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The use of odd random phase electrochemical impedance spectroscopy to study lithium-based corrosion inhibition by active protective coatings

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ABSTRACT

In this work, the study of the time-dependent behaviour of lithium carbonate based inhibitor technology for the active corrosion protection of aluminium alloy 2024-T3 is presented. Odd random phase electrochemical impedance spectroscopy (ORP-EIS) is selected as the electrochemical tool to study the corrosion protective properties of a model organic coating with and without lithium carbonate as a function of immersion time, by examination of the non-linearities and non-stationarities in the system. A dedicated qualitative and quantitative analysis allows linking the presence of non-stationarities in a certain frequency range with the (un)stable behaviour of different electrochemical processes. Monitoring of the system with and without lithium corrosion inhibitors during the first 12 h after immersion in a 0.05 M NaCl aqueous solution and modelling the ORP-EIS data with equivalent electrical circuit (EEC) models revealed a relation between the trends in the parameter evolution and the (un)stable behaviour of the morphological changes taking place. This paper shows that the ORP-EIS based methodology allows us to study the behaviour of corrosion inhibitors in an alternative way; the time-dependent behaviour of corrosion inhibitor containing electrochemical systems is highlighted, proving that this a useful approach for further corrosion inhibitor and active protective coating research.

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1. Introduction

Among the wide variety of electrochemical techniques, electrochemical impedance spectroscopy (EIS) has proven to be a suitable and powerful technique to screen corrosion inhibitors and study the protective properties and efficiency of (self-healing) coatings on metal substrates over time [1–3]. EIS can provide both qualitative and quantitative information. The qualitative description refers to monitoring the efficiency of electrochemical systems by comparing, e.g., the magnitude of the impedance modulus at low frequencies, i.e., the polarization resistance. Any decrease or increase in the polarization resistance can be related to a decrease or increase in corrosion protection, respectively [1–3]. Quantitatively, the system can be studied by fitting the experimental data to an equivalent electrical circuit (EEC) model

describing the physical phenomena occurring in the electrochemical system, in such a way that the individual contributions to the global system's performance can be studied [1,3]. This makes EIS a very powerful technique to study electrochemical systems. Garcia et al. studied the corrosion inhibition mechanism of cerium-based bi-functional inhibitors on AA2024-T3 alloy with EIS, proposing a systematic strategy in selecting the most probable EEC. Doing so, it is crucial that the most probable EEC has a physical meaning, with minimal model error and parameter errors on all circuit elements [4]. Balaskas et al. applied EIS to study the effect of various organic compounds on the corrosion process of AA2024-T3 alloy, in order to rank them according to the degree of corrosion protection they provide [5]. Lamaka et al. screened different organic corrosion inhibitors for aluminium 2024 alloys with EIS to reveal the effectiveness and working mechanism of each inhibitor [1]. In a later study, EIS was used to study the synergistic effect of inhibitor mixtures for the protection of AA2024-T3 [6]. Lopez-Garrity et al. completed a similar study, to reveal the mechanism of the protective action of sodium

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molybdate corrosion inhibitor on AA2024-T3 alloys [7].

Recently, lithium-based corrosion inhibitor technology has become of interest as possible alternative to chromium based corrosion inhibitor technology and protect aluminium AA2024-T3 against (localized) corrosion [8–10]. Visser et al. have proven that when dispersed in a model organic coating, lithium carbonate and lithium oxalate pigments can ensure fast and effective corrosion protection in an artificial damage under neutral salt spray (NSS) exposure according to ASTM B-117 [11]. These lithium-salts are able to leach from the coating matrix through a specific leaching mechanism, providing active corrosion protection by rapid formation of a three-layered morphology, consisting of an inner dense layer close to the aluminium alloy metal surface, a porous middle layer and a very porous columnar outer layer [12,13]. The coverage, growth process and surface chemistry of the protective layer were studied in detail with a variety of surface analysis and spectroscopic techniques [13,14]. Finally, electrochemical impedance spectroscopy (EIS) was used to study the electrochemical properties of the generated three-layered protective morphology, its formation and properties as a function of NSS exposure time [15]. However, a more in depth study of the initial stability as a function of time of this protective layer after NSS is required. Since corrosion processes are intrinsically de facto non-linear and non-stationary, these phenomena can only be described adequately by means of EIS if it is proven that the system is linear and stationary within the measurement time, since these are crucial requirements to have reliable EIS measurements [16].

The application of Kramers-Kronig (K-K) transforms could provide a possible solution to verify electrochemical impedance data with respect to the conditions of causality, linearity and time-invariance. If a system fulfils these conditions and if the impedance is finite in the frequency domain under investigation, the EIS data will transform following the K-K relationships. On the contrary, the converse is not true [17,18]. It has been demonstrated that the linearity can always be guaranteed, but that the conformity with the causality and time-invariance conditions is more difficult, limiting the K-K transforms' applicability [17–19]. Besides, with that approach it is not possible to quantify the level of non-linear and non-stationary distortions at each frequency.

Odd random phase electrochemical impedance spectroscopy (ORP-EIS) is an electrochemical tool providing linearity and time-invariance information that can be used to evaluate the suitability of the equivalent electrical circuit models. ORP-EIS is a different technique to measure impedance compared to the classical EIS method. Rather than exciting the system at each subsequent frequency, as in classical EIS, the system is excited with a multisine signal over the entire frequency range. This periodic broadband signal consists of harmonically related sine waves whereof only the odd harmonics are excited and out of every group of three consecutive odd harmonics, one is randomly omitted [20]. This method provides two benefits. Firstly, applying a broadband rather than a single sine signal decreases the measurement time drastically while exciting the higher frequencies even more. This reduces the standard deviation, compared to a single-sine excitation, since the standard deviation is inversely proportional to the number of samples taken. Secondly, through a dedicated data analysis procedure, extra information regarding the noise, non-linearities and non-stationarities present in the system under investigation can be evaluated and quantified [21–24]. To investigate the reliability of the modelling results, it is important to verify whether the experimental data are correct and to evaluate whether the EEC model is able to describe the experimental data within the experimental error. This information is also available by the application of the ORP-EIS technique. The concept of ORP-EIS has already demonstrated to be a successful tool for a number

of practical applications. Van Gheem et al. studied non-linear and non-stationary electrochemical systems using an especially designed excitation signal [21]. By exciting the system with an odd random phase multisine with a random harmonic grid, it was possible to detect both non-linearities and non-stationarities, as was concluded from the application on the pitting corrosion of aluminium in an aerated sodium chloride solution [22]. Breugelmans et al. successfully applied it as a rapid corrosion screening test of metal-coated steel [25] and to analyse (self-healing) organic coatings [20]. Hauffman et al. employed ORP-EIS to investigate the time-varying process of self-assembling monolayers on aluminium oxide, a process which is essentially non-stationary [26,27]. In addition, a detailed study of the early stages of copper corrosion and the mechanism of adsorption on copper by ORP-EIS has been reported [28,29].

In this paper, ORP-EIS is used to study the initial stability as a function of time of the protective morphology formed in coating defects of model coatings with and without lithium leaching coating technology on an AA2024-T3 substrate. The application of this technique is crucial to investigate the initial stages of the stability of the multi-layered protective morphology provided by inhibitor based corrosion protective technologies and to achieve more reliable measurements for corrosion inhibitor systems in general. In a first step, the experimental data are examined, both qualitatively and quantitatively, through the analysis of the additional information regarding the non-linearities and non-stationarities provided by ORP-EIS about the correctness of the data. Furthermore, the impact and advantages of using the additional information regarding the non-linearities and non-stationarities in the modelling is assessed in order to study and improve the modelling reliability. A parallel is drawn between the stationarity of the different electrochemical processes and the parameter evolution of the equivalent electrical circuit elements.

