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## **Comparison of EIS and Ramlog Measurements of Spread Resistance and Polarisation Impedance for Steel Exposed in Artificial Soil Solutions with and without Scaling Capacity at 50 Hz AC**

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### **Keywords:**

*Electrochemical Impedance Spectroscopy (EIS), Ramlog recordings, spread resistance, polarisation impedance*

### **Abstract**

Comparative studies on the applicability of electrochemical impedance spectroscopy and the Ramlog recording instant OFF technique have been made in two 120-h parallel experiments conducted in a scaling solution as well as a non-scaling solution.

The AC current measured by the Ramlog technique correlated fine with measurements using a Fluke multimeter.

In accordance with established DC polarisation curves, calculations from the Ramlog recordings showed that the polarisation impedance decreased throughout time in the scaling environment but remained constant in the non-scaling environment.

Exact calculation of the spread resistance cannot be done from the Ramlog recordings, however, quite accurate assessments (accuracy > 80%) can be made at 50 Hz. In comparison, the degree of accuracy obtained for measurements of the spread resistance using a frequency around 108 Hz were only improved by a few percent. Consequently, the Ramlog recordings provide a quite fair assessment of the spread resistance in particular when bearing in mind that the spread resistance may vary within several orders of magnitude in practice.

## Introduction

Electrochemical impedance spectroscopy (EIS) has previously been used with a certain success to describe the ohmic resistance – or spread resistance –  $R_s$  of an electrode system as well as the polarisation conditions for said electrode. However, the EIS technique cannot be used to monitor the change of these quantities directly throughout time during an experiment in which an electrode is subjected to a DC- and AC load.

Instant OFF techniques applied continuously throughout an experiment in which a sample is subjected to DC and AC may provide some information regarding these quantities.

The aim of the present study was to make a comparison between spread resistance measured by EIS and calculated from an instant OFF technique (the Ramlog Correal recorder) as well as the polarisation conditions assessed from these two techniques. The comparative study was made in solution with a scaling capacity (i.e. the spread resistance was expected to increase throughout the test period), as well as in solution without scaling capacity (no increase in spread resistance).

## Experimental

Two parallel experiments were conducted throughout a 120h period. The set-ups of these experiments were identical. Traditional electrochemical three-electrode arrangements were assembled in 2-liter glass vessels each equipped with a 1-cm<sup>2</sup> steel sample as working electrode, a large (500 cm<sup>2</sup>) titanium-mesh as counter electrode, and a saturated calomel electrode (SCE, +242 mV vs. SHE) as reference electrode.

One experiment was conducted in a solution with chemical composition according to table 1. It was expected in advance that when cathodically protecting the steel sample, hydroxides and perhaps carbonates of the earth-alkaline cations would precipitate on the steel surface.<sup>1</sup> This solution is accordingly denoted “scaling solution”. The initial pH was measured to be around 7.8, whereas the initial conductivity was around 1900  $\mu\text{S/cm}$ .

Component	Concentration (mg/L)	Concentration (mol/L)
MgSO <sub>4</sub> , 7H <sub>2</sub> O	617	$2.5 \cdot 10^{-3}$
CaSO <sub>4</sub> , 2H <sub>2</sub> O	430	$2.5 \cdot 10^{-3}$
NaHCO <sub>3</sub>	210	$2.5 \cdot 10^{-3}$
CaCl <sub>2</sub>	554	$5.0 \cdot 10^{-3}$

*Table 1. Chemical composition of the scaling solution. Initial pH = 7.8, initial conductivity = 1900  $\mu\text{S/cm}$ .*

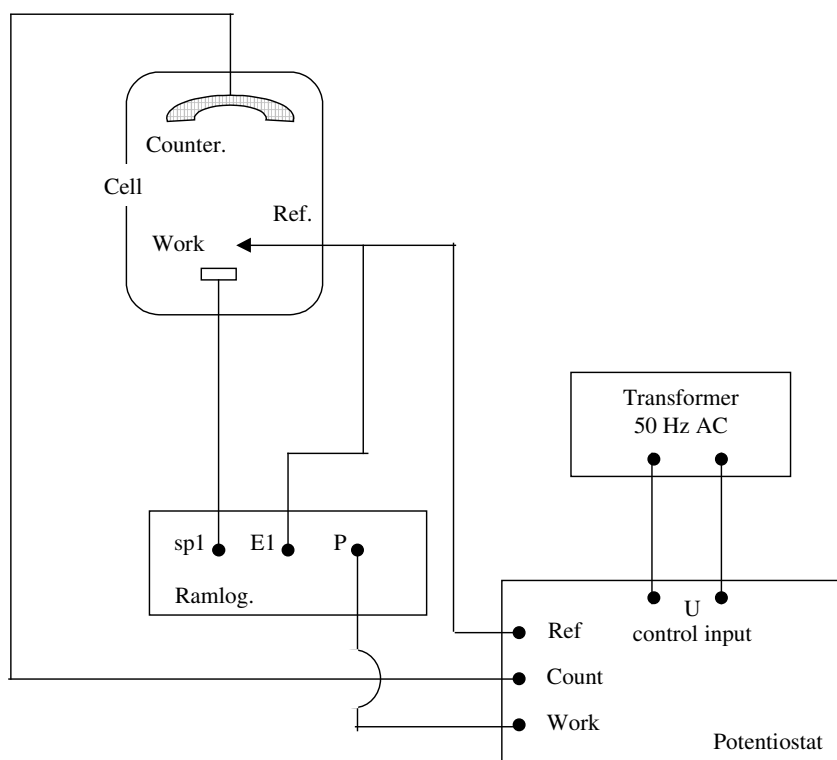
The other experiment was conducted in a chemical solution according to table 2. This solution is identical to the scaling solution with respect to concentration of an-ions, however, earth-alkaline cat-ions (Mg, Ca) were replaced by Na instead. It was expected in advance that this solution did not have the same scaling potential,<sup>1</sup> and the solution is accordingly denoted “non-scaling solution”. The initial pH was measured to be around 8.2, whereas the initial conductivity was around 2530  $\mu\text{S}/\text{cm}$ .

Component	Concentration (mg/L)	Concentration (mol/L)
$\text{Na}_2\text{SO}_4$	710	$5.0 \cdot 10^{-3}$
$\text{NaHCO}_3$	210	$2.5 \cdot 10^{-3}$
$\text{NaCl}$	585	$1.0 \cdot 10^{-2}$

*Table 2. Chemical composition of the non-scaling solution. Initial pH = 8.2, initial conductivity = 2530  $\mu\text{S}/\text{cm}$ .*

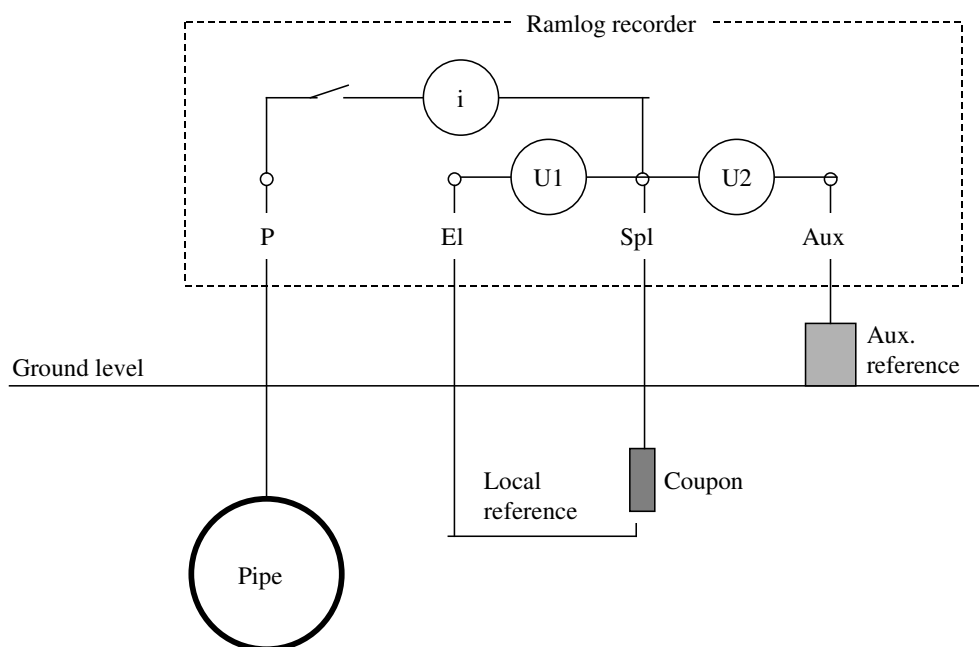
Both solutions were purged with nitrogen gas throughout the test period.

The steel samples were controlled to a DC offset potential of  $-850 \text{ mV SCE}$  using a conventional potentiostat. This DC-offset was superimposed by an AC voltage of 2 V (RMS) by connecting a transformer to the potentiostat. The applied electrical circuit is sketched in figure 1.



