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FAST IMPEDANCE ANALYSER FOR CORROSION MONITORING

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Abstract: *Frequency Response Analysers (FRA) are commonly employed to monitor the corrosion state of metallic antiquities. Commercial devices, though very accurate and versatile, are often rather costly and require a long time to complete the Electrochemical Impedance Spectroscopy (EIS). This paper describes a low cost and portable alternative to commercial FRAs that also embeds the potentiostatic function and therefore can be used in the field without requiring external devices. The proposed instrument is based on a compact DSP board and employs a sine-fit algorithm for the impedance measurement; the paper also describes a fast algorithm to obtain the results without requiring long measuring sessions. The proposed instrument automatically performs a simple coating test and is equipped with a digital interface so that it can be connected to a personal computer to carry out a complete frequency analysis and to perform more complex data processing.*

Keywords: Spectroscopy, Impedance measurement, Corrosion Monitoring.

1 INTRODUCTION

Metallic antiquities and works of art suffer from corrosion, which depends on environmental humidity and pollutants [1]. Several organic coatings have been proposed which exert a barrier effect against air, acid gases, oxygen and other aggressive pollutants. Unfortunately most common good coatings, which provide a durable protection, are often difficult to remove in case of necessity and this limits their use on valuable antiquities. Wax-based coatings are easy to remove and can be an interesting alternative, but their duration as well as protection efficiency needs to be tested at regular intervals.

Several techniques can be used to carry out these tests as well as to investigate the corrosion conditions of the surface. Among these techniques, the Electrochemical Impedance Spectroscopy (EIS) [2] is the only that can be carried out in the field with compact and portable instruments.

The EIS is carried out by contemporaneously employing an instrument referred to as Frequency Response Analyser in conjunction with a potentiostat, which is responsible for the DC polarisation. The EIS consists in the measurement of modulus and phase of the surface impedance of the metallic object whose coating has to be tested. The measurement is carried out by employing an electrochemical cell whose working electrode is the antiquity.

The stimulation voltage is composed of a small AC component superimposed to a DC voltage that is used to polarise the electrochemical interface. The stimulus is applied between the antiquity and the other electrode, which is referred to as counter electrode. A third electrode, referred to as reference electrode, is used to measure the actual stimulus applied to the coating, getting rid of the resistance between counter-electrode and solution. The potentiostat is used to keep the DC voltage between reference and working electrodes constant. The coating surface impedance $\mathbf{Z}_{RW}$ is obtained as the ratio between the applied voltage $\mathbf{V}_{RW}$ and the current $\mathbf{I}_{W}$ that flows through the cell.

The impedance is typically measured in the extended frequency range of 1 mHz to 100 kHz even though frequency ranges below 10 mHz and above 10 kHz are often considered of less importance for corrosion monitoring. The expected impedance, for cells having an electrode surface of 10 cm^2 on coated surfaces, is in the range of 10 kΩ to 10 GΩ.

2 BASICS OF THE PROPOSED EIS SYSTEM

The FRA the authors has designed does not require the measurement of the applied voltage $\mathbf{V}_{RW}$ and determines the unknown impedance by means of a substitution method. The AC stimulus voltage is applied in sequence to the cell and to a known standard resistor R_S. In the proposed circuit, the potentiostat circuitry (Fig. 1), in addition to the polarisation control, is used to ensure that the same voltage is applied between reference and working electrode and on the standard resistors. The two measured current values $\mathbf{I}_W$ and $\mathbf{I}_S$ can be employed to determine the impedance as:

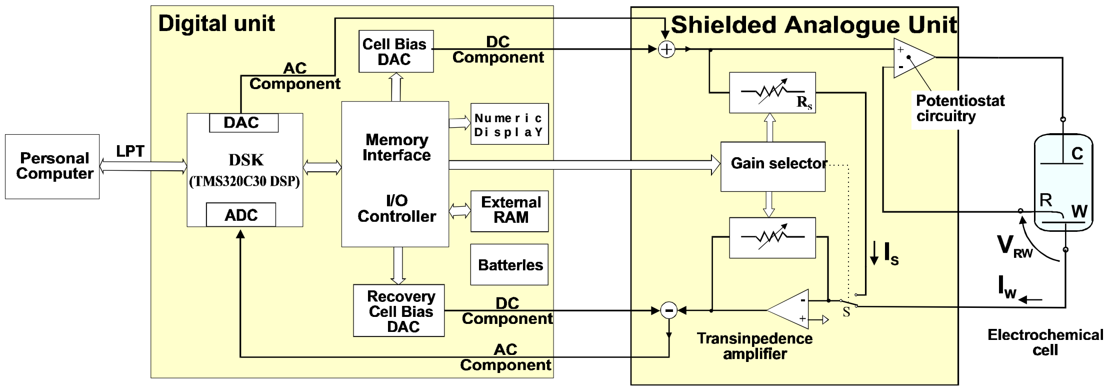

Figure 1. The block diagram of the EIS system.