2. Experimental details

2.1. Materials and sample preparation

AA2024-T3 aluminium alloy with nominal composition from Alcoa was anodized in tartaric-sulfuric acid (TSA) according to aerospace requirements (AIPI 02-01-003). The anodized samples were coated with a polyurethane based model coating (Table 1) with a dry film thickness of 20–25 μm [15]. Coatings without corrosion inhibitors, used as non-inhibited reference, and lithium carbonate containing coatings were applied. To study the active corrosion protective properties of these coatings, an artificial damage from corner to corner was made with a mechanical milling device yielding a U-shaped scribe of 1 mm width and approximately 100–150 μm depth. Afterwards, the scribed lithium carbonate containing samples were exposed to the neutral salt spray

Table 1
Composition of the organic model coatings with and without lithium carbonate.

	Without corrosion inhibitors	Lithium carbonate
Component A		
N-Butylacetate	75.0 g	75.0 g
Desmophen 650MPA	47.7 g	47.7 g
Lithium carbonate		23.6 g
Magnesium oxide	16.4 g	16.4 g
Tioxide TR 92	5.9 g	5.9 g
Blanc Fixe N (Ba(SO ₄))	66.0 g	15.4 g
Component B		
Tolonate HDB 75 MX	28.5 g	28.5 g
Dynasilan Glymo	5.2 g	5.2 g

test (NSS) according to ASTM B-117 for 168 h [11]. The 0.05 M NaCl solution used during the ORP-EIS measurements was prepared from J.T. Baker NaCl crystals with a purity of at least 99% and demineralized water.

2.2. Odd random phase electrochemical impedance spectroscopy (ORP-EIS)

A typical three electrode set-up was used for the electrochemical experiments with an Ag/AgCl 3 M KCl reference electrode (RE), a platinum grid as the counter electrode (CE) and the mechanically scribed coated AA2024-T3 sample as the working electrode (WE) with an exposed area of 3.14 cm^2 and a scribed area of 0.48 cm^2 . The set-up was placed in a Faraday cage. Measurements were recorded immediately after immersion in 0.05 M NaCl and for 12 subsequent hours. In the case of the system without corrosion inhibitors, a measurement was taken every 10 min and, in the case of the lithium carbonate inhibited system, a measurement was taken every 15 min.

The ORP-EIS measurements were performed with a MATLAB controlled set-up composed of a Bio-Logic SP-200 potentiostat and a National Instruments PCI-6110 DAQ-card. The frequency range is from 10^{-2} Hz to $2 \cdot 10^3 \text{ Hz}$. The amplitude of the excitation signal was set to 10 mV (7.07 mV RMS) applied at the free corrosion potential, to have a good signal-to-noise ratio while keeping the non-linearities confined. The MATLAB written software to build the odd random phase multisine excitation signal, record the impedance measurements and perform the modelling was developed at the Vrije Universiteit Brussel. A more detailed description of the technique can be found elsewhere [16,21].

3. Results and discussion

3.1. Qualitative interpretation of ORP-EIS noise distortions

To study the system's evolution in meeting the three requirements needed for a correct EIS measurement, both the system without corrosion inhibitors and the lithium carbonate inhibited system were intensively monitored during the first hours after immersion in the electrolyte. In Fig. 1, the ORP-EIS results of the coated AA2024-T3 sample without inhibitors after 0, 2, 4 and 6 h of immersion in 0.05 M NaCl are presented. The black line and the grey line correspond to the magnitude of the impedance modulus and the phase angle, respectively, as usually plotted by classical EIS. The other characteristics of the experimental data of an ORP-EIS measurement are provided by the curves representing the noise, the noise plus the non-linearities and the noise plus the non-stationarities [30,31]. Data interpretation can be described in the following way. The system is fully linear if the noise curve and the noise + non-linearities curve overlap; the system is fully time-invariant (stationary) if the noise curve and the noise + non-stationarities curve overlap.

For the first measurement at Time = 0 (Fig. 1a), neither the noise + non-linearities curve nor the noise + non-stationarities curve overlap the noise curve. This suggests the presence of significant non-linearities and non-stationarities in the system right at the start. After 2 h of immersion (Fig. 1b), the noise + non-linearities curve approaches the noise curve, almost fulfilling the condition of linearity. Nevertheless, the noise + non-stationarities curve does not overlap the noise curve, indicating that the system behaves non-stationary. After 4 h (Fig. 1c), the noise + non-linearities curve overlaps completely the noise curve, indicating a linear behaviour

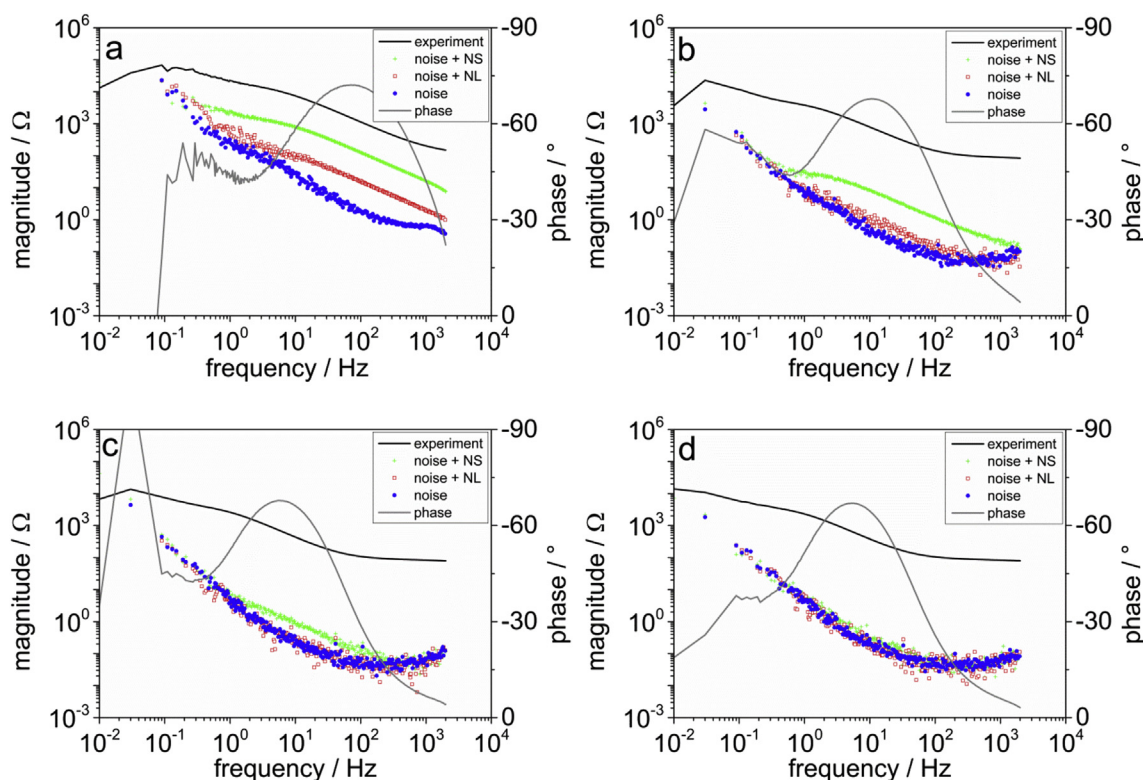


Fig. 1. Bode plots of the system without corrosion inhibitors after 0 h (a), 2 h (b), 4 h (c) and 6 h (d) in 0.05 M NaCl with the experimental impedance and noise distortion curves.

