosion detection and prevention. That is one of the reasons why electrochemical noise (*ECN*) investigations have become more and more popular among material scientists and chemists recently. *ECN* methods offer results, even in cases, where traditional methods fail. There are different useful techniques to yield *ECN* information. The IM6 system **supports all common techniques** - but that is not all. Moreover, Zahner developed ***CorrElNoise.*** This revolutionary new method is superior to common *ECN* techniques by avoiding most of their typical problems.

As usual with the IM6, **additional channels** can be recorded parallel to the noise for monitoring e.g. temperatures, pH-values or any other analog or digital signal.

Method	Advantages	Disadvantages	Scheme
OCPN **Open circuit or galvanostatic potential noise** • no probe	• potential course including long term DC-components can be recorded	• sensitivity relatively low • not useful for electrochemical objects with very low noise amplitudes • no current noise can be recorded in parallel	
PCCN **Current noise under potentiostatic control** • no probe	• current course including long term DC-components can be recorded	• low sensitivity • not useful for electrochemical objects with very low noise amplitudes • no potential noise can be recorded in parallel	
UCPN **Uncorrelated three electrode current- and potential noise** • with probe	• high sensitivity • automatic suppression of long-term drift signals • only changes are recorded	• information of the DC-component is lost • poor correlation between current and potential • additional hardware needed	
CorrElNoise **Correlated two electrode current- and potential noise** • with probe	• sensitivity and suppression of long-term drift signals • unique generation of correlated signals for both potential and current which come from one electrochemical source • current and potential signals can be used to record noise power, which is a highly significant corrosion indicator • equivalent impedance can be evaluated additionally	• additional hardware needed	

All noise acquisition methods require IM6/6e + NProbe + EPC40 **!**

CorrElNoise

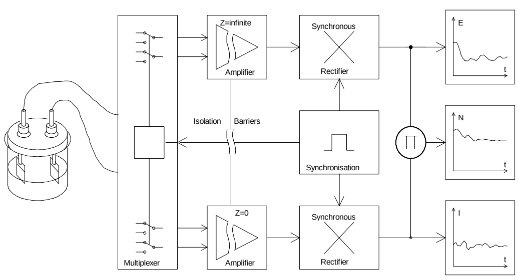
Noise based corrosion research using conventional electrochemical methods focus on the fact that the initial redox processes are related to the charge transfer of the metal dissolution-deposition processes. Distinct areas of the object surface can be viewed as local galvanic elements that contribute to the total measured potential. Since many of these local elements are superimposed, the fluctuation of the potential (and the current, if the electrode is polarized) is low. Traditional electrochemical methods are based on this „steady state“ behavior. However, inhomogeneous corrosion attack, which is particularly important in the nucleation phase, does not conform to these conditions. Traditional methods such as impedance or Tafel techniques will fail for such inhomogeneous corroding objects, because the measurement signals become more and more noisy. In this case noise measurements quantify these discrete events that are disturbing the continuous methods.

For analysis, it is of great value to measure both current and potential noise. The problem is that measurement of current noise essentially requires a short circuit condition, whereas potential noise must be measured with a high impedance load. The standard method for solving this problem is to measure two identical systems, one under open circuit, the other under short circuit condition. A common experimental arrangement uses three identical electrodes, where one pair acts as a current noise source under short - circuit conditions, the second as a potential noise source under open circuit condition. One electrode acts as a common electrode.

This arrangement is often used in monitoring applications, and can be set up with the IM6. However, this method has a significant disadvantage in that the measured current and potential noise do not come from the same electrochemical system. Even though it is assumed that the corrosion behavior of both systems is identical, the current and the potential are not correlated. This means that only the scalar rms.-values can be related, and vector operations like power calculation are meaningless.

There is a solution for the problem, based on the fact that corrosion-related noise is observed mainly in the low frequency range. To a first approximation, the noise source may be described as a low frequency noise oscillator in series with a source resistance. Therefore it is possible to sample both current and potential signals by rapid switching between the two modes (*open circuit* and *short circuit*). If the switching/sampling frequency is high relative to the highest noise frequency of interest, this technique works without loss of information.