$$\mathbf{Z}_{RW} = \frac{\mathbf{I}_S}{\mathbf{I}_W} R_S \qquad (1)$$

By using this technique, both the generated voltage and the actual measuring chain characteristics need not to be precisely known, and only one measuring systems is required, thus greatly simplifying the instrument design and lowering its cost.

The EIS is based on a completely digital technique: the stimulus is generated by means of a Digital to Analog Converter (DAC), while the currents are determined by processing a stream of samples acquired by an Analog to Digital Converter (ADC). Both converters run from the same clock, so that a synchronous acquisition is performed. This allows a simplified three-parameter sine-fit algorithm to be employed since the frequency is a-priori known. Offset A_0, sine A_S and cosine A_C components can be estimated from N samples as:

$$\left[\tilde{A}_0, \tilde{A}_S, \tilde{A}_C\right]^{\mathbf{t}} = \left(\mathbf{U}^{\mathbf{t}}\mathbf{U}\right)^{-1}\mathbf{U}^{\mathbf{t}}\mathbf{S} \qquad (2)$$

where **S** is the vector of samples and **U** is a matrix built as described in appendix A. Current amplitude $\tilde{A}$ and phase $\tilde{\varphi}$ can be eventually obtained as:

$$\tilde{A} = \sqrt{\tilde{A}_C^2 + \tilde{A}_S^2} \quad ; \quad \tilde{\varphi} = \tan^{-1}\left(\frac{\tilde{A}_C}{\tilde{A}_S}\right) + m\pi \qquad (3)$$

where m=-1, 0, +1 depending on $\tilde{A}_S$ and $\tilde{A}_C$ signs.

Eqn. 2 allows the estimation to be performed regardless of the observation duration, but, if the N samples span exactly an integer number of periods n_P, the estimation simplifies and a remarkable insensitivity with respect to the harmonic distortion is obtained. The estimation in this case becomes:

$$\tilde{A}_0 = \frac{1}{N}\sum_{i=0}^{N-1} S_i \quad ; \quad \tilde{A}_S = \frac{2}{N}\sum_{i=0}^{N-1} \sin(2\pi n_P \frac{i}{N}) \cdot S_i \quad ; \quad \tilde{A}_C = \frac{2}{N}\sum_{i=0}^{N-1} \cos(2\pi n_P \frac{i}{N}) \cdot S_i \qquad (4)$$

where S_i is the i-th acquired sample.

The described approach is quite effective with respect to both noise and distortion effects [3], but is sensitive with respect to non periodic signals and transient signals. The algorithm therefore needs to operate in the absence of transient and this requires a wait interval after changing the stimulation frequency in order to allow the transient component to vanish.

Problems related to the transient presence can be severe especially when poorly coated antiquities are tested. Good coatings can be approximately modelled as a small capacitor of the order of 1 nF and are characterised by a very high impedance. The time constant of the current transient is related to the output resistance of the stimulus generator and is very short, so that the transient vanishes after few milliseconds. Damaged coatings present some delaminated areas where pollutants can penetrate.

The electrochemical impedance of a damaged coating at low-frequency can be approximately modelled as in Fig. 2: R_S models the resistance of the solution that fills the pores of the coating and takes values in the range of some kiloohms; R_P models the resistance of the solution inside the delaminated areas and takes values in the range of some tens of kiloohms, and C_P models the double layer capacitance into the delaminated areas and takes values of several microfarads.

The electrochemical impedance in this case is:

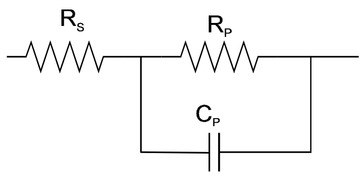

Figure 2. Low-frequency equivalent circuit for a damaged coating.

$$\mathbf{Z}(s) = R_S \frac{s+b}{s+a} \quad ; \quad a = \frac{1}{R_P C_P} \quad ; \quad b = \frac{R_S + R_P}{R_S R_P C_P} \tag{5}$$

The transient time constant of the current $\tau = 1/b$ (see appendix C) can easily become greater than one second, so that an intolerably long waiting time is required for the transient to vanish.