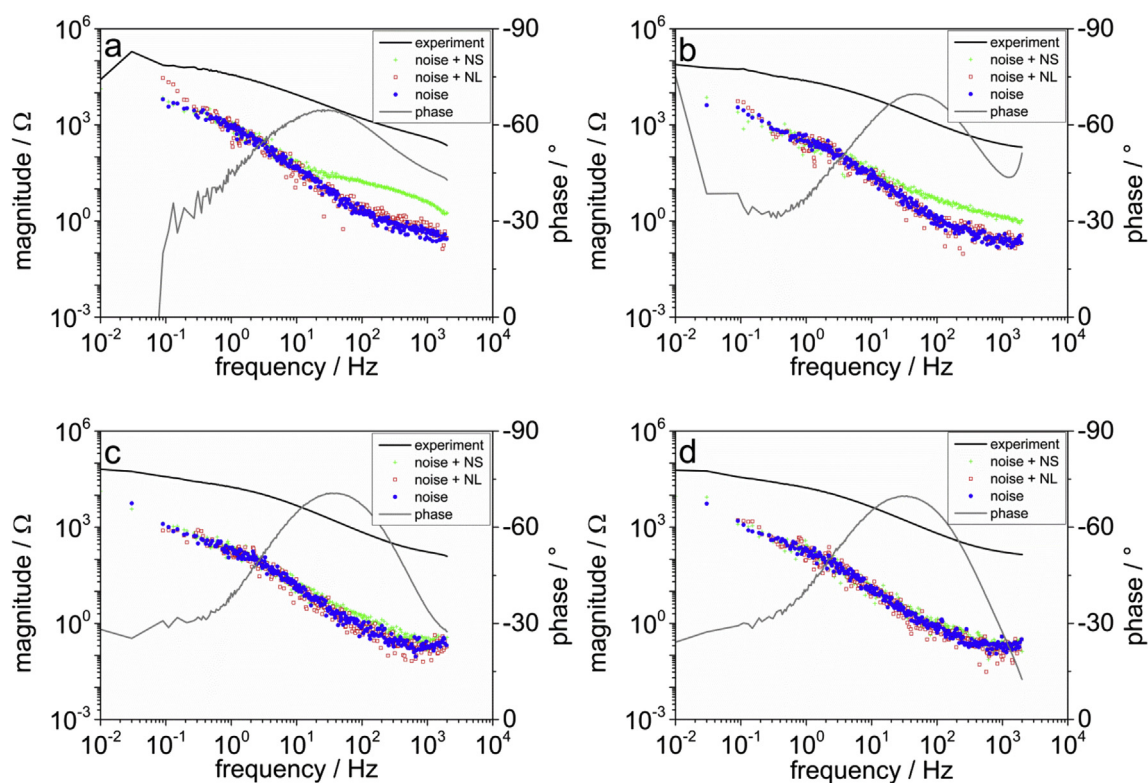


Fig. 2. Bode plots of the lithium carbonate inhibited system after 0 h (a), 2 h (b), 4 h (c) and 6 h (d) in 0.05 M NaCl with the experimental impedance and noise distortion curves.

of the system. The *noise + non-stationarities* curve does not overlap the noise curve yet, meaning the stationarity condition still must be fulfilled. After 6 h of immersion (Fig. 1d), the system behaves fully linearly and stationary, as observed by the overlap of the noise, *noise + non-linearities* and *noise + non-stationarities* curves.

In Fig. 2, the ORP-EIS results of the sample with the lithium carbonate containing coating after different times of immersion in 0.05 M NaCl are presented. It can be seen that, right at the start of the measurement, neither the *noise + non-linearities* curve nor the *noise + non-stationarities* curve completely overlaps the noise curve (Fig. 2a). The system did not reach the linearity and stationarity condition yet. In the case of the *noise + non-stationarities* curve, the mismatch is especially apparent at high frequencies, from 20 Hz to 2 kHz. The non-stationarities observed at the higher frequencies suggest that the electrochemical processes with low characteristic time constants (fast processes) mainly cause the time-variant behaviour of the system. After 2 h of immersion (Fig. 2b), the *noise + non-linearities* curve clearly overlaps the noise curve, meaning that the system has a linear behaviour under the given experimental conditions. However, the same observation about the stationarity condition can be made as before, with the non-stationary behaviour related to the high frequency region and thus the unstable behaviour linked to the electrochemical processes with low characteristic time constants. After 4 h of immersion (Fig. 2c), the *noise + non-stationarities* curve approaches the noise curve, indicating that the system has reached the condition of stationarity. After 6 h of immersion (Fig. 2d), the system behaves fully linearly and stationary, since the *noise + non-linearities* curve and the *noise + non-stationarities* curve overlap with the noise curve.

From this qualitative interpretation, it can be seen that for both the system without corrosion inhibitors and the lithium carbonate inhibited system, it takes approximately 6 h to reach a stationary

behaviour and, thus, fulfil the condition of time-invariance. At this point, both systems also behave linearly. This time designates the duration to reach a stable degradation process of the (native) oxide on the sample without corrosion inhibitors or the three-layered protective morphology formed during 168 h of NSS on the lithium carbonate inhibited sample. It corresponds to the stabilization time needed before a reliable EIS measurement is obtained. However, the non-linear and non-stationary behaviour of both systems in the initial hours of immersion requires further study by means of a quantitative interpretation of the noise distortions in the ORP-EIS data.

3.2. Quantitative interpretation of ORP-EIS noise data

The qualitative analysis of the experimental data obtained for both the system without corrosion inhibitors and the inhibitor containing systems provides an estimation of the time each system needs to 'stabilize' and fulfil the conditions of linearity and time-invariance. Yet, in order to study the reliability of EIS data in more detail, the information in Figs. 1 and 2 regarding the noise, non-linearities and non-stationarities present in the system needed to be quantified. The discrete information was calculated for each measurement separately by a numerical integration through interpolation using the trapezoidal rule [32]. The individual contributions of the noise, non-linearities and non-stationarities were calculated, as absolute values, by subtracting the noise curve from the *noise + non-linearities* and the *noise + non-stationarities* curve. This information was then expressed relative to the magnitude of the impedance modulus ($N/|Z|$; $NL/|Z|$; $NS/|Z|$), which is also quantified by a numerical integration through interpolation. This approach was followed for the first 12 hours of every measurement, both for the system without corrosion inhibitors and the lithium carbonate inhibited system. The resulting curves of the relative

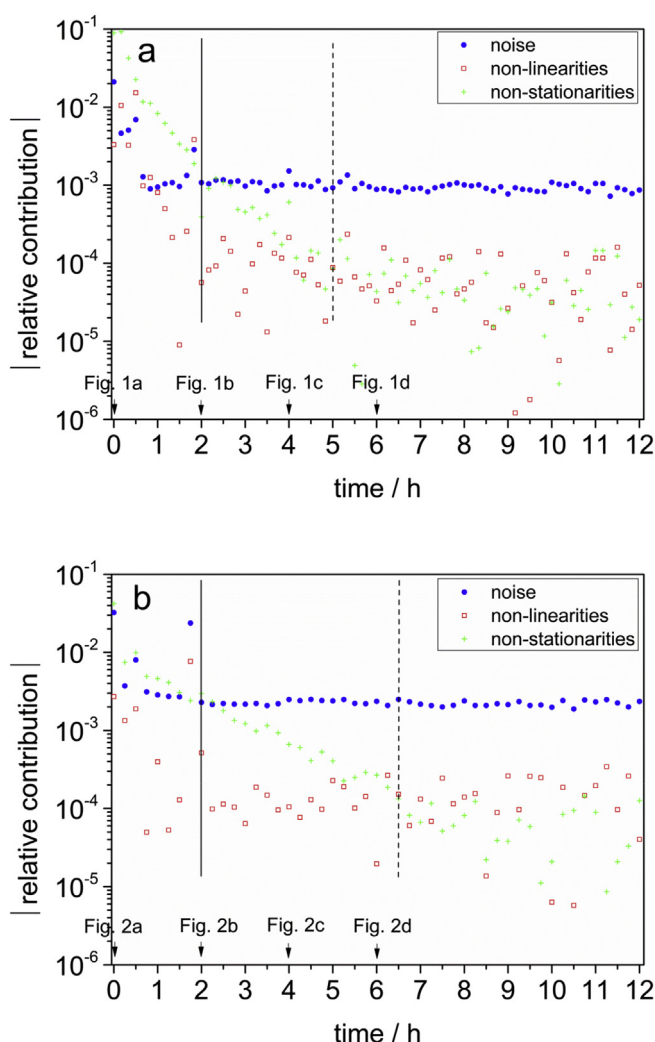


Fig. 3. Evolution of the contribution of the noise (N), non-linearities (NL) and non-stationarities (NS) relative to the impedance modulus for (a) the system without corrosion inhibitors and (b) the lithium carbonate inhibited system for the first 12 h of immersion in 0.05 M NaCl. The full- and dashed-vertical line represent the point in time where the system is fully linear and fully stationary, respectively.

contributions of the noise, non-linearities and non-stationarities as a function of time are presented in Fig. 3.