*Figure 1. The electrical wiring diagram used to control the electrical conditions on the working electrodes.*

Throughout the experimental period, the average ON-potential, instant OFF-potential and instant current values were followed using a Ramlog recorder, the applicability of which has been presented by Pourbaix et al.<sup>2</sup> The Ramlog recorder was originally designed for recording the said electrical conditions for a coupon connected to a pipeline by inserting the Ramlog in-between the pipe and the coupon as illustrated in figure 2. The Ramlog recorder is equipped with four terminals; P connected to the pipe, E1 connected to a local reference electrode placed nearby the coupon, Sp1 connected to the coupon, and Aux connected to an auxiliary reference placed on ground. In principle, the P and Sp1 terminals are connected allowing for current to flow between the pipe to the coupon. At certain programmable time intervals, the connection is instantly disrupted for a short period of time, allowing for the instant OFF potential of the coupon to be measured. Figure 3 illustrates the Ramlog measuring cycle as it is presented in the manual.<sup>3</sup>



*Figure 2. Schematic illustration of the principle of the Ramlog recorder.*

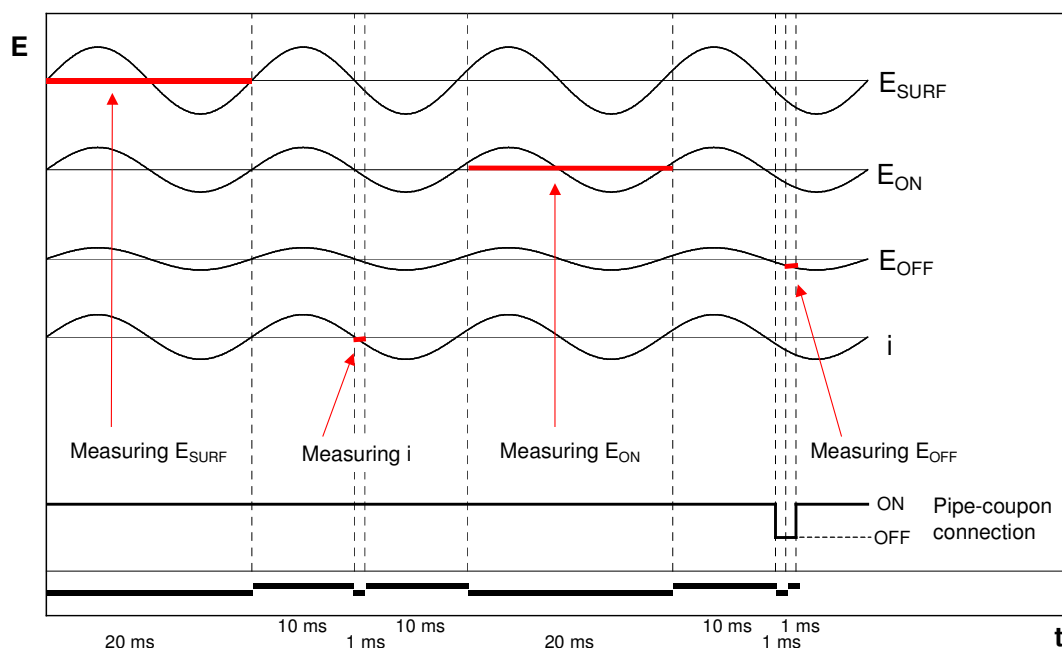


Figure 3. Ramlog recorder measuring cycle. Redrawn from manual.<sup>3</sup>

One cycle of measurements has duration of 73 milliseconds (ms). During the initial 20 ms (corresponding one cycle of 50 Hz AC), 300 measurements of the ON potential is measured with respect to the auxiliary reference electrode and the average. After a 10 ms stabilisation period the current is measured during a 1 ms period. The current so measured then becomes an approximated instant value. After another 10 ms of stabilisation, the average ON potential is then measured over a 20 ms period (one cycle of 50 Hz AC). After yet another 10 ms of stabilisation, the current (pipe-coupon connection) is disrupted for two ms in order to obtain an IR-free measurement of the instant OFF potential made during the last ms with respect to the local reference.

In the present study, the Ramlog recorder was connected as illustrated in figure 1. The auxiliary reference electrode terminal was not in action. Measurements according to the measuring cycle were made every 5 minutes throughout the 120h test period.

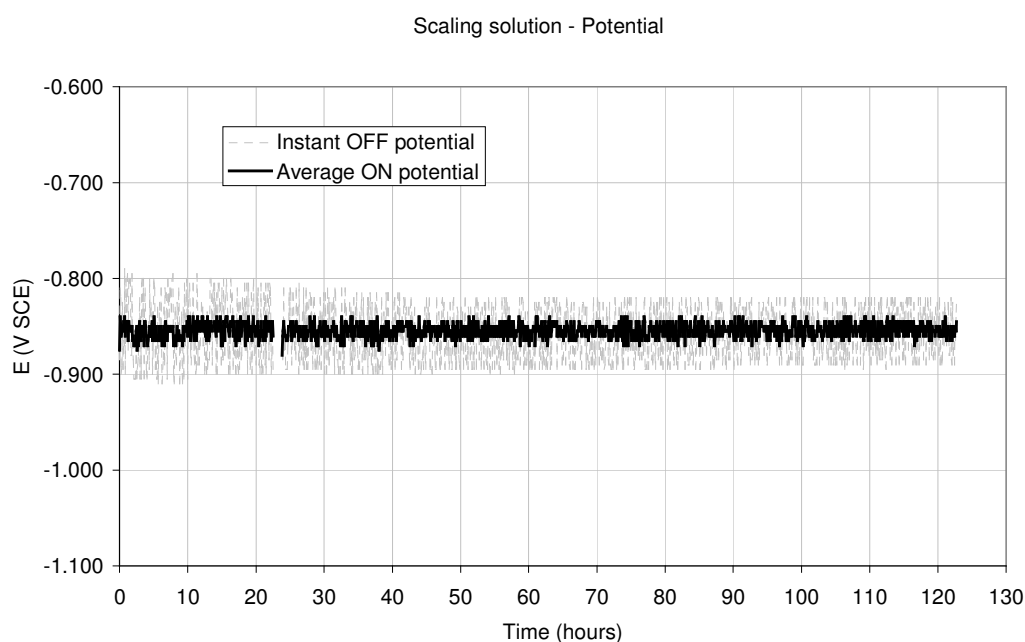
Electrochemical impedance spectroscopy (EIS) measurements were made prior to imposing the electrical conditions on the coupons, after some 20 hours of test (electrical circuit disconnected throughout the test), and at the end of the test. All EIS measurements were made at  $-850$  mV DC offset potential and with amplitude of 10 mV. At the same times, DC polarisation curves were established in the ON-potential region  $-1500$  mV to 0 mV by holding the potential fixed in steps of 100 mV and recording the current throughout five minutes at each step. Both DC curves and EIS measurements were performed with Gamry equipment.

Frequently throughout the test period, the AC-voltage and AC-current was measured using a Fluke multimeter.

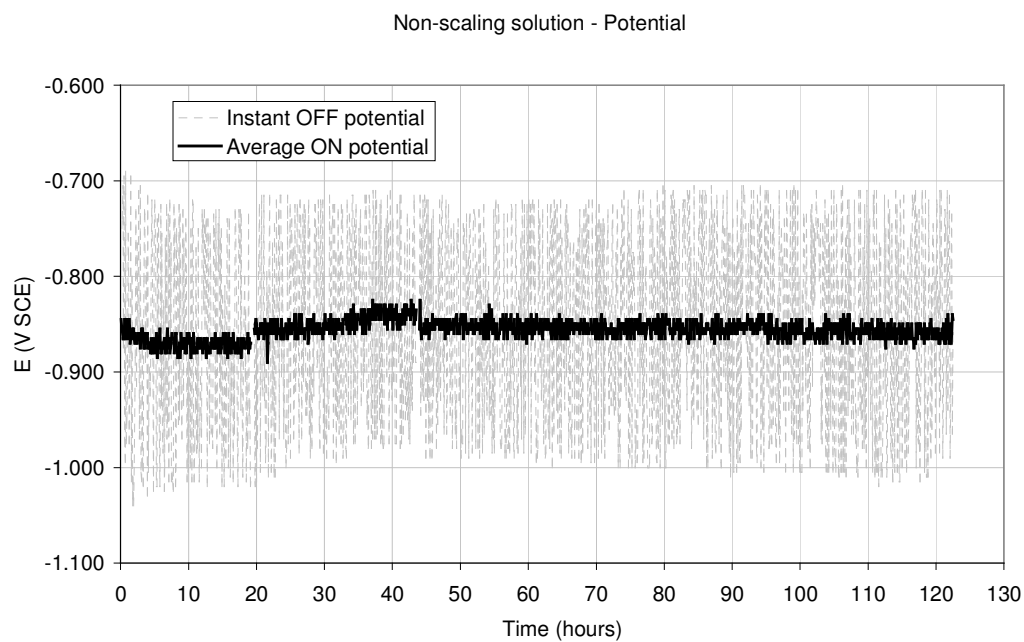
## Results

The Ramlog potential recordings made throughout time is shown in figure 4 (scaling solution), and figure 5 (non-scaling solution). The corresponding Ramlog current recordings are shown in figures 6 and 7 respectively.