If an estimation of τ is available, the transient can be greatly reduced by employing a stimulus signal in the form of (appendix C):

$$v(t) = V_P \sin(2\pi ft + \varphi)u(t) \tag{6}$$

where $u(t)$ is the unit step, f is the stimulus frequency, and φ is the initial signal phase computed as:

$$\varphi = \tan^{-1}(2\pi f \tau) \tag{7}$$

This kind of stimulus has another advantage: if it is applied on an integral number of half-periods, it does not generate transients at signal end so that a new stimulus, with a different frequency, can be applied immediately, without having to wait for the circuit to settle.

The low-transient stimulus signal can therefore be expressed as:

$$v(t) = V_P \sin(2pft + j)\left(u(t) - u\left(t - \frac{n_h}{2f}\right)\right) \tag{8}$$

where n_h is the number of half periods generated.

The shortest stimulus, which can be applied without generating large transients, has therefore duration equal to half a period. By employing such short signals, and in the absence of waiting time between measurements, the EIS can become rather fast, but two problems arise that are related to the possible signal distortion and to the uncorrected transients.

When the sine-fit algorithm is employed to estimate amplitude and phase on half period signals, its insensitivity with respect to the distortion disappears. The worst effect is due to the second harmonic that can produce errors on the estimated amplitude values twice its relative amplitude. Fortunately, the actual signal distortion and therefore the expected estimation errors can be evaluated by performing a simplified Discrete Fourier Transform of the sine-fit residual:

$$\mathbf{R} = \mathbf{S} - \mathbf{U} \cdot \left[\tilde{A}_0, \tilde{A}_S, \tilde{A}_C\right]^t \tag{9}$$

The transient cancellation depends on the accuracy of the estimation of the zero position and on the ratio between the estimation frequency and the zero frequency $f_b = \frac{1}{2\pi\tau}$. Fig. 3 shows the errors on estimated impedance amplitude and phase as a function of the error of the zero position in the worst case of $R_P >> R_S$. Errors are maximum for stimulus frequencies close to the zero frequency: amplitude errors of about 10% and phase errors of about 10° are expected for a 30% error in the zero frequency estimation. If the zero is not correctly estimated, the current ends with transient whose amplitude is related

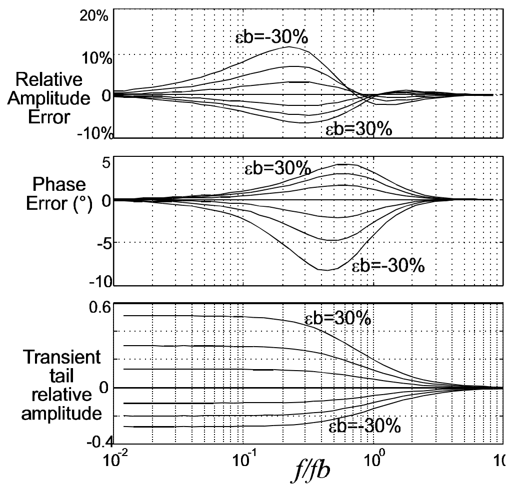

Figure 3. Effects of an error in the hypothesised zero position.

to the error in the zero position estimation. The analysis of such a transient may allow one to estimate zero error sign and value and to estimate the error on impedance amplitude and phase. Bottom traces of Fig. 3 show the expected ending transient tail amplitude as a function of the error in the zero position. One should note that the traces shown in Fig. 3 can be used as a rough, though reasonable, estimation even though the actual coating behaviour cannot be exactly modelled by the system of Eqn. 5

The zero position can be estimated by starting the measurement session from the higher frequencies and extrapolating amplitude and phase traces from the already determined points. The estimation can then be refined both using the new measured points and by applying correction related to the amplitude of the ending transient. In addition, a loop could be designed to adjust the zero estimation until the tail amplitude decreases below a predefined threshold, even though the time required for the loop execution should waste most of the speed gain achieved with the proposed solution.