3.2.1. ORP-EIS noise data analysis of the system without corrosion inhibitors

For the system without corrosion inhibitors (Fig. 3a), it can be observed that in the first hour after immersion, the non-stationarities have the highest relative contribution of the three, with an absolute value only 1 order of magnitude lower than the magnitude of the Bode impedance modulus, corresponding to a contribution of almost 10%. For the noise, the contribution is almost 2 orders of magnitude lower compared to the magnitude of the impedance modulus and for the non-linearities almost 3 orders of magnitude. All contributions tend to fluctuate during the initial stages.

Following the initial stages after immersion, all individual contributions start decreasing over time. The relative contribution of the noise decreases quite strongly, before reaching a stable value after nearly 1 h, approximately 3 orders of magnitude lower than the measured impedance modulus, corresponding to approximately 0.1%. Afterwards, the noise contribution remains stable for

the rest of the measurement time.

The relative contribution of non-linearities decreases strongly in the first 2 h, reaching a relative contribution of approximately $2 \cdot 10^{-4}$ or less until the end of the measurement, corresponding to approximately 0.02% or less of the impedance modulus. This point in time is indicated by the full vertical line in Fig. 3a and from this point, the system behaves fully linearly.

The contribution of the non-stationarities decreases from only 1 to almost 3 orders of magnitude difference compared to the impedance modulus during the first 2 h of immersion. Afterwards, its contribution keeps decreasing up to 5 h after immersion, reaching a relative contribution of approximately 4 orders of magnitude lower than the impedance modulus, comparable to what is observed for the non-linearities. This point in time is indicated by the dashed vertical line in Fig. 3a, corresponding to a fully time-invariant behaviour of the system from this moment on.

The high relative contributions and high fluctuations during the initial stages of immersion are due to the unstable behaviour of the system right after immersion in the electrolyte. Considering these trends, the system's behaviour can be described as non-linear and non-stationary during the initial stages. The non-stationarities represent the main contributor to the system's distortion. After 2 h, the system's behaviour is still unstable, but the system behaves fully linearly with an excitation signal amplitude of 10 mV.

The information concerning the non-stationarities accounts for the instability of the electrochemical processes. Yet, processes with different time constants are visible in different frequency regions of the impedance spectrum; thus, non-stationarities in a certain frequency region could be associated to a particular electrochemical process. To analyse the contribution of the different processes to the overall system stability, the data regarding the non-stationarities was also quantified per frequency decade. The impedance data were, therefore, divided into 6 frequency decades. The first frequency decade, from 10 mHz to 100 mHz, was included in this analysis, because there were only three data points present, providing no statistically significant information. In addition to that, the data between 1 kHz and 2 kHz were not taken into account, since they comprise only one tenth of a frequency decade. The relative contribution (NS/|Z|) is calculated for each frequency decade separately and displayed in Fig. 4.

It can be observed that the contribution of the non-stationarities decreases for every frequency decade with time (Fig. 4a). For the highest (V) and the lowest (II) frequency decades it strongly decreases in the first hours and stabilizes after approximately 4 h. On the other hand, for the two mid frequency regions (III and IV) it decreases more slowly and stabilizes after more than 6 h. This corresponds to what is already observed in a qualitative way: after 2 h (Fig. 1b) the system behaves non-stationary over the entire frequency range, while after 4 h (Fig. 1c), the system behaves only non-stationary in the 1 Hz - 100 Hz range. Consequently, the electrochemical processes with time constants corresponding to the mid-frequency regions take the longest to stabilize, prolonging the instability of the system.

3.2.2. ORP-EIS noise data analysis of the lithium carbonate loaded system

For the lithium carbonate loaded system (Fig. 3b), the relative contributions of the noise and non-stationarities are the highest right after the start of immersion, about 3–4%. The relative contribution of the non-linearities, on the other hand, is already 2 orders of magnitude lower than the impedance modulus.

During the initial stages, the individual contribution of the noise undergoes some fluctuations, before decreasing to a stable value after 2 h of immersion, more than 2 orders of magnitude lower than the impedance modulus with a relative contribution of

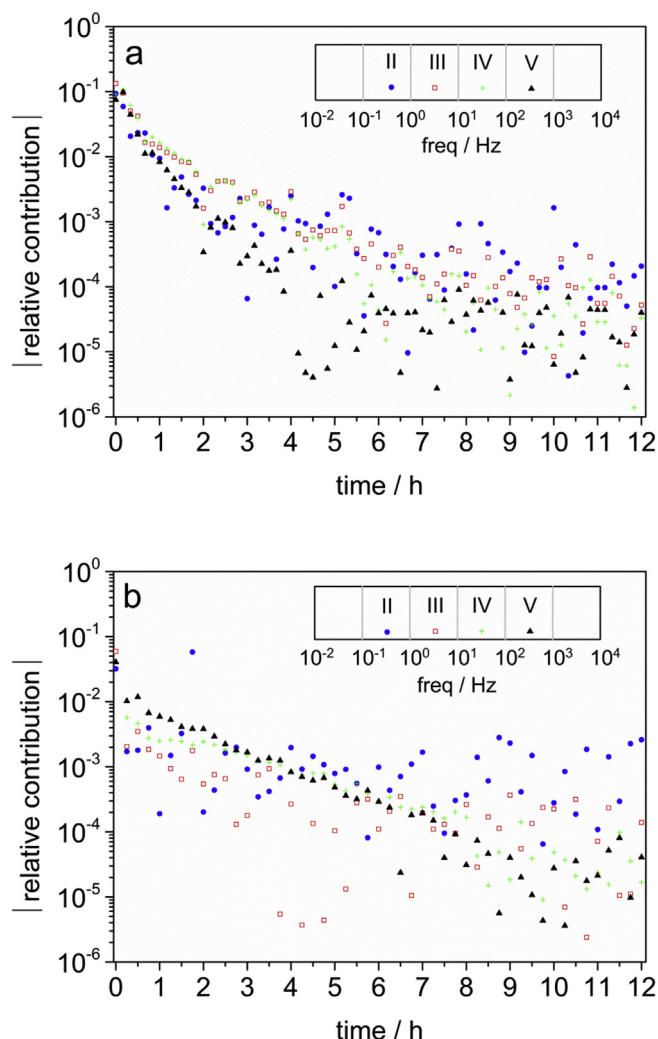


Fig. 4. Evolution of the relative contribution of the non-stationarities for the different frequency decades for (a) the system without corrosion inhibitors and (b) the lithium carbonate inhibited system for the first 12 h of immersion in 0.05 M NaCl.

approximately 0.3%. The noise relative contribution remained equal for the remaining time of the measurement. The contribution of the non-linearities is only present in the first hours after immersion and rapidly decreases over time, reaching a stable contribution with a value of $3 \cdot 10^{-4}$ or less after 2 h of immersion. This point in time is indicated by the full vertical line in Fig. 3b and from this moment on, the system behaves fully linearly. Here again the non-stationarities account for the largest contribution right after the start of immersion, with less than 2 orders of magnitude difference with the impedance modulus, corresponding to approximately 4%. However, this contribution decreases as a function of time, more than 3 orders of magnitude lower after 3 h and reaches a stable contribution with a value of $1 \cdot 10^{-4}$ or less after 6.5 h, fulfilling the condition of time-invariance. This point in time is indicated by the dashed vertical line in Fig. 3b.

Similarly to the system without corrosion inhibitors, the same quantification per decade was carried out for the contribution of the non-stationarities of the lithium carbonate loaded system. In Fig. 4b, it can be observed that for the lowest (II) frequency decade, the contribution of the non-stationarities remains the same over time, while for the other frequency decades, the contribution of the non-stationarities decreases for each frequency decade with time.

The contribution of the non-stationarities of frequency decade III decreases rapidly and reaches a more or less stable value after approximately 4 h. The contribution of the non-stationarities of frequency decades IV and V decreases more slowly and reaches a pseudo-plateau between 6 and 8 h and stabilizes around 8 h after immersion. The trend for the frequency decades IV and V is in accordance with what is observed in a qualitative way (Fig. 2), with a non-stationary behaviour in the higher frequency decades initially. This implies that the electrochemical processes with characteristic time constants related to frequency decades IV and V dominate the overall instability of the system.