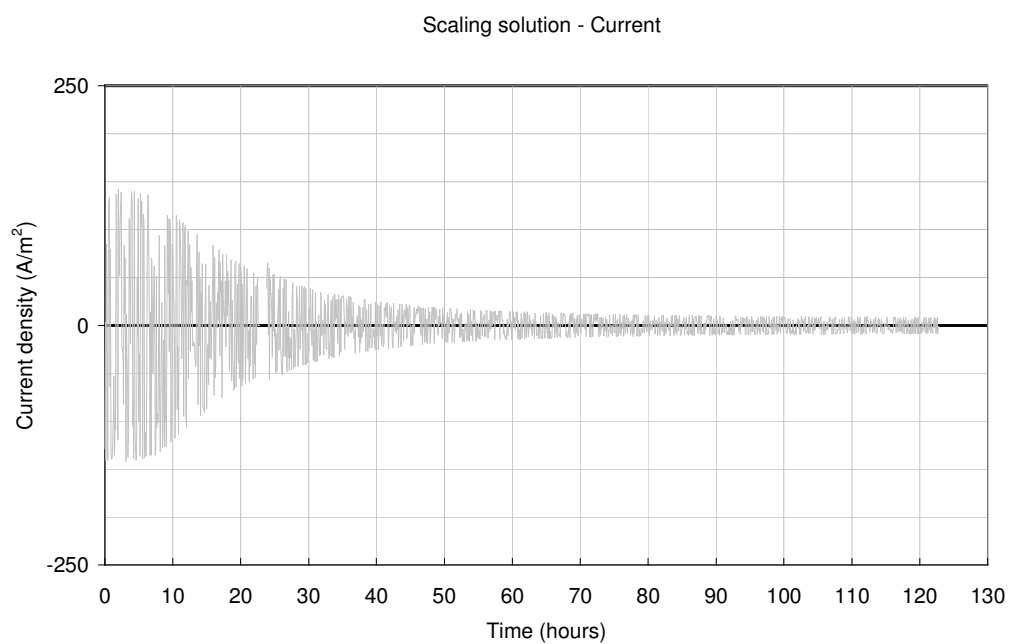
The Ramlog current recordings in particular show a fundamentally different behaviour between the scaling- and the non-scaling solution. In the scaling solution the current decreases considerable throughout the test period, whereas the current is fairly constant in the non-scaling solution.



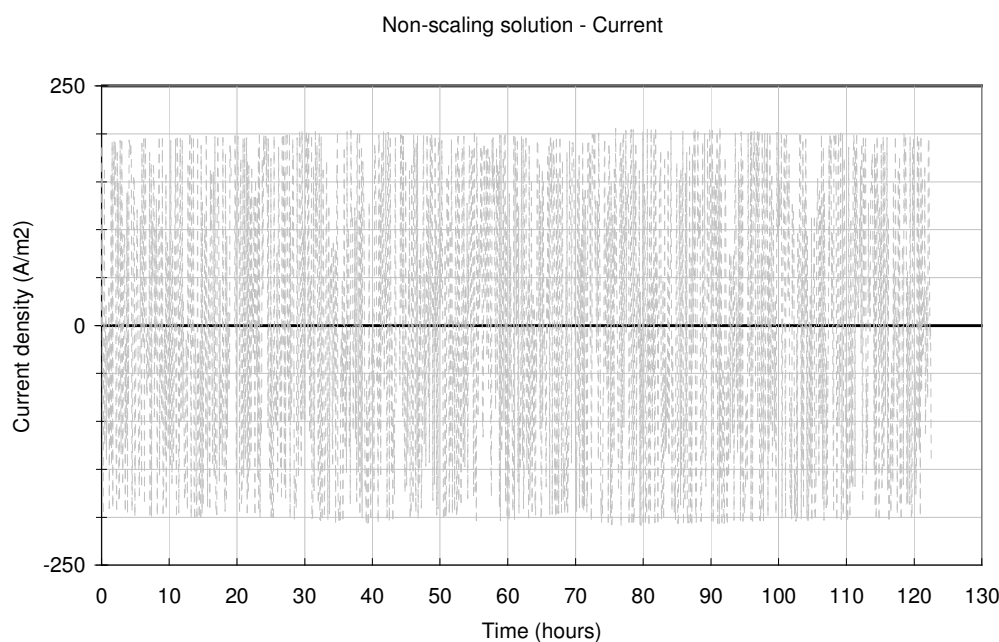
*Figure 4. Ramlog potential measurements – scaling solution.*



*Figure 5. Ramlog potential measurements – non-scaling solution.*



*Figure 6. Ramlog current measurements – scaling solution.*



*Figure 7. Ramlog current measurements – non-scaling solution.*

The electrochemical impedance measurements are presented in figure 8 (Nyquist plots for both solutions) and in figure 9 (Bode plots for both solutions).

In the Nyquist plots are indicated general diffusion tails in all experiments. In the scaling solution, an increase in ohmic resistance is indicated in particular for the 120h test. Both plots are kept in the same scale to indicate that the impedance in general is higher in the scaling environment.

The increase in ohmic resistance is more evident from the Bode plots, showing that the increase in the scaling environment is found also from the 0h test to the 20h test. In the non-scaling environment it is clear that no increase in ohmic resistance takes place. In all cases, the diffusion tail at lower frequencies is sustained, since the phase does not find distinct maximum value as in a completely activation controlled processes. Local maximum values indicate presence of an activated reaction followed by diffusion control at lower frequencies.



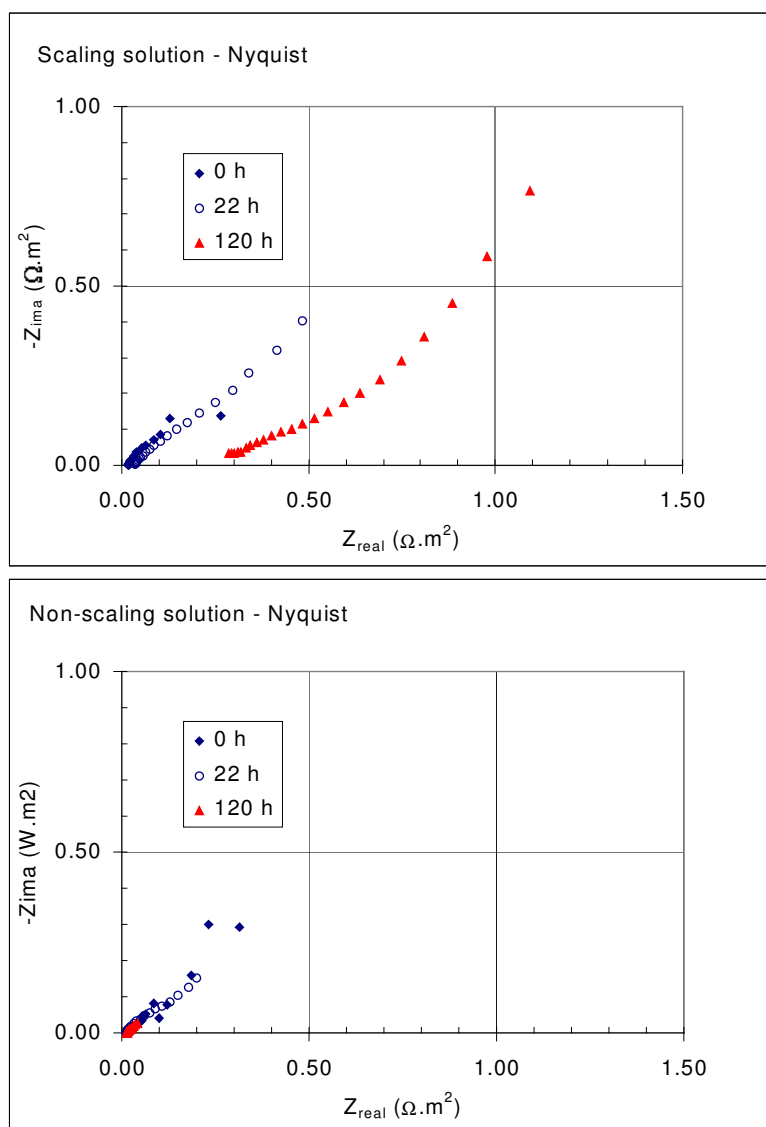


Figure 8. Nyquist plots resulting from EIS measurements. Scaling solution (upper) and non-scaling solution (lower).