3 EIS PROTOTYPE

A prototype of the EIS has been arranged according to the block diagram of Fig. 1 by employing a commercial board from Texas Instruments (DSK C30) which contains a floating point processor (TMS320C30 DSP) and an Analog Interface Circuit that embeds a 14 bit DAC and a 14 bit ADC. The prototype is split into two sections allocated inside two separate containers (see Fig. 4)

The Digital unit contains the DSK, an external 32kWord memory, an alpha-numeric display, and two additional DACs. One DAC (cell bias DAC) is employed to supply the DC component of the stimulus signal, and the other (recovery cell bias DAC) to remove the DC component from the acquired signal. In addition, the digital unit contains a set of rechargeable batteries and a parallel interface, which is used for PC connection.

The shielded analogue unit contains the potentiostat circuitry, the variable gain input amplifiers, and the standard resistors used for the substitution measurement.

The electrochemical cell used for the tests is also shown in Fig. 4. It is composed of a plexiglas basement and a plexiglas cylinder. The sample whose coating has to be tested is inserted between cylinder and basement and the cylinder is filled with the electrolytic solution. Reference and Counter electrodes are inserted from the top of the cylinder.

4 EXPERIMENTAL RESULTS

A preliminary characterisation has been carried out by measuring a known network that simulates the electrochemical impedance of a damaged coating (Fig. 5).

The network parameters has been chosen to describe a 12 μm thick, damaged coating, with permittivity ε_r=5, and 1% of delaminated surface. The cell surface has been set to 10 cm^2 and the solution resistivity to 2 $k\Omega \cdot cm^2$, therefore obtaining:

- R_S= 400 Ω (counter/reference solution resistance);
- Cp_2= 5 nF (coating capacitance);
- R_P=20 kΩ (solution resistance inside delaminated areas);
- R_{S2}= 10 kΩ (pore resistance, corresponding to three delaminated areas, pores of 20 μm diameter

Figure 4. The frequency response analyser.

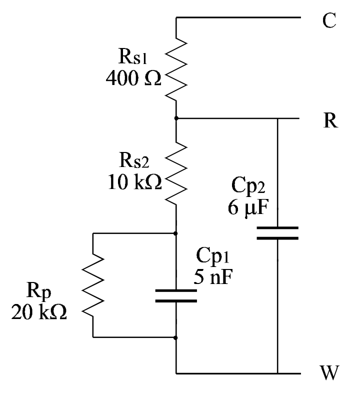

Figure 5. Electric equivalent circuit of a damaged coating.

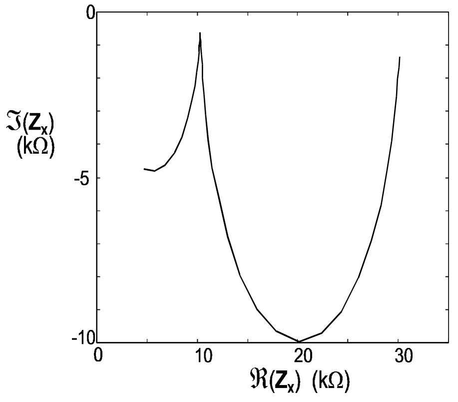

Figure 6. Nyquist plot for a delaminated coating.

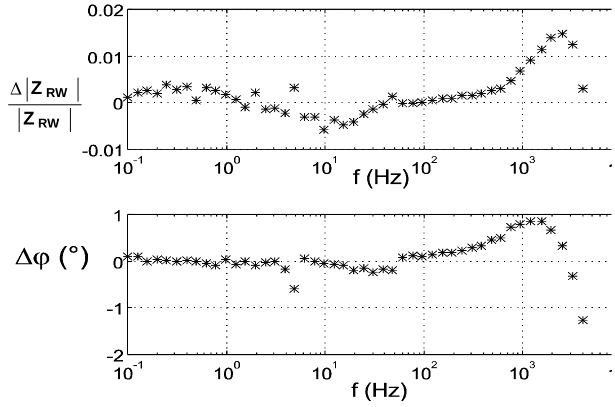

Figure 7. Amplitude and phase errors.

and solution conductance of 0.01 S·cm^{-1});

- C_{P1}= 6 µF (double layer capacitance for specific capacitance of 60 $\mu F \cdot cm^{-1}$).

Figs. 6 and 7 shows the obtained results and the difference with respect to the values obtained by means of a impedance analyser, which amplitude and phase uncertainties are about 0.2% and 0.2°. Amplitude and phase differences below 2% and 1° have been obtained in the entire frequency range.