When studying the data quality of the ORP-EIS measurements in a quantitative way, the point in time when the three requirements for a reliable classical EIS measurement are fulfilled can be determined more adequately. This information must be used correctly in practice when fitting the experimental data to an equivalent electrical circuit (EEC). This will be discussed in the next section.

3.3. Corrosion protective properties of the system without corrosion inhibitors and the lithium carbonate inhibited system

The ORP-EIS data of the system without corrosion inhibitors were fitted with an equivalent electrical circuit (EEC1) with two time-constants to model quantitatively the behaviour of the (native) oxide layer on aluminium alloys in a defect without the presence of corrosion inhibitors [6,15]. In EEC1 (Fig. 5a), R_s is the electrolyte resistance, R_{oxide} is the resistance of the oxide layer consisting of the native oxide layer and the formed corrosion products upon exposure to the electrolyte, $\text{CPE}_{\text{oxide}}$ is the constant phase element representing the capacitive behaviour of this oxide layer, R_{pol} is the polarization resistance and CPE_{dl} is the constant phase element accounting for capacitive behaviour of the double layer [15]. A constant phase element (CPE) rather than a capacitor is chosen here to allow deviations from the ideal capacitive behaviour [18]. The impedance of a constant phase element (Z_{CPE}) is given by:

$$Z_{\text{CPE}} = \frac{1}{(j\omega)^n Q} \quad (1)$$

where Q is the CPE-constant, n is the power value ($0 < n \leq 1$), j is the imaginary number ($j^2 = -1$) and ω is the angular frequency.

During the first 5 h of immersion, the system without corrosion inhibitors does not meet the requirements of a reliable impedance measurement, as discussed above, and the straightforward application of the EEC models is not possible. Initially, the system behaves both non-linearly and non-stationary and it only meets the linearity and stationarity conditions after 2 and 5 h, respectively. Moreover, the individual contribution of the non-stationarities is always predominant over that of the non-linearities. This must be taken into account in the modelling and an alternative fitting approach has to be followed for the first hours of immersion. Because the non-stationary contribution is dominant over the non-linearity contribution, the experimental data are weighted according to the *noise + non-stationarities* in every frequency point rather than with the magnitude of the impedance modulus, as commonly used for EIS fittings. The quality of the fitting can be determined by the evaluation of the model residual, i.e., the difference between the best-fit model and the experiment curves [33]. The approach is illustrated in Fig. 6 for the impedance after 1 h of immersion. It can be seen that the model residual and the *noise + non-stationarities* curves are laying around the same level, indicating that the only difference between the experimental data and the fitting results can be associated to the measurement of the noise present in the system and the non-stationarity behaviour of the system. The parameter values of the circuit elements and their

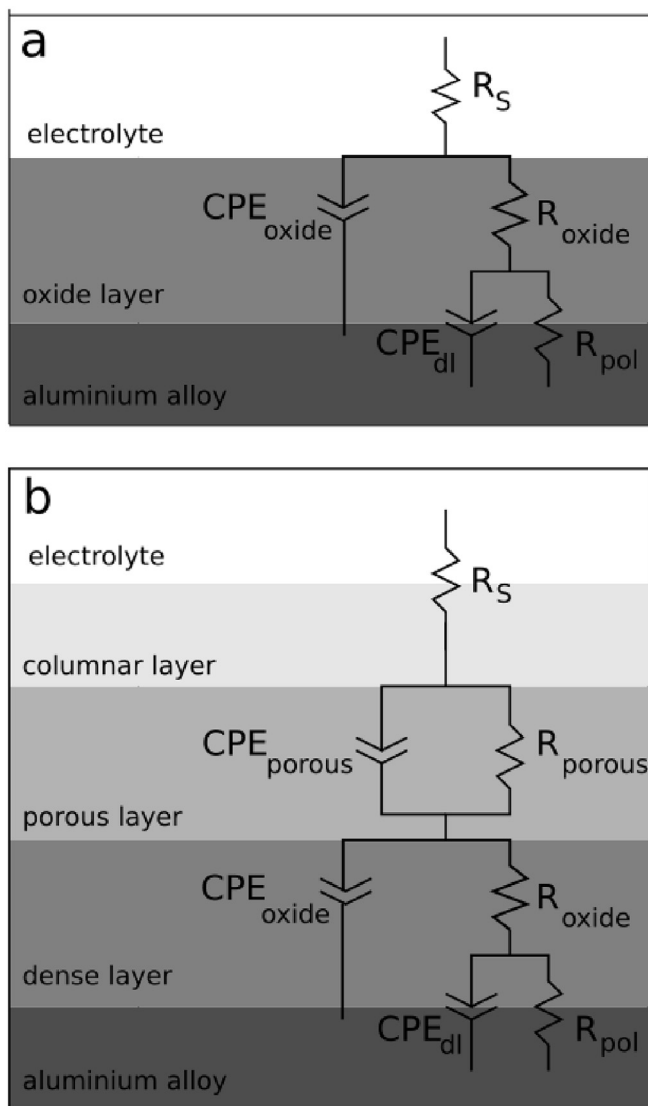


Fig. 5. The equivalent electrical circuit used to perform the fittings for (a) the system without corrosion inhibitors (EEC1) and (b) the lithium carbonate inhibited system (EEC2).

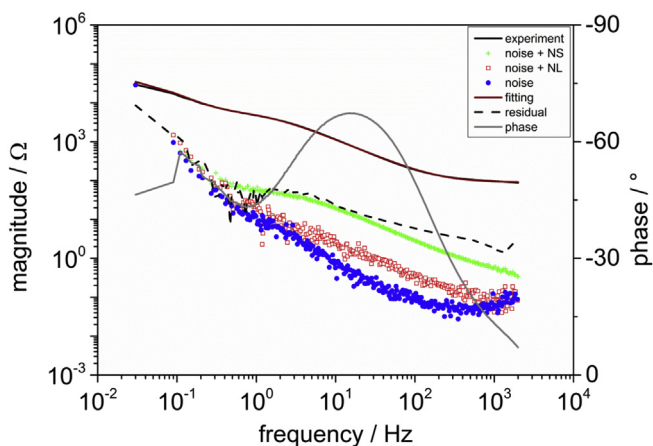


Fig. 6. Bode plot of the system without corrosion inhibitors after 1 h of immersion in 0.05 M NaCl with the experimental impedance and noise distortion curves and the fitted impedance and model residual curves.

Table 2

Fitting results of the system without corrosion inhibitors after 1 h and 8 h of immersion in 0.05 M NaCl, showing the parameter values and the relative errors on each of the circuit elements, respectively.

		1 h		8 h	
		value	error (%)	value	error (%)
R_s	$\Omega \cdot \text{cm}^2$	44.26	0.16	41.48	0.30
R_{oxide}	$\text{k}\Omega \cdot \text{cm}^2$	3.67	0.54	2.10	0.67
Q_{oxide}	$\text{Ss}^n \cdot \text{cm}^{-2}$	$4.83 \cdot 10^{-5}$	0.80	$1.53 \cdot 10^{-4}$	0.57
n_{oxide}		0.87	0.18	0.89	0.25
R_{pol}	$\text{k}\Omega \cdot \text{cm}^2$	19.47	11.46	6.03	9.63
Q_{dl}	$\text{Ss}^n \cdot \text{cm}^{-2}$	$1.61 \cdot 10^{-4}$	2.94	$1.26 \cdot 10^{-3}$	9.59
n_{dl}		0.94	1.90	0.97	3.23

relative errors for the system without corrosion inhibitors after 1 h of immersion are shown in Table 2. For all the EIS data during the first 5 h of immersion, similar modelling results are obtained. Besides, all model parameters are estimated with low relative errors, below 5% for R_{oxide} , Q_{oxide} , n_{oxide} and n_{dl} , below 10% for Q_{dl} and below 20% for R_{pol} . So, the proposed EEC1 model is able to match the experimental data within the level of the noise distortions and the model can be accepted.