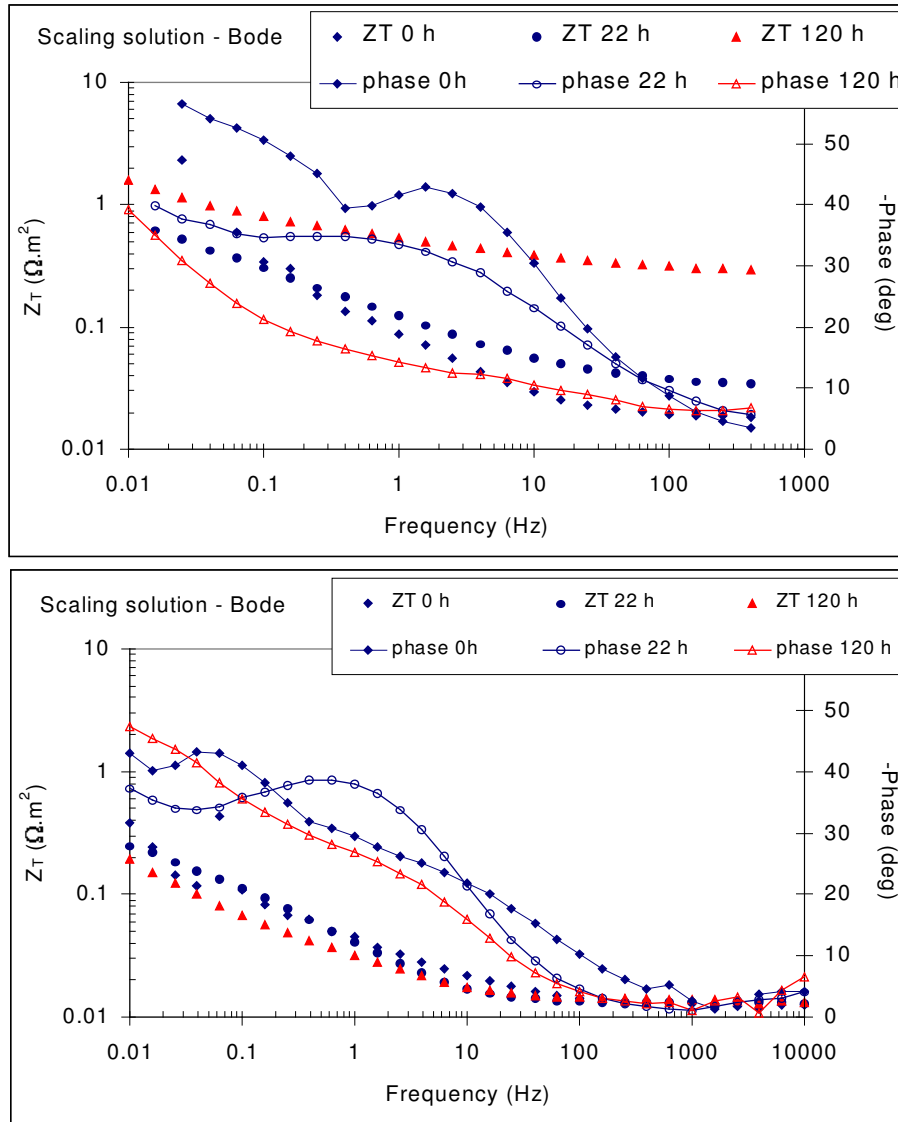


Figure 9. Bode plots resulting from EIS measurements. Scaling solution (upper) and non-scaling solution (lower).

Tables 3 (scaling solution) and 4 (non-scaling solution) draw out some characteristics of the EIS measurements.  $R_s$  is the ohmic resistance (spread resistance) extracted at high frequency. In addition, real part ( $Z_R$ ), imaginary part impedance ( $-Z_i$ ), and total impedance ( $Z_T$ ), as well as corresponding phase is given for different frequencies in the 50 Hz region. These quantities are outlined for the discussion. The capacitance estimations are made according to the equation:

$$C = \frac{1}{2 \cdot \pi \cdot f \cdot (-Z_i)} \quad (1)$$

The usual way of assessing the capacitance requires the total impedance at the maximum phase, but since the maximum phase is not quite clear in all experiments, the assessment has been made according to (1).

Time Hours	$R_s$ $\Omega.m^2$	Freq. Hz	$Z_R$ $\Omega.m^2$	$-Z_i$ $\Omega.m^2$	$Z_T$ $\Omega.m^2$	-Phase degrees	C F/m <sup>2</sup>
0	0.0184	40	0.0205	0.0055	0.0212	15.1	0.72
0	same	63	0.0198	0.0041	0.0203	11.6	0.62
0	same	100	0.0192	0.0029	0.0194	8.8	0.55
0	same	158	0.0188	0.0020	0.0189	6.1	0.50
22	0.0348	40	0.0409	0.0103	0.0422	14.0	0.39
22	same	63	0.0390	0.0079	0.0398	11.4	0.32
22	same	100	0.0371	0.0064	0.0377	9.7	0.25
22	same	158	0.0362	0.0050	0.0365	7.9	0.20
120	0.2897	40	0.3315	0.0473	0.3348	8.1	0.08
120	same	63	0.3201	0.0391	0.3225	7.0	0.06
120	same	100	0.3106	0.0356	0.3127	6.5	0.04
120	same	158	0.3025	0.0336	0.3043	6.3	0.03

Table 3. Characteristic EIS quantities (scaling solution).

Time Hours	$R_s$ $\Omega.m^2$	Freq. Hz	$Z_R$ $\Omega.m^2$	$-Z_i$ $\Omega.m^2$	$Z_T$ $\Omega.m^2$	-Phase degrees	C F/m <sup>2</sup>
0	0.0124	40	0.0157	0.0043	0.0163	15.3	0.92
0	same	63	0.0148	0.0033	0.0151	12.7	0.77
0	same	100	0.0140	0.0025	0.0142	10.2	0.63
0	same	158	0.0135	0.0019	0.0137	8.0	0.53
22	0.0133	40	0.0139	0.0022	0.0141	9.1	1.81
22	same	63	0.0135	0.0015	0.0136	6.4	1.68
22	same	100	0.0134	0.0011	0.0135	4.5	1.45
22	same	158	0.0133	0.0007	0.0133	3.1	1.44
120	0.0132	40	0.0148	0.0019	0.0150	7.2	2.09
120	same	63	0.0146	0.0014	0.0147	5.6	1.80
120	same	100	0.0144	0.0010	0.0144	4.1	1.59
120	same	158	0.0143	0.0008	0.0143	3.1	1.26

Table 4. Characteristic EIS quantities (non-scaling solution).

Figure 10 shows the polarisation curves obtained for both solutions throughout the test period. Again, a quite different development takes place in the two environments.

In the scaling environment, the current in general decreases throughout time indicating ever-increasing effect of the ohmic resistance. In contrast, the potential-current characteristics are fairly stable in the non-scaling environment.

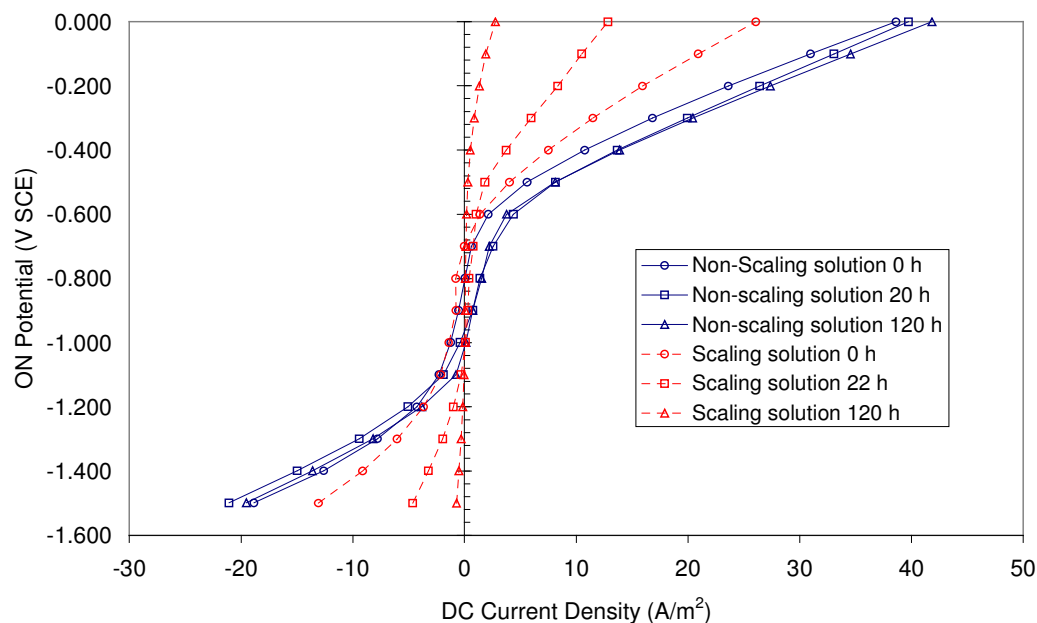


Figure 10. DC-polarisation curves in the scaling- and in the non-scaling solution.

Table 5 shows the multimeter measurements made occasionally during the tests. As observed, the AC voltage remains stable (as programmed into the potentiostat). The AC current decreases steady in the scaling environment, but stays fairly constant in the non-scaling environment. It is noted that a control measurement of the solution conductivity after the tests showed no decrease as compared with prior to the tests in any of the solutions.

Time Hours	Scaling solution		Non-scaling solution	
	$U_{AC,ON}$ (RMS)	$I_{AC}$ (RMS)	$U_{AC,ON}$ (RMS)	$I_{AC}$ (RMS)
	V	A/m <sup>2</sup>	V	A/m <sup>2</sup>
0	2.0	105	2.0	143
20	2.0	48	2.0	144
44	2.0	16	2.0	146
70	2.0	9	2.0	141
120	2.0	6	2.0	137

Table 5. Multimeter measurements of the AC conditions throughout test period.