5 CONCLUSIONS

A low-cost and portable instrument that can be used to monitor the coating status of metallic antiquities and works of art has been described in this paper. The proposed instrument implements a complete EIS system providing both the Frequency Response Analyser and the potentiostat. Uncertainty of some percent on the amplitude and of a few degrees on the phase are obtained in the frequency range of 0.1 Hz to 5 kHz by employing a sine-fit algorithm that can operate on half signal period. A model of the impedance is estimated and updated during the measurement process and used to adjust the stimulation signal, thus reducing the transients to a low value and speeding up the complete measurement process that lasts less than one minute.

APPENDIX A: Sine-fit (integer number of periods)

A sinusoidal biased signal with frequency f can be written as a sum of a sinusoidal, a cosinusoidal and an offset component:

$$s(t) = A_0 + A_C \cos(2\pi ft) + A_S \sin(2\pi ft) \tag{10}$$

where A_0, A_S and A_C are the offset, the sinusoidal and cosinusoidal parameters. If N samples $S_0, \ldots, S_{N-1}$ of s(t) are obtained at frequency fs, the parameters A_0, A_S and A_C can be estimated by means of a three parameters sine-fit algorithm [4]:

$$\left[\tilde{A}_0, \tilde{A}_S, \tilde{A}_C\right]^{\mathbf{t}} = \left(\mathbf{U}^t\mathbf{U}\right)^{-1}\mathbf{U}^t\mathbf{S} \tag{11}$$

where

$$\mathbf{U} = \begin{bmatrix} 1 & 0 & 1 \\ 1 & \sin(k) & \cos(k) \\ \vdots & \vdots & \vdots \\ 1 & \sin((N-1)k) & \cos((N-1)k) \end{bmatrix} \quad ; \quad \mathbf{S} = [S_0, S_1, \ldots, S_{N-1}]^t \quad ; \quad k = 2\pi\frac{f}{f_S} \tag{12}$$

Eqn. 4 is obtained from Eqn. 11 if the N samples span an integer number of periods

APPENDIX B: Sine-fit (half period)

If the N samples are acquired on a half period of the signal so that $(N-1)k = \pi$, then:

$$\left(\mathbf{U}^t\mathbf{U}\right)^{-1} = \begin{bmatrix} c_{11} & c_{12} & 0 \\ c_{21} & c_{22} & 0 \\ 0 & 0 & c_{33} \end{bmatrix} \tag{13}$$

where:

$$c_{11} = \frac{(N-1)/2}{\Delta} \quad ; \quad c_{12} = c_{21} = -\frac{\mathrm{ctg}\left(\frac{\pi}{2(N-1)}\right)}{\Delta} \quad ; \quad c_{22} = \frac{N}{\Delta} \quad ; \quad c_{33} = \frac{2}{(N-1)} \tag{14}$$
$$\Delta = \frac{(N-1)N}{2} - \mathrm{ctg}^2\left(\frac{\pi}{2(N-1)}\right)$$

The estimated sinusoidal parameters became

$$\tilde{A}_0 = \sum_{i=0}^{N-1}\left(c_{11} + c_{12}\sin\left(\pi\frac{i}{N-1}\right)\right)S_i$$
$$\tilde{A}_S = \sum_{i=0}^{N-1}\left(c_{21} + c_{22}\sin\left(\pi\frac{i}{N-1}\right)\right)S_i \quad ; \quad \tilde{A}_C = \sum_{i=0}^{N-1} c_{33}\cos\left(\pi\frac{i}{N-1}\right)S_i \tag{15}$$

APPENDIX C: Time response of a zero-pole impedance

If an impedance $\mathbf{Z}(s) = R_S\frac{s+b}{s+a}$ is stimulated with a voltage signal $v(t) = V_P\sin(\omega t + \varphi)u(t)$, the current signal is composed of a transient component $i_T(t)$ and a permanent regime component $i_{PR}(t)$: $i(t) = i_{PR}(t) + i_T(t)$, where:

$$i_{PR}(t) = \frac{V_P}{R_S}\sqrt{\frac{w^2 + a^2}{w^2 + b^2}}\sin(wt + j + a)u(t)$$
$$a = \tan^{-1}(w/a) - \tan^{-1}(w/b) \tag{16}$$
$$i_T(t) = \frac{V_P}{R_S}\frac{a-b}{b^2+w^2}w\cos j\left[1 - \frac{b}{w}\tan j\right]e^{-bt}u(t)$$

The transient component nullifies if stimulus phase is

$$j = \tan^{-1}\left(\frac{w}{b}\right) \tag{17}$$

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