After 5 h of immersion, the system without corrosion inhibitors behaves in a fully linear and time-invariant manner, as shown in Fig. 3a. Since the requirements for a correct EIS measurement are fulfilled, a classical data fitting approach can be followed and a weighting factor corresponding to the inverse of the magnitude of the impedance modulus in each frequency point is attributed. Yet, here again, the reliability of the fitting procedure must be evaluated. The model residual is evaluated and compared to the noise curve in this case. The approach is illustrated in Fig. 7 for the impedance after 8 h of immersion. The model residual overlaps the noise curve only in the low frequency region, and differs from it in the middle and high frequency regions. Nevertheless, the model residual relative to the impedance magnitude is always below 10%, relative to the impedance magnitude, proving the EEC is statistically correct. The parameter values and the relative errors on each of the circuit elements for the system without corrosion inhibitors after 8 h of immersion are shown in Table 2. For all the EIS data obtained between 5 and 12 h after immersion, similar modelling results are obtained. In any case, all model parameters are estimated with low relative errors, below 5% for R_{oxide} , Q_{oxide} , n_{oxide} and n_{dl} , and below 15% for R_{pol} and Q_{dl} .

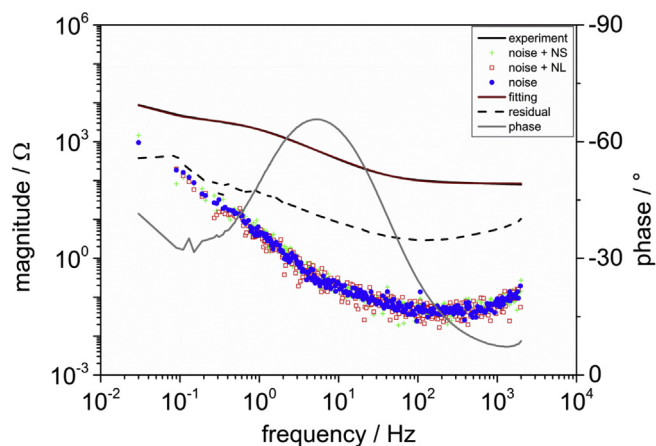


Fig. 7. Bode plot of the system without corrosion inhibitors after 8 h of immersion in 0.05 M NaCl with the experimental impedance and noise distortion curves and the fitted impedance and model residual curves.

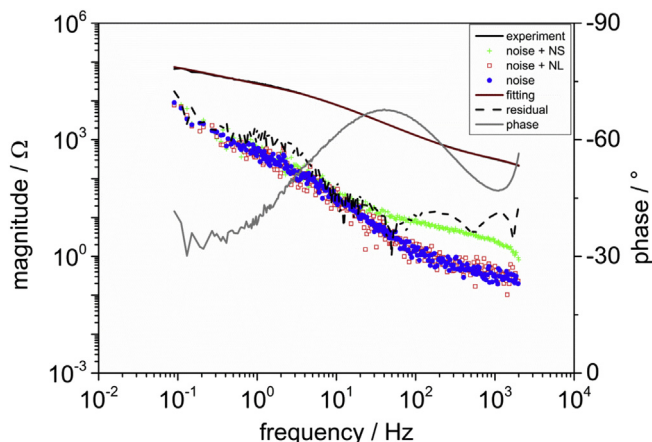


Fig. 8. Bode plot of the lithium carbonate inhibited system after 1 h of immersion in 0.05 M NaCl with the experimental impedance and noise distortion curves and the fitted impedance and model residual curves.

In order to quantitatively describe the electrochemical behaviour of the system during the first hours of immersion in the electrolyte, the ORP-EIS data obtained for the lithium carbonate inhibited system were fitted with an alternative circuit (EEC2) (Fig. 5b), which has been introduced by Visser et al. [15]. The extra time constant present in the EEC2 accounts for the resistive and capacitive behaviour of the porous middle layer. In this electrical circuit, R_s stands for the resistance of the electrolyte, R_{porous} and CPE_{porous} represent the contribution of the porous middle layer, R_{oxide} and CPE_{oxide} stand for the contribution of the dense inner (oxide) layer and R_{pol} and CPE_{dl} represent the charge transfer at the interface between the metal and the oxide [15]. Note that the columnar outer layer found in the hydrated aluminium oxide layer formed in the defect area [13] is not present in the proposed EEC2, since this layer is too porous and, therefore, its contribution is not distinguishable on the ORP-EIS data.

During the first hours of immersion, the lithium carbonate inhibited system does not meet the requirements of a correct EIS measurement (Fig. 3b). The linearity and stationarity condition are met after 2 and 6.5 h, respectively. Since the non-stationarity contribution is dominant over the linearity contribution, the experimental data is weighted according to the *noise + non-stationarities*. This approach is illustrated for a measurement recorded 1 h after immersion in the electrolyte (Fig. 8). Again, the modelling quality can be evaluated by means of the model residual. It can be seen that the model residual curve and the *noise + non-stationarities* curve are situated around the same level, meaning that the

Table 3

Fitting results of the lithium carbonate inhibited system after 1 h and 8 h of immersion in 0.05 M NaCl, showing the parameter values and the relative errors on each of the circuit elements, respectively.

		1 h		8 h	
		value	error (%)	value	error (%)
R_s	$\Omega \cdot \text{cm}^2$	27.89	7.43	53.49	2.18
R_{porous}	$\Omega \cdot \text{cm}^2$	84.07	5.27	11.41	2.18
Q_{porous}	$\text{Ss}^n \cdot \text{cm}^{-2}$	$1.26 \cdot 10^{-6}$	7.04	$2.14 \cdot 10^{-7}$	16.83
n_{porous}		1	2.55	0.99	5.63
R_{oxide}	$\text{k}\Omega \cdot \text{cm}^2$	13.67	4.19	10.85	1.10
Q_{oxide}	$\text{Ss}^n \cdot \text{cm}^{-2}$	$6.52 \cdot 10^{-6}$	2.19	$1.37 \cdot 10^{-5}$	1.91
n_{oxide}		0.86	0.31	0.87	0.21
R_{pol}	$\text{k}\Omega \cdot \text{cm}^2$	35.06	16.30	28.42	7.78
Q_{dl}	$\text{Ss}^n \cdot \text{cm}^{-2}$	$2.96 \cdot 10^{-5}$	31.00	$6.99 \cdot 10^{-5}$	4.54
n_{dl}		0.71	7.52	0.72	2.44

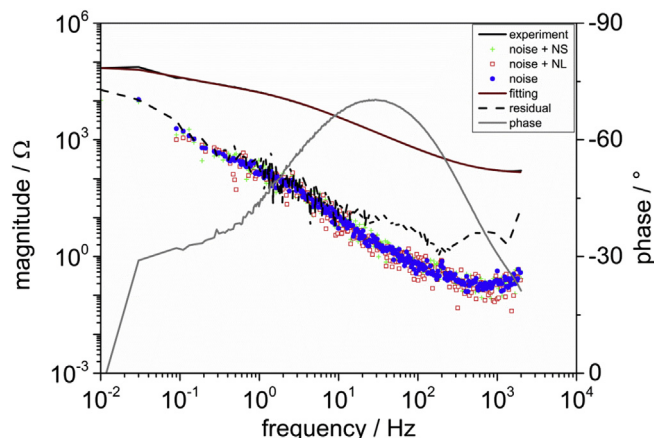


Fig. 9. Bode plot of the lithium carbonate inhibited system after 8 h of immersion in 0.05 M NaCl with the experimental impedance and noise distortion curves and the fitted impedance and model residual curves.

model is able to represent the experimental data within the noise distortions. The parameter values and their relative errors of the circuit elements for the lithium carbonate inhibited system after 1 h of immersion are shown in Table 3. In this case, a value close to 1 is obtained for n_{porous} , nevertheless a CPE element is selected over a capacitance in EEC2, since it shows a better compatibility overall. For all the EIS data during the first 6.5 h of immersion, similar modelling results are obtained. The model parameters are determined with uncertainty levels below or equal to 10% for R_{oxide} , Q_{oxide} , n_{porous} , n_{oxide} and n_{dl} , 20% for R_{porous} , 25% for Q_{porous} and Q_{dl} and 45% for R_{pol} .

