



HAL
open science

Impedance analysis of film-forming amines for the corrosion protection of a carbon steel

Jordan Baux, Nicolas Causse, Jérôme Esvan, S. Delaunay, J. Tireau, M. Roy, D. You, Nadine Pebere

► To cite this version:

Jordan Baux, Nicolas Causse, Jérôme Esvan, S. Delaunay, J. Tireau, et al.. Impedance analysis of film-forming amines for the corrosion protection of a carbon steel. *Electrochimica Acta*, 2018, 283, pp.699-707. hal-01883111v1

HAL Id: hal-01883111

<https://cea.hal.science/hal-01883111v1>

Submitted on 5 Nov 2019 (v1), last revised 27 Sep 2018 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterization by EIS and XPS of an organic inhibitive thin film formed on a carbon steel surface

Jordan Baux^{1,2}, Nicolas Causse¹, Jérôme Esvan¹, Sophie Delaunay², Jonathan Tireau²,
Marion Roy³, Dominique You³, Nadine Pébère^{1*}

¹Université de Toulouse, CIRIMAT, UPS/INPT/CNRS ENSIACET, 4 allée Emile Monso, 31030 Toulouse Cedex 4, France.

²EDF R&D / Chemistry and Corrosion Group, Avenue des Renardières, 77818 Moret-sur-Loing Cedex, France.

³Den – Service d'Etude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France.

* Corresponding authors.

E-mail address: nadine.pebere@ensiacet.fr

Abstract

Octadecylamine is a well-known organic inhibitor for carbon steel protection for industrial boilers functioning at various temperatures in alkaline media. In the present study, we focus on the analysis of electrochemical impedance spectroscopy (EIS) data to extract physical parameters of the ODA thin film that forms on a P275 carbon steel surfaces. First, surface observations and contact angle measurements showed clearly the modification of the surface after treatment linked to the adsorption of an organic translucent and hydrophobic thin film. X-ray photoelectron spectroscopy (XPS) confirmed the presence of a very thin covering organic layer and shows the presence of iron oxide underlying the ODA film. The EIS data analysis allows the determination of physical parameters considering an in-depth power-law distribution of resistivity in the dielectric film. The values of the permittivity and thickness of the film are extracted. Finally, the in-depth resistivity profile have been calculated. It highlights a high resistivity value corresponding to the thickness of an ODA monolayer.

Keywords

Film-forming amine, 1-octadecylamine, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, organic inhibitor.

1. Introduction

During shutdown periods of pressurized water reactors (PWR) for maintenance operation, corrosion phenomena can appear due to oxygen entrance. Use of environmentally friendly corrosion inhibitors such as film-forming amines (FFA) is a promising approach to reduce or to stop the corrosion of carbon steel, which constitute the major part of the PWR secondary circuit [1,2]. A key benefit of film-forming amines is to improve the corrosion protection during frequent startups and shutdowns of the PWR and, as a consequence, high steam quality can be obtained quicker during startup, leading to significant economic repercussions [1]. Even though FFA have been used successfully for decades to treat boiler feed water in industrial power plants [3], its behaviour is not well understood as well as the physical characteristics of the film formed on the carbon steel surface. Octadecylamine (ODA), $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$, is a well-known FFA that has been used as corrosion inhibitor for steel in nuclear power plants and fossil fuel power plants for years [1,4–11,3,12]. The molecule has both a hydrophilic head and a hydrophobic tail, which after film-formation creates a physical barrier that impedes water, oxygen or other corrosive agents to reach the metal surface and also probably impedes dissolution of iron from the material. The protective film is often described as a monolayer formed on the steel surface [2,9,13,14] but no proof of the film thickness has been provided. The determination of the film thickness would be of great interest to better control the ODA addition in the circuit. However, *in situ* determination of the thickness of organic ultra-thin films on non-ideal surfaces such as metallic substrates remains quite challenging [15–17]. Mechanical and optical profilometry are not sensitive enough to investigate the film thickness at a submicrometric scale. Other optical techniques, such as ellipsometry, require the knowledge of physical quantities (refractive index, for example) and the use of modeling to extract the film thickness from the experimental data. Atomic force microscopy (AFM) can be used for measuring very thin film thickness but the

measurements are strongly sensitive to the substrate roughness. For an ODA film deposited on mica, Patil et al. [18] have measured a thickness of about 20-30 nm by AFM in humid conditions. On the other hand, spectroscopic techniques such as x-ray photoelectron spectroscopy (XPS) and secondary ion-mass spectroscopy (SIMS) are powerful *ex situ* techniques that allow surface characterization and thickness measurement at a nanometric scale. However, the erosion rate, which depends on the material, must be known for an accurate thickness determination.