CorrElNoise, developed by the specialists at Zahner, is based on these principles. *CorrElNoise* stands for the measurement of ***CORR***elated ***EL***ectrochemical current and potential ***NOISE*** coming from the same source. The method is available both as a plug-in for the IM6 and as a stand-alone-system. It enables the user to record current, potential and power noise in the frequency range from DC up to about 5 Hz. Furthermore *CorrElNoise* benefits from the chopper principle. This means that electronic offset and drift problems, as well as line frequency



Principle of the CorrElNoise technique

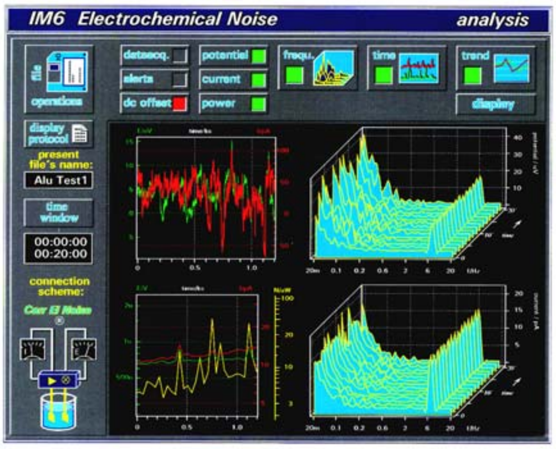
interference, are automatically suppressed.

As noise measurements normally have a long acquisition time there is a lot of data to be handled. The *NOISE* software allows to save measurement data in two ways: Normally the software reduces the flood of data by a factor of 260. Then you have access to the most often used analysis mode, the frequency spectrum of the noise signal. In addition the time-domain signal can be saved so that any other analysis method can be applied after the acquisition. Time-domain data are compressed with a factor of 8.

NOISE

Analysis

There are different types of analysis methods and corresponding online data reduction algorithms implemented in the *NOISE* software.



If maximum flexibility is needed to process the data in both time and frequency domain only a little data reduction should be done in order to avoid any loss of information. The adequate technique of the IM6 *NOISE* software is the ***Real Time Acquisition Mode***: The time course of potential and/or current is sampled with 8-fold oversampling. The signals will be limited in bandwidth online by a FIR filter which is responsible for an 8-fold decimation of the oversampled data. This reduced data stream is stored on harddisk in blocks of 2048 16-bit-words per channel. The time course will not be interrupted during acquisition. So, at a chosen bandwidth of 10 Hz, 80 bytes per second will be written for example. This sums to about 80 Mbytes per day. For monitoring purpose with acquisition periods of several days, in this mode the flood of data is too big.

Therefore well adapted online data reduction algorithms are implemented. The ***Frequency Acquisition Mode*** provides a data reduction by a factor of 260. The result is a representation of the noise data in the frequency domain. The 60 samples are equidistant in a logarithmic scale and correspond to the 2048 time domain samples.

For extremely long acquisition periods an even more effective data reduction is necessary. In the ***rms. Acquisition Mode*** the power frequency data are integrated to rms. values, yielding a reduction factor of 16384. A weighting filter can be used optionally to suppress defined interfering frequencies and to emphasize relevant areas. The same factor of data reduction (16384) is achieved by calculating the ***Standard Deviation*** from the time domain data.

While the acquisition is running, additional calculations can be done online. They are recorded as ***Alert Event Count***. There are various options to define those alert events. One class detects violations of reference values. They can be set for amplitudes, rms. or standard deviation. The second class does an on-line comparison with a reference signal by checking the cross-correlation amplitude against a reference value. A third class will register an alert event if the frequency spectrum envelopes are showing *pink noise* behavior.

With its sophisticated measurement and analysis methods the *NOISE* module for the electrochemical workstation IM6 will cause a big step forward in electrochemical noise applications.

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