## Discussion

From the Ramlog current recordings (figures 6 and 7) the RMS AC current density can be calculated according to the equation:

$$i_{AC,RMS} = \frac{\max(i_n \dots i_{n+x}) - \min(i_n \dots i_{n+x})}{2 \cdot \sqrt{2}} \quad (2)$$

where  $\max(i_n \dots i_{n+x})$  and  $\min(i_n \dots i_{n+x})$  denotes the maximum and minimum current respectively measured throughout  $x$  current measurements. Dividing this value by 2 gives the current amplitude, and dividing by  $\sqrt{2}$  gives the RMS value. In the present case, the calculation has been made from the spreadsheet to which all Ramlog measurements are transferred. The RMS AC current at time  $t$  has been found based on the maximum- and minimum current values in the time interval  $\pm 1$  hour from  $t$ . Since recordings are made every 5 minutes, the total number of recordings ( $x$ ) involved in the establishment of the RMS current value is 25.

The results of this procedure is shown in figure 11 (both solutions), in comparison with the multimeter measurements. A quite good correlation is shown. Again, the decrease in the current density in the scaling environment is obvious.

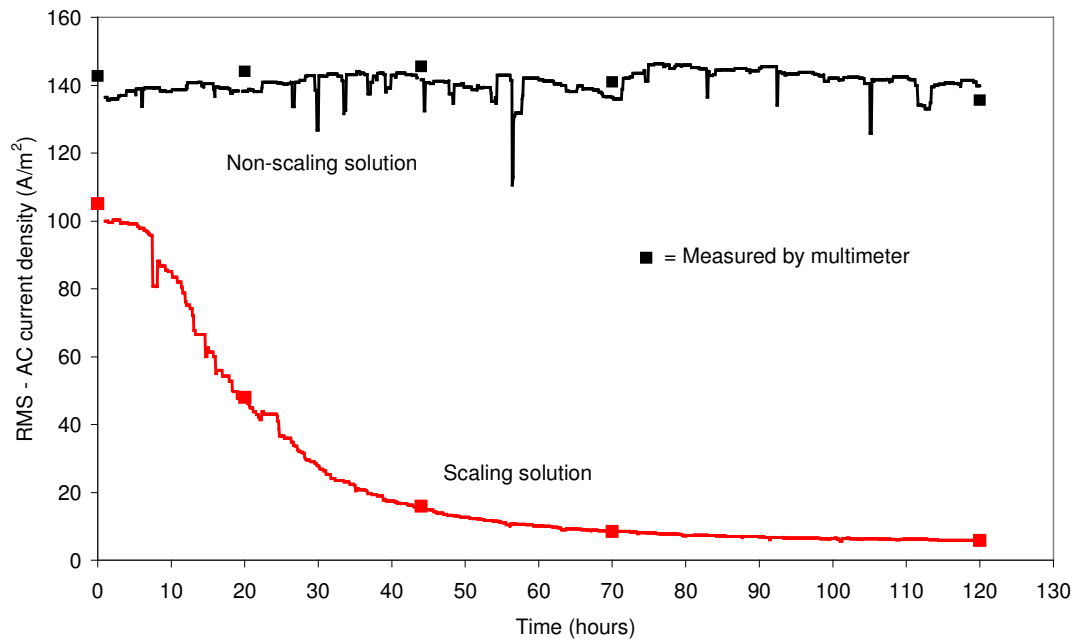


Figure 11. Comparison of the Ramlog current recordings with multimeter measurements.

The total impedance  $Z_T$  of the electrodes can be calculated according to equation 3:

$$Z_T (\Omega \cdot m^2) = \frac{U_{AC,ON} (V)}{i_{AC} (A/m^2)} \quad (3)$$

In this equation,  $U_{AC,ON}$  is the controlled AC voltage (2 V RMS). The AC current density refers to measurements by the multimeter, or the values established from Ramlog recordings (figure 11). Figure 12 illustrate the development in total electrode impedance throughout time based on the Ramlog measurements.

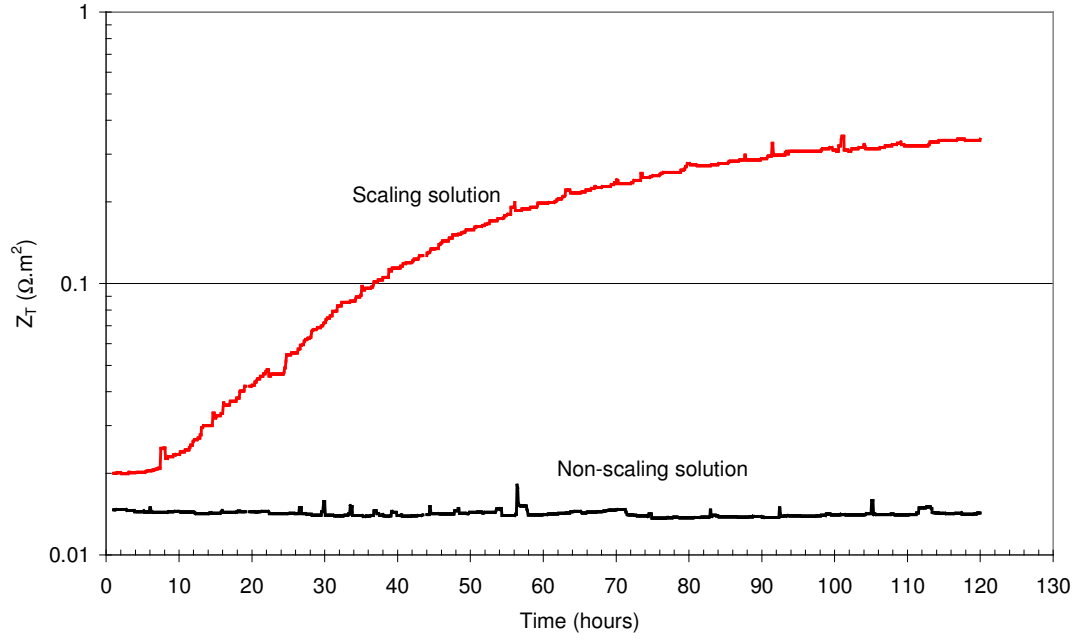


Figure 12. Total electrode impedance throughout time based on Ramlog measurement.

As observed, the total electrode impedance increases by more than a decade in the scaling environment, whereas no detectable increase is found in the non-scaling environment.

Similar to the RMS AC current, the IR-free RMS AC voltage ( $U_{AC,OFF,RMS}$ ) can be calculated according to the equation:

$$U_{AC,OFF,RMS} = \frac{\max(E_{OFF,n} \dots E_{OFF,n+x}) - \min(E_{OFF,n} \dots E_{OFF,n+x})}{2 \cdot \sqrt{2}} \quad (4)$$

Figure 13 shows the results of this procedure (both solutions).

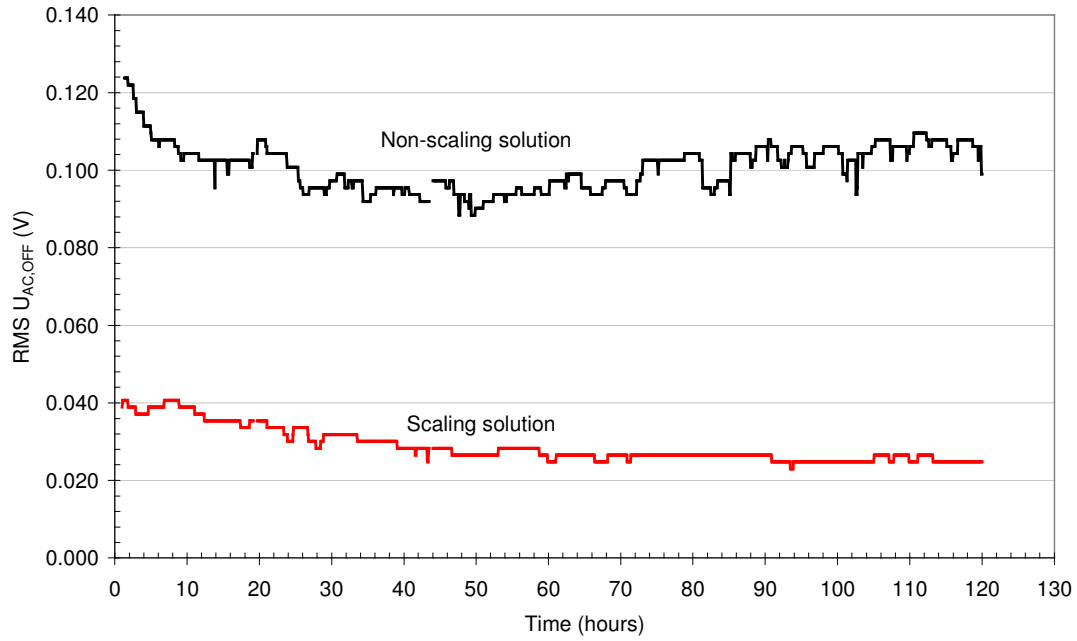


Figure 13. RMS AC (OFF) voltage established from the Ramlog measurements.