Electrochemical impedance spectroscopy (EIS), is a widely use technique for the assessment of corrosion protection by inhibitors or coatings. This technique allows *in situ* measurements in controlled experimental conditions which can be representative of real environment [19–23]. Recently, good agreement has been found between results obtained from EIS data and XPS analysis for the determination of a thin passive oxide layer film thickness [24,25]. The aim of the present work was to determine the thickness of an ODA film formed on a carbon steel surface at 80 °C in an alkaline solution representative of the PWR secondary circuit. First, the film formed on a carbon steel electrode was characterized by *ex situ* observations and XPS analysis. Then, the EIS diagrams obtained in the presence of ODA was modelled to determine the film thickness and other physical parameter (e.g. permittivity). From the impedance diagrams obtained at the corrosion potential with and without ODA, the inhibitor efficiency for the corrosion protection of the carbon steel was determined.

2. Impedance diagrams analysis

The impedance results are usually analyzed by using electrical equivalent circuits (EEC). However, it is observed that resistances and capacitances, which are associated with different steps of the corrosion process, inhibitor or coating properties do not accurately describe the experimental impedance data. In these cases, constant phase element (CPE) were used instead of capacitance to take into account the non-ideal behaviour of the system. The CPE impedance is expressed in terms of model parameters α and Q as:

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

It is possible to graphically determine the α parameter by plotting the logarithm of the imaginary part of the impedance with respect to the logarithm of the frequency (Eq. 2) [26]. Then, Q is expressed as a function of α and impedance data with the following relationship :

$$\alpha = \frac{d \log(-Z_j)}{d \log(f)} \quad (\text{Eq. 2})$$

$$Q = \sin\left(\frac{\alpha\pi}{2}\right) \frac{-1}{Z_i(f)(2\pi f)^\alpha} \quad (\text{Eq. 3})$$

However, the CPE parameters have no physical meaning and, in the case of a 3D dielectric layer at the surface of a conducting electrode, cannot be directly related to the physical properties of the layer. In the case of oxide films or organic coatings, the complex capacitance representation can exhibit the effective capacitance of the dielectric layer [24,27]. An ohmic drop correction is necessary to properly study the dielectric properties of the system at high frequency, that may be hidden by the electrolyte resistance contribution.

The latter is obtained by extrapolation at high frequency on the real axis on the Nyquist plot.

The complex capacitance plots corresponding to EIS data is obtained using the following transformation (Eq. 4).

$$C(\omega) = \frac{1}{j\omega[Z(\omega) - R_e]} \quad (\text{Eq. 4})$$

with C, the capacitance as a function of $\omega = 2\pi f$. Z, the impedance data and R_e , the electrolyte resistance. The thickness of the dielectric layer can then be calculated using the following relationship :

$$\delta = \frac{\varepsilon\varepsilon_0}{C_f} \quad (\text{Eq. 5})$$

ε is the permittivity of the film, ε_0 , the permittivity of vacuum, C_f , the effective capacitance of the film determined from the extrapolation at high frequency and δ , its thickness.

Power-law model

Recently, different studies suggested that the origin of the CPE behaviour observed with oxide films or organic coatings may be the consequence of a normal distribution of their resistivity along the film thickness according the model developed by Hirschorn et al. [28,29].