After 6.5 h of immersion, when the requirements for a correct EIS measurement are fulfilled, a similar procedure can be followed as for the system without corrosion inhibitors. The approach is illustrated in Fig. 9 for the impedance after 8 h of immersion. It can be seen that the model residual curve and the noise curve are situated around the same level, meaning that the model is able to represent the experimental data within the noise distortions. The parameter values and the relative errors on each of the circuit elements for the lithium carbonate inhibited system after 8 h of immersion are shown in Table 3. For all the EIS data between 6.5 and 12 h after immersion, similar modelling results are obtained. In any case, all model parameters are estimated with relative errors below or equal 10% for R_{oxide} , Q_{oxide} , n_{oxide} , n_{dl} and n_{porous} , 15% for R_{porous} , 25% for Q_{porous} and Q_{dl} and 45% for R_{pol} .

Before accepting the validity of the model, the estimated model parameters must be assessed to confirm that the model is physically plausible. On the one hand, the parameters values should show the differences between the systems with and without lithium carbonate. On the other hand, the time evolution of the model parameters must be physically meaningful.

To make a useful analysis and compare the different impedance results obtained, the effective capacitance of each CPE needs to be considered. Hirschhorn et al. successfully derived a mathematical equation to estimate the effective capacitance C starting from the CPE parameters (Q and n) and the resistance R associated with the same time-constant, for a normal time-constant distribution through a surface layer [34]:

$$C = R^{\frac{(1-n)}{n}} Q^{\frac{1}{n}} \quad (2)$$

Using this approach, the effective dense oxide layer capacitance (C_{oxide}), the double layer capacitance (C_{dl}) and the porous outer layer capacitance (C_{porous}) were calculated.

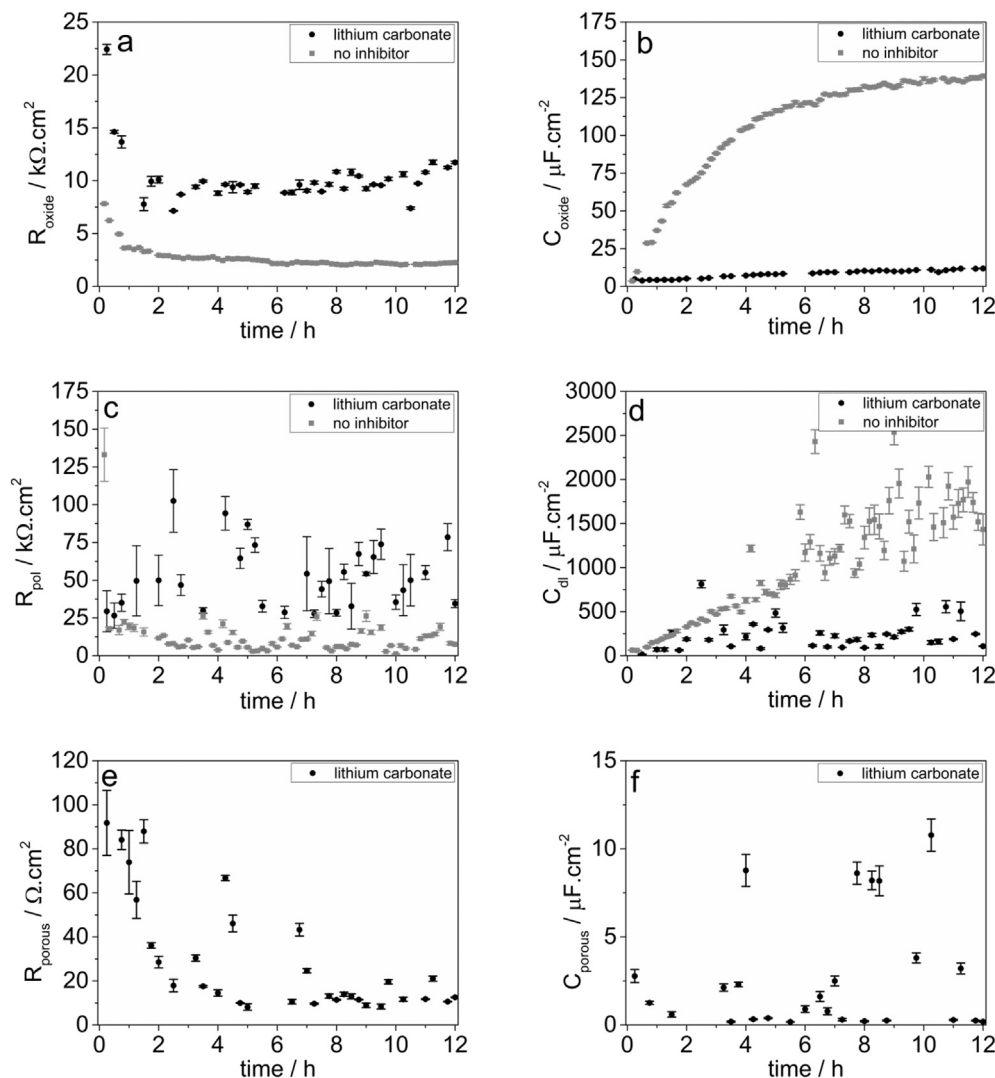


Fig. 10. Evolution of the parameters (a) R_{ox} , (b) C_{ox} , (c) R_{pol} , (d) C_{dl} , (e) R_{porous} and (f) C_{porous} as a function of time for the system without corrosion inhibitors and the lithium carbonate inhibited system.

Fig. 10 shows the evolution of the resistance and capacitance of the oxide layer, the polarization resistance and the double-layer capacitance and the resistance and capacitance of the porous layer as a function of time for the system without corrosion inhibitors and the lithium carbonate inhibited system. For the system without corrosion inhibitors, the resistance and capacitance of the porous layer do not apply. The resistance of the oxide R_{oxide} (Fig. 10a) is $22.43 \pm 0.48 \text{ k}\Omega \text{ cm}^2$ right at the start and decreases drastically in the first 6 h after immersion, reaching a stable value of $10.11 \pm 0.31 \text{ k}\Omega \text{ cm}^2$. Simultaneously, the capacitance of the oxide layer C_{oxide} (Fig. 10b) increases from $3.60 \pm 0.05 \text{ }\mu\text{F cm}^2$ right at the start to a value of $137.55 \pm 1.24 \text{ }\mu\text{F cm}^2$ after 10 h of immersion. The polarization resistance R_{pol} (Fig. 10c) rapidly decreases during the first 2 h of immersion and stabilizes afterwards at $11.70 \pm 0.23 \text{ k}\Omega \text{ cm}^2$. The double layer capacitance C_{dl} (Fig. 10d) increases from $62.85 \pm 1.67 \text{ }\mu\text{F cm}^2$ right at the start to $1732.96 \pm 179.86 \text{ }\mu\text{F cm}^2$ after 10 h of immersion in the electrolyte.

For the protective layer developed from the lithium carbonate leaching coating after 168 h NSS, it can be seen that the contribution of the resistance of the porous middle layer R_{porous} (Fig. 10e) starts at $91.76 \pm 14.76 \text{ }\Omega \text{ cm}^2$ and rapidly decreases in the first couple of hours before reaching a stable value of $10.58 \pm 1.04 \text{ }\Omega \text{ cm}^2$

after 6.5 h of immersion. The coupled capacitance of the porous layer C_{porous} (Fig. 10f) is around $1\text{--}3 \text{ }\mu\text{F cm}^2$, except for some fluctuations occurring during the first 12 h. The resistance of the dense inner oxide layer R_{oxide} (Fig. 10a) is $22.43 \pm 0.48 \text{ k}\Omega \text{ cm}^2$ right at the start and decreases afterwards, reaching a stable value of $10.11 \pm 0.31 \text{ k}\Omega \text{ cm}^2$ after 2 h and for the remaining of the measurement. Simultaneously, the capacitance of the oxide layer C_{oxide} (Fig. 10b) increases progressively from an initial value of $4.82 \pm 0.19 \text{ }\mu\text{F cm}^2$ to a value of $11.90 \pm 0.16 \text{ }\mu\text{F cm}^2$ after 12 h of immersion. The polarization resistance R_{pol} (Fig. 10c) is $29.42 \pm 13.60 \text{ k}\Omega \text{ cm}^2$ for the initial stages and fluctuates around $30\text{--}80 \text{ k}\Omega \text{ cm}^2$ for the remaining of the first 12 h of immersion. The double layer capacitance C_{dl} (Fig. 10d) is $13.73 \pm 3.42 \text{ }\mu\text{F cm}^2$ right at the start and increases afterwards to a fluctuating value between 150 and $300 \text{ }\mu\text{F cm}^2$.