Both solutions show a fairly stable  $U_{AC,OFF,RMS}$  throughout time, however, considerably lower (1/3) in the scaling solution.

Dividing the  $U_{AC,OFF,RMS}$  values so established by the  $i_{AC,RMS}$  values established in figure 11 gives the polarisation impedance:

$$Z_p = \frac{U_{AC,OFF,RMS}}{i_{AC,RM}} \quad (5)$$

Figure 14 gives this polarisation impedance throughout time. As observed, correlating with the decreased in AC current density caused by the increase in total electrode impedance, the polarisation impedance in the scaling solution increases steady throughout time, whereas the polarisation impedance in the non-scaling environment remains constantly lower.

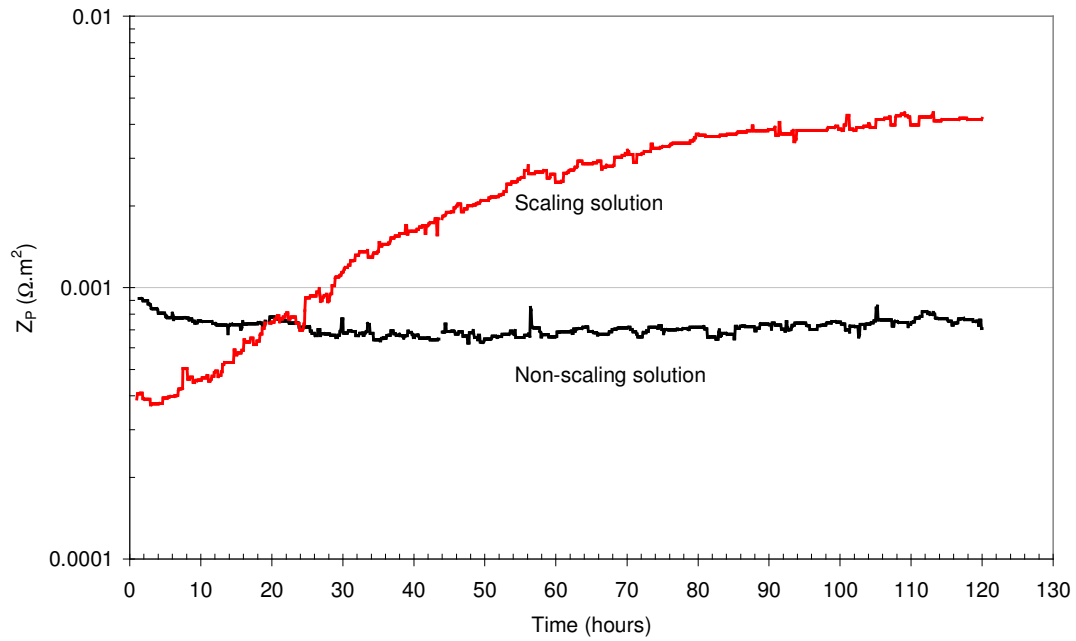


Figure 14. Polarisation impedance in both solutions throughout time.

The electrode impedance can – as generally accepted - be regarded as a series couple of the ohmic resistance with the polarisation impedance (the latter being a non-linear impedance describing the impedance of electrochemical processes), regardless of whether or not the polarisation impedance includes a Warburg diffusion element (figure 15).

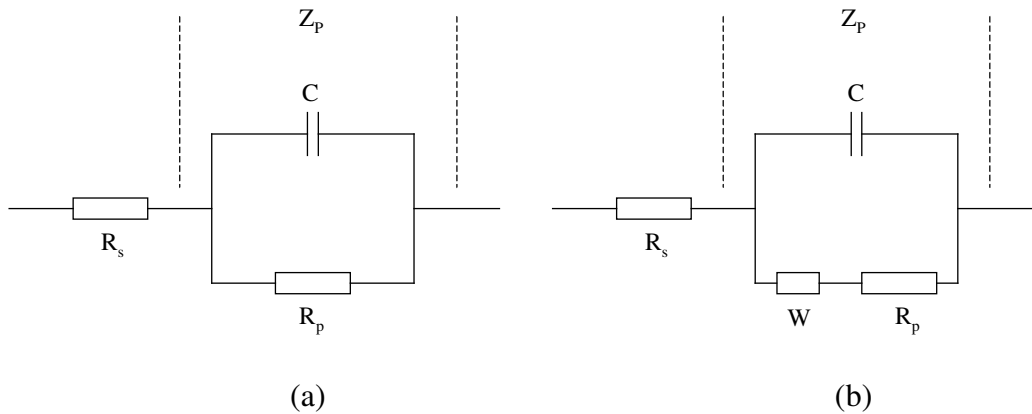


Figure 15. Randles circuit without (a) and with (b) Warburg diffusion element.

For this reason, it would be tempting to extract the ohmic resistance from the Ramlog measurements simple by subtracting the polarisation impedance from the total electrode impedance as described by the equation:

$$R_s = \frac{U_{AC,ON,RMS} - U_{AC,OFF,RMS}}{i_{AC,RMS}} = Z_T - Z_p \quad (6)$$



Doing this, however, it is forgotten that the polarisation- as well as the total electrode impedance are in fact impedances which probably are out of phase as well as out of phase with the ohmic resistance of the system. This can be illustrated from the typical Nyquist plot (figure 16, a recording from the present study) in which the impedances resulting from 4 different frequencies in the region of 50 Hz are plotted.

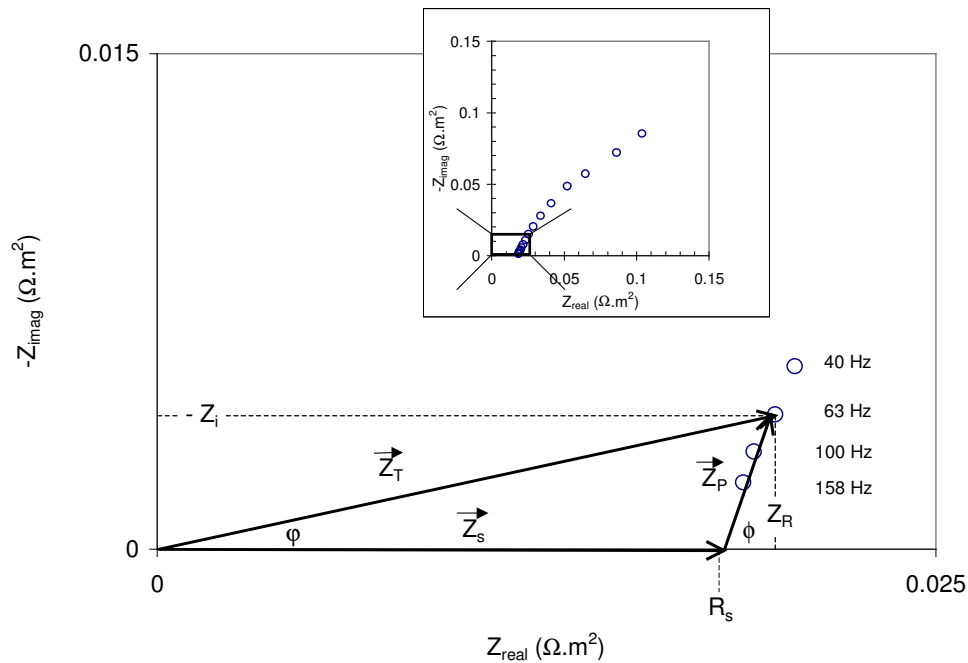


Figure 16. Nyquist plot illustrating the impedance for 4 different frequencies around 50 Hz.

Three vectors are defined:

$$\vec{Z}_T = \begin{pmatrix} Z_R \\ -Z_i \end{pmatrix} \text{ having length } Z_T = \sqrt{Z_R^2 + Z_i^2} \quad (7)$$

$$\vec{Z}_s = \begin{pmatrix} R_s \\ 0 \end{pmatrix} \text{ having length } R_s \quad (8)$$

$$\vec{Z}_p = \begin{pmatrix} Z_R - R_s \\ -Z_i \end{pmatrix} \text{ having length } Z_p = \sqrt{(Z_R - R_s)^2 + Z_i^2} \quad (9)$$

From this, it is evident that the total impedance is a vector  $\vec{Z}_T$  given by the sum of the other two vectors,  $\vec{Z}_s$  and  $\vec{Z}_p$  :

$$\vec{Z}_T = \begin{pmatrix} Z_{T,real} \\ Z_{T,ima} \end{pmatrix} = \vec{Z}_s + \vec{Z}_p = \begin{pmatrix} R_s \\ 0 \end{pmatrix} + \begin{pmatrix} Z_{p,real} \\ Z_{p,ima} \end{pmatrix} = \begin{pmatrix} R_s + Z_{p,real} \\ Z_{p,ima} \end{pmatrix} = Z_T \cdot \begin{pmatrix} \cos(\varphi) \\ \sin(\varphi) \end{pmatrix} \quad (10)$$

From equation (10) and figure 16, it is evident that the correct way of calculating the ohmic resistance is by the following equation:

$$R_s = Z_T \cdot \cos \phi - Z_P \cdot \cos \phi \quad (11)$$

Since the phase angle is not registered by the Ramlog recording, equation (11) cannot be applied on data from the Ramlog.