The parameter values obtained for the system without corrosion inhibitors in this work are similar to the ones obtained by Visser et al. after 4–8 h of immersion in the electrolyte [15]. In the case of the system without corrosion inhibitors, values of $3.85 \text{ k}\Omega \text{ cm}^2$ and $102.82 \text{ }\mu\text{F cm}^2$ were obtained for the oxide resistance and capacitance, respectively, which have a good agreement with the values of 2.59 ± 0.02 to $2.10 \pm 0.01 \text{ k}\Omega \text{ cm}^2$ and 104.86 ± 0.92 to

$132.51 \pm 0.75 \mu\text{F cm}^{-2}$ after 4 and 8 h of immersion in this work. For the polarization resistance and double layer capacitance, $9.68 \text{ k}\Omega \text{ cm}^2$ and $553.08 \mu\text{F cm}^{-2}$ were obtained, compared to 3.78 ± 0.29 to $6.03 \pm 0.58 \text{ k}\Omega \text{ cm}^2$ and 628.12 ± 30.91 to $1341.72 \pm 128.70 \mu\text{F cm}^{-2}$ after 4–8 h in this work.

In the case of the lithium carbonate inhibited system, a similar comparison can be made. For the resistance and capacitance of the porous layer, Visser et al. obtained values of $17.00 \text{ k}\Omega \text{ cm}^2$ and $0.83 \mu\text{F cm}^{-2}$ after 168 h exposure in the NSS testing and after 4–8 h of immersion in the electrolyte, compared with 14.53 ± 1.45 to $11.41 \pm 0.25 \text{ k}\Omega \text{ cm}^2$ and a stable value of around $1\text{--}3 \mu\text{F cm}^{-2}$ in this work, under the same conditions [15]. For the contribution of the oxide layer, $29.64 \text{ k}\Omega \text{ cm}^2$ and $27.04 \mu\text{F cm}^{-2}$ were obtained, compared to 8.82 ± 0.20 to $10.85 \pm 0.12 \text{ k}\Omega \text{ cm}^2$ and a progressive increase from 7.23 ± 0.09 up to $10.35 \pm 0.20 \mu\text{F cm}^{-2}$ after 4–8 h of immersion in the electrolyte in this work. The polarization resistance and double layer capacitance were $237.43 \text{ k}\Omega \text{ cm}^2$ and $46.14 \mu\text{F cm}^{-2}$ compared to $30\text{--}80 \text{ k}\Omega \text{ cm}^2$ and $150\text{--}300 \mu\text{F cm}^{-2}$ in this study. The differences in the oxide resistance and capacitance and the polarization resistance and double layer capacitance are remarkable. Nevertheless, the evaluation of the fitting quality by means of the model residual shows that the model is able to represent the experimental data within the noise distortions. This proves that the EEC is statistically correct and that these parameter values can be considered more realistic.

It is interesting to link the resistance and the capacitance of the porous layer to the observations made in the quantitative interpretation of the ORP-EIS noise data of the lithium inhibited system. The analysis of the relative contribution of the non-stationarities shows that the system behaves non-stationary for the first 6.5 h after immersion in the electrolyte. On the other hand, the non-stationary behaviour is predominant at the highest 2 frequency decades (IV and V), i.e., frequencies ranging from 10 Hz up to 1 kHz (Fig. 4b). Considering the physical behaviour of the electrochemical system and the proposed electrical circuit, the non-stationarities at high frequencies can be related to the time-varying behaviour of the porous layer. This behaviour is translated into unstable, decreasing values for the resistance of the porous layer in the first 6.5 h. Afterwards, when the whole system, and the porous layer in particular, behaves stationary, a stable value of around $10 \text{ k}\Omega \text{ cm}^2$ for R_{porous} is obtained.

Regarding the parameters related to the dense oxide layer, for the system without corrosion inhibitors, the decrease in resistance and the increase in capacitance demonstrate the degradation of the native oxide layer during the first hours of immersion. A similar observation can be made for the lithium carbonate inhibited system, with a degradation of the inner dense oxide layer in the first 2 h. This coincides with the non-stationary behaviour in the frequency region from 1 Hz to 10 Hz (decade III) (Fig. 4b). A stable value of around $10 \text{ k}\Omega \text{ cm}^2$ is obtained for the oxide resistance of the inhibited system, more than 4 times higher than the $2.20 \text{ k}\Omega \text{ cm}^2$ for the system without corrosion inhibitors. Moreover, the oxide capacitance of the system without corrosion inhibitors increases more rapidly than the oxide capacitance of the inhibited system, which is related to the fast degradation of the native oxide layer for the system without corrosion inhibitors and the slower degradation of the dense layer formed during NSS for the inhibited system. This corresponds with the observations made in our previous work [15].

The corrosion activity is described by the low frequency time constant [35]. The polarization resistance of the lithium inhibited containing coating is more than 3 times higher, compared to the system without corrosion inhibitors. The double layer capacitance

of the system without corrosion inhibitors, similar to the oxide capacitance, increases more rapidly than the inhibited system, up to values at least 5 times higher after 12 h of immersion. This confirms the protective properties of the layer generated by the lithium leaching coating technology, in agreement with earlier observations [11,14,15].

The modelling residual is low compared to either the level of noise + non-stationarities or the noise level, dependent on the system's stability, for both the system without corrosion inhibitors and the lithium carbonate inhibited system. Moreover, the estimated parameters are physically meaningful and the proposed EEC models are physically plausible. Consequently, it is concluded that the proposed EEC models can be accepted.

4. Conclusions

The qualitative analysis of the ORP-EIS data of the system without corrosion inhibitors and the lithium carbonate inhibited system revealed the presence of both non-linearities and non-stationarities in the early stages after immersion in the electrolyte. For both systems, it is observed quantitatively that the presence of non-stationarities is linked to the overall instability of the electrochemical system during the first 5 and 6.5 h, respectively. These correspond to the time needed to reach a stable degradation process of the oxide on the system without corrosion inhibitors or the multi-layered protective morphology on the lithium carbonate inhibited system. The quantification per frequency decade of the information regarding the non-stationarities of the system without corrosion inhibitors leads to the conclusion that the electrochemical processes related to the dense oxide layer, occurring in the mid-frequency region, take the longest to stabilize. In the case of the lithium carbonate inhibited system, the electrochemical processes in the porous layer, occurring in the high frequency regions prolong the system's instability.

From the monitoring of the system without corrosion inhibitors and the lithium carbonate inhibited system during the first 12 h of immersion in 0.05 M NaCl, the parameter evolutions of the respective equivalent electrical circuits elements are extracted. The observed trends can be explained by the evolution of the level of non-stationarities in the corresponding frequency decade(s) and they can be linked to the morphological changes happening during immersion in the electrolyte. Particularly, the non-stationary behaviour of the lithium carbonate inhibited system in the mid frequency region from 1 to 10 Hz in the first 2 h and in the highest two frequency decades in the first 6.5 h can be related to the unstable, decreasing values of the resistance of the oxide- and the porous layer in the first 2 and 6.5 h, respectively. When the lithium carbonate based protective morphology becomes stable as a function of immersion time, stable parameter values are obtained for the respective EEC model elements.

This paper shows that the ORP-EIS based methodology allows us studying the behaviour of corrosion inhibitors in an alternative way. The time-dependent behaviour of electrochemical systems containing corrosion inhibitor is highlighted, proving the great value of the approach for further corrosion inhibitor research.

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