However, the EIS data can give some idea of the error made by using equation (6) on the Ramlog data – although, off course, it is recognised that the EIS data are obtained using a voltage amplitude different from the amplitude of the AC-voltage applied throughout the test period. Based purely on the EIS data, tables 6 (scaling solution) and 7 (non-scaling solution) assemblies, as a function of the co-ordinate frequencies (40, 63, 100, and 158 Hz), the following quantities:

- The “true” ohmic resistance according to EIS data,
- The total impedance  $Z_T$ ,
- The polarisation impedance  $Z_P$  calculated according to equation (9),
- The difference between these impedances ( $Z_T - Z_P$ , representing the approximate ohmic resistance calculated according to equation (6), i.e. a measure of the ohmic resistance using this equation on the Ramlog data),
- The fraction  $(Z_T - Z_P)/R_s$  representing the degree of accuracy to which the ohmic resistance calculated according to equation (6) can be assessed in comparison with the “true”  $R_s$ .

Time Hours	$R_s$ $\Omega.m^2$	Freq. Hz	$Z_T$ $\Omega.m^2$	$Z_P$ $\Omega.m^2$	$Z_T - Z_P$ $\Omega.m^2$	$(Z_T - Z_P)/R_s$ %
0	0.0184	40	0.0212	0.0059	0.0153	83.1
0	same	63	0.0203	0.0043	0.0159	86.6
0	same	100	0.0194	0.0030	0.0164	88.8
0	same	158	0.0189	0.0021	0.0168	91.6
22	0.0348	40	0.0422	0.0120	0.0302	86.9
22	same	63	0.0398	0.0089	0.0307	88.6
22	same	100	0.0377	0.0068	0.0309	88.7
22	same	158	0.0365	0.0052	0.0313	90.0
120	0.2897	40	0.3348	0.0631	0.2717	93.8
120	same	63	0.3225	0.0495	0.2729	94.2
120	same	100	0.3127	0.0413	0.2714	93.7
120	same	158	0.3043	0.0359	0.2684	92.6

Table 6. Characteristic EIS quantities (scaling solution).

Time Hours	$R_s$ $\Omega.m^2$	Freq. Hz	$Z_T$ $\Omega.m^2$	$Z_P$ $\Omega.m^2$	$Z_T - Z_P$ $\Omega.m^2$	$(Z_T - Z_P)/R_s$ %
0	0.0124	40	0.0163	0.0054	0.0109	87.6
0	same	63	0.0151	0.0041	0.0110	89.2
0	same	100	0.0142	0.0030	0.0112	90.7
0	same	158	0.0137	0.0022	0.0115	92.5
22	0.0133	40	0.0141	0.0023	0.0118	88.7
22	same	63	0.0136	0.0015	0.0121	91.2
22	same	100	0.0135	0.0011	0.0124	93.6
22	same	158	0.0133	0.0007	0.0126	95.1
120	0.0132	40	0.0150	0.0025	0.0125	94.4
120	same	63	0.0147	0.0020	0.0127	96.0
120	same	100	0.0144	0.0015	0.0129	97.3
120	same	158	0.0143	0.0013	0.0130	98.2

Table 7. Characteristic quantities calculated from the EIS measurements (non-scaling solution).

In other words, the table seeks to make an assessment of the degree of accuracy one would expect if the Ramlog data are used to assess the ohmic resistance according to equation (6). The index of accuracy ( $(Z_T - Z_P)/R_s$ ) from the above tables are graphically illustrated in figures 17 and 18.

#### Scaling solution

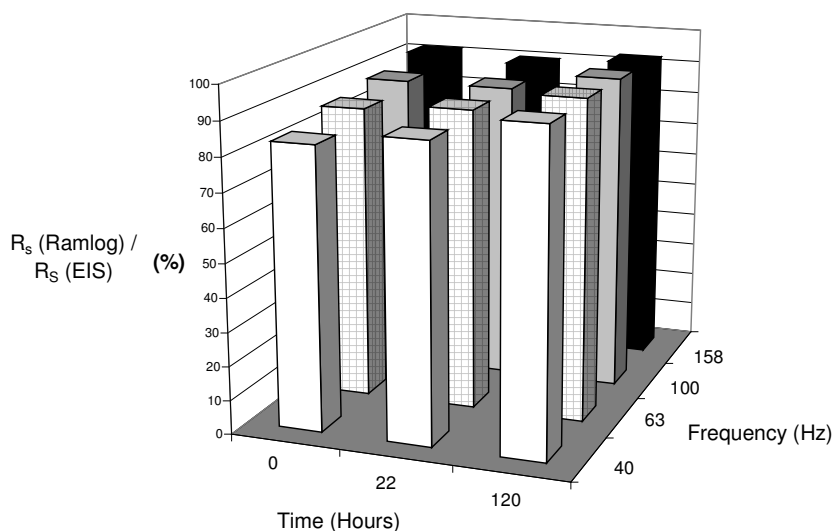


Figure 17.  $R_s$  calculated from equation (6) – denoted “Ramlog” although calculated from EIS data - compared with the “true”  $R_s$  at high frequency – scaling solution.

### Non-scaling solution

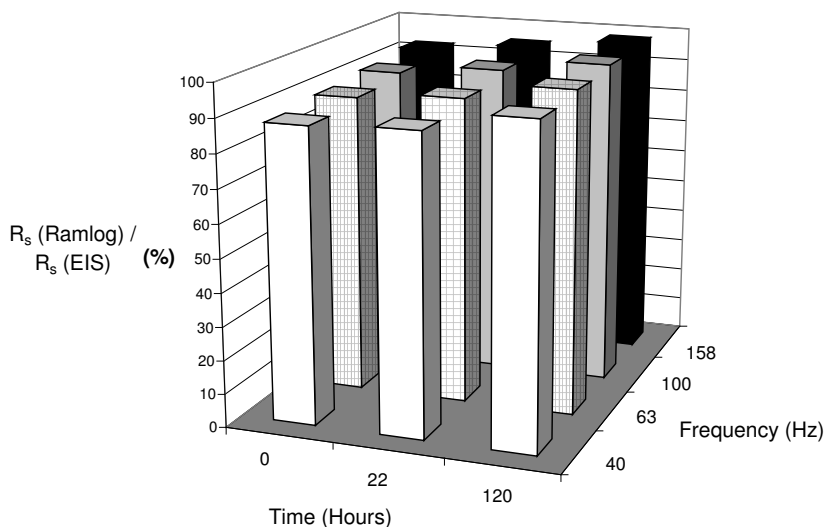


Figure 18.  $R_s$  calculated from equation (6) – denoted “Ramlog” although calculated from EIS data - compared with the “true”  $R_s$  at high frequency – non-scaling solution.

Frequencies have been selected in a range below 50 Hz to above 108 Hz, the latter being the frequency often used in equipment for 4 point Wenner measurements.

It is clear from the above analysis that applying equation (6) on Ramlog data, the  $R_s$  estimation is expected to be made with accuracy  $> 80\%$  in relation to the true  $R_s$ . Taking into account that measuring the  $R_s$  value at the usual frequency applied in 4 point Wenner equipment only improves the accuracy by approximately 5%, it is suggested that using equation (6) on Ramlog data will provide a useful measure of the ohmic resistance. Further, the accuracy should be compared with the range within ohmic resistances are expected to be found. Figure 19 illustrates the actual outcome of using the equation (6) on Ramlog data. EIS data have been added for comparison. Actually, the EIS data give (for the scaling solution in particular) slightly lower values of the ohmic resistance, but generally a good correlation is found. The reason for the lower values found using EIS data may be found in the fact that the Ramlog data has been obtained using a higher AC voltage, and this undoubtedly creates a different ionic composition of the environment nearby the electrode surface, e.g. through the creation of hydrogen gas. Concerning the ohmic resistance in general, it is clear that the chemical composition of the environment close to the electrode surface plays a key role for the magnitude of the ohmic resistance. A raise in ohmic resistance of more than a decade is created in the scaling solution although the solution conductivity did not change throughout the experimental period. This underlines that the ohmic resistance should not be confused with, nor tried calculated on the basis of, the solution resistance. In addition to the effect of the nearby environment, the effect of the electrode area has been shown to play a major role on the magnitude of the ohmic resistance.<sup>4</sup> Increasing the electrode area from  $0.01 \text{ cm}^2$  to  $4 \text{ cm}^2$  gave an almost 20-fold decrease in ohmic resistance. The term “spread resistance” rather than

the somewhat more neutral term “ohmic resistance” is accordingly highly justified, whereas the term “solution resistance” may be directly misleading, or at least covering a different quantity. The initial spread resistance measured in the solutions reflects the differences in solution conductivity, but eventually, as cathodic scaling is precipitated on the electrode exposed in the scaling solution, the spread resistance is far from a reflection of the solution resistance.

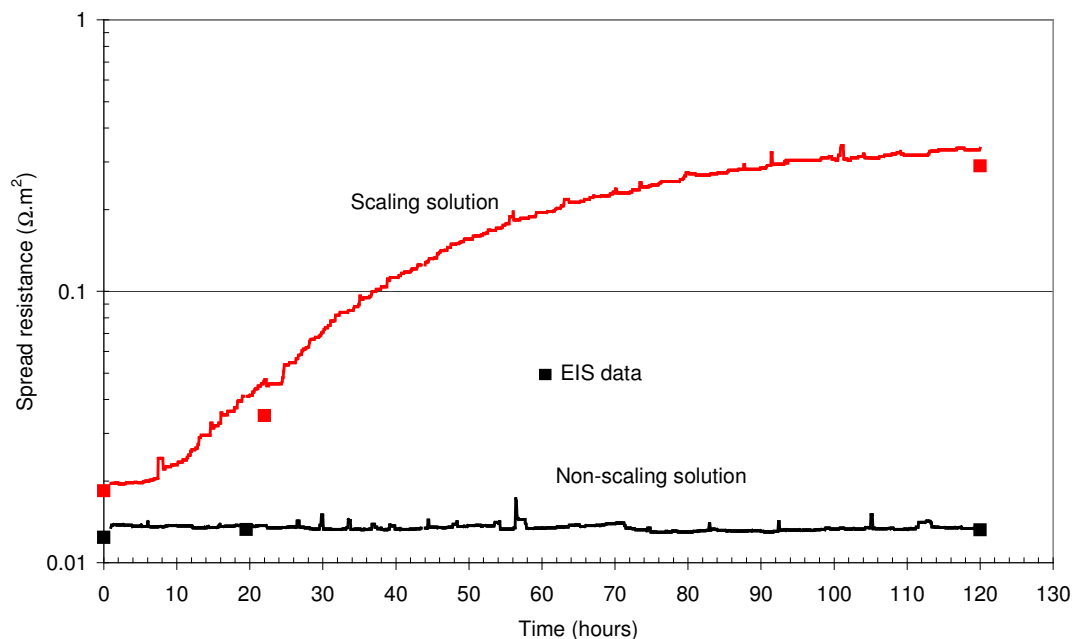


Figure 19. Spread (ohmic) resistance calculated based on Ramlog data according to equation (6). EIS data on  $R_S$  values are added for comparison.

Returning finally to the polarisation impedance,  $Z_p$ , one finds from figure 14 that the polarisation impedance increase in tact with the spread resistance in the scaling solution, suggesting that the scale developed on the electrode has an impact on the polarisation impedance as well. This comes as no surprise, however, since once again the Ramlog recorder does not detect the phase between current and voltage, it cannot be verified from the Ramlog data whether this development in polarisation impedance is caused by decrease in capacitance, or by an increased polarisation resistance. The capacitance calculated (using the EIS data) by equation (1) and displayed in tables 3 and 4 gives a hint that the capacitance is actually decreasing throughout time in the scaling solution. This alone would cause an increase in polarisation impedance. From the present EIS data, no polarisation resistance ( $R_p$ ) has been extracted, but it seems plausible that the scaling also reduces the activity of the electrode processes. Some help may be gathered from the DC-polarisation behaviour (figure 10), but these curves are not corrected from the IR drop. Adjusting the potential according to the equation:

$$E_{\text{OFF}} = E_{\text{ON}} - i \cdot R_S \quad (12)$$

the curves in figure 20 are obtained. Since  $R_s$  is measured at a DC offset potential around  $-850$  mV, one should be cautious in making the above correction. Especially

in the anodic region, the spread resistance is expected to decrease due to production of ferrous ions causing enhancement of the nearby solution conductivity. Regarding the 120h-curve the overestimation of the IR-drop is evident in the anodic region where the curve bends over. However, at low anodic currents where the IR-drop plays only a minor role, it is indicated that the electrode activity is actually decreased. In the cathodic region where the IR estimation is expected to be considerably more accurate, the decreased electrode activity is clear. On this basis, quite strong evidence of increased polarisation resistance in the scaling system is provided. In the non-scaling solution, there seems to be a fairly constant polarisation resistance throughout time. In this system however, it appears from table 4 that the capacitance increases throughout time causing a decrease in polarisation impedance, but also an increase in the electrode time constant. The latter can be identified as a displacement of the phase towards lower frequencies in the Bode plot (figure 9).

So, in conclusion to the polarisation impedance, it is evident that although the Ramlog recordings are capable of providing a measure of this quantity, one cannot from such measurements alone establish the relative influence of capacitance and polarisation resistance, since the phase is not detected.

Further, it is pointed out that when making electrochemical measurements in general on systems imposed by AC, the electrochemical response reflects the sum of all active processes, whether or not these include the most interesting of all when dealing with AC corrosion; the irreversible oxidation of iron. As a natural consequence, one cannot expect to extract any data from electrochemical measurements giving rise to assessments of the corrosion rate under AC load.

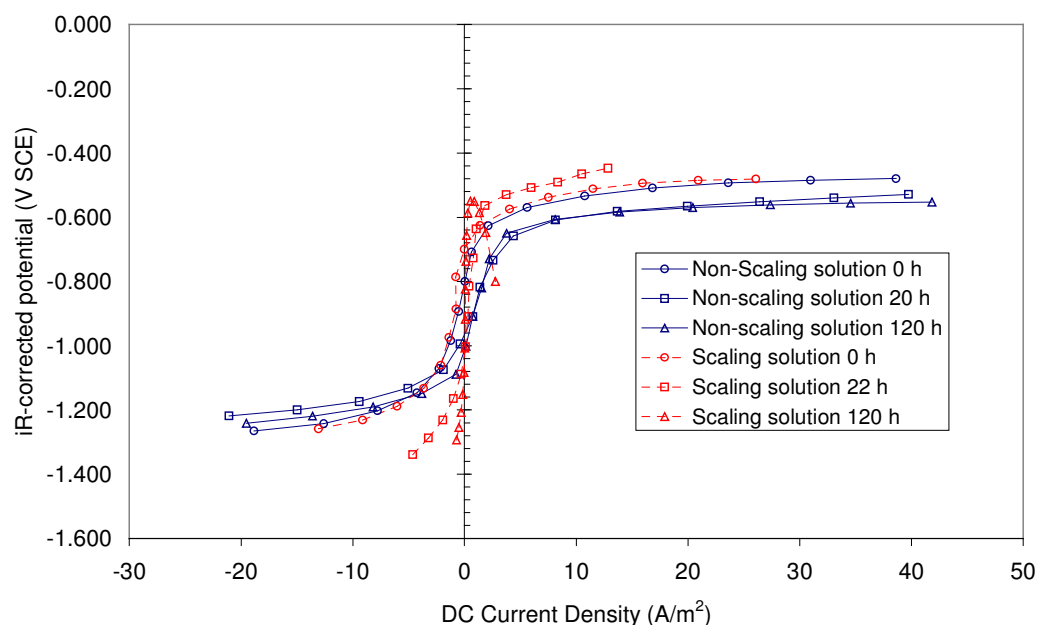


Figure 20. DC-polarisation curves attempted corrected from iR-drops.

## **Conclusions**

- Comparative studies on the applicability of electrochemical impedance spectroscopy and the Ramlog recording instant OFF technique have been made in two 120-h parallel experiments conducted in a scaling solution as well as a non-scaling solution.
- In the scaling solution, the AC current measured by the Ramlog technique decreased over time whereas a steady current density was found in the non-scaling solution. These measurements were confirmed by simple measurements of the AC current using a Fluke multimeter. Accordingly, the Ramlog recorder proved to be able to assess with accuracy the AC current flowing to a sample.
- Regarding polarisation impedance of the electrodes, it was shown from the OFF potential recordings of the Ramlog recordings that the polarisation impedance in the scaling environment increased throughout time whereas this impedance remained fairly constant in the non-scaling environment. This was in accordance with DC polarisation curves established three times during the tests.
- Using vector analysis, it was shown that the exact calculation of the spread resistance of the electrode systems cannot be done from the Ramlog recordings since recordings of the phase between current and voltage is not made, however, quite accurate assessments are made at 50 Hz AC by just subtracting ON and OFF AC voltages and dividing by the AC current density. Using this procedure, the assessments of spread resistance were quite close to the spread resistance measurements performed by EIS. The error made by calculating the spread resistance from the Ramlog recordings was assessed from the EIS measurements. In both solutions, this procedure gave values for spread resistance that correlated to a degree of around 90% of the true spread resistance as measured by electrochemical impedance spectroscopy at very high frequency. In comparison, the EIS measurements were used as well to calculate the degree of accuracy obtained for measurements of the spread resistance using a frequency around 108 Hz (which is applied in common four point Wenner instrumentation). These calculations showed that the degree of accuracy obtained using measurements of said higher frequency were only improved by a few percent. Accordingly, the Ramlog recordings provide a quite fair assessment of the spread resistance in particular when bearing in mind that the spread resistance may vary within several orders of magnitude depending on electrode area (size of coating defect), the initial conductivity of the environment as well as the scaling potential of the chemistry nearby the surface of the sample.

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