The resistivity $\rho(\xi)$, with $\xi = \frac{x}{\delta}$, is expressed (Eq. 6) as a function of the thickness of the layer δ , the depth x in the layer, the limit values of the resistivity ρ_0 and ρ_δ at the interfaces $x = 0$ and $x = \delta$ respectively and γ which is derived from the CPE parameter α such as $\alpha = \frac{(\gamma-1)}{\gamma}$.

$$\frac{\rho(\xi)}{\rho_\delta} = \left(\frac{\rho_\delta}{\rho_0} + \left(1 - \frac{\rho_\delta}{\rho_0}\right) \xi^\gamma \right)^{-1} \quad (\text{Eq. 6})$$

For a frequency $f < \frac{1}{2\pi\varepsilon\varepsilon_0\rho_\delta}$, the corresponding impedance can be determined using an integral expression (Eq. 7).

$$Z_f(\omega) = \delta \int_0^1 \frac{1}{\frac{1}{\rho_0} + j\omega\varepsilon\varepsilon_0 + \left(\frac{1}{\rho_\delta} - \frac{1}{\rho_0}\right) \xi^\gamma} d\xi \quad (\text{Eq. 7})$$

Regression of EIS data with the power-law model allows the extraction of physical parameters related to the film such as the permittivity, the thickness and the resistivity at the interfaces, which are not easily accessible by other techniques.

According to the power-law model, values of the CPE parameters are correlated to the physical properties of the film [28] using Eq. 8.

$$Q = \frac{(\varepsilon\varepsilon_0)^\alpha}{g\delta\rho_\delta^{(1-\alpha)}} \quad (\text{Eq. 8})$$

With g a function depending on α given by Eq. 9 and ρ_δ the resistivity at the interface film/electrolyte as discussed above.

$$g = 1 + 2.88(1 - \alpha)^{2.375} \quad (\text{Eq. 9})$$

The resistivity at the metal/film interface ρ_0 can be calculated using Eq. 10 with the characteristic frequency f_0 determined at the maximum of the imaginary part of the impedance.

$$\rho_0 = \frac{1}{2\pi\varepsilon\varepsilon_0f_0} \quad (\text{Eq. 10})$$

In this paper, impedance results in the presence of ODA were analyzed in two successive steps in order to estimate the film thickness. The first approach was based on the graphical method, independent of any physical model [24,26,27]. The second approach was focused on the use of the power-law resistivity model developed by Hirschorn et al. [28,29]. The agreement between graphical estimated parameters and fitted parameters was verified in order to validate the model.

3. Experimental

3.1. Materials

The P275 low carbon steel was supplied by EDF (France) as representative material of PWR. Its composition is reported in Table 1. The steel sample was machined to obtain a cylindrical rod of 1.13 cm in diameter (surface area = 1 cm²). The lateral part of the rod was covered with a heat-shrinkable insulating sheath, leaving only the tip of the carbon steel in contact with the solution. Before the deposition step, the surface was wet ground with silicon carbides (SiC) papers down to grade 4000, cleaned ultrasonically with ethanol, rinsed with deionized water and dried.

The chosen FFA was octadecylamine (ODA) in the form of ODACON[®], a commercial emulsion (≈ 50 g/L FFA) supplied by REICON[™] mainly constituted of ODA and hexadecylamine (HDA) in smaller proportion.

The test solution was prepared from analytical grade Na₂SO₄ 10⁻³ M and deionized water in equilibrium with air ([O₂]_{25 °C} = 8 mg.kg⁻¹). pH was adjusted at 10 with ammonia. The choice of this medium was based upon its low electrical conductivity, close to that encountered in industrial water circuit, its low corrosiveness toward carbon steel and because it is an easily reproducible baseline solution. The same solution was used for the deposition step and for electrochemical analysis.

3.2. Deposition conditions and film formation

The deposition conditions were determined from a preliminary experiment. In the present study, the ODA film was formed with the following parameters (Table 2). With these parameters, a complete and protective ODA film was formed on the carbon steel surface in less than 30 minutes.

3.3. Surface characterizations

Optical observations were performed with a binocular loupe and an Olympus PMG3 optical microscope. The contact angles were measured using a Digidrop Contact Angle Meter from GBX Scientific Instruments. The protocol consisted in depositing a deionized water drop of an accurate volume of 2 μL on the sample surface (bare metallic surface or treated surface with ODA) and then measuring the static contact angle (θ) 60 s after the deposition. The contact angle value was obtained by calculating the slope of the tangent to the drop at the liquid-solid interface thanks to the GBX software. To assess the homogeneity of the surface properties, 20 measurements were performed on different locations on the samples surface and the average contact angle was calculated with the standard deviation. All the experiments were performed at room temperature.

The chemical composition of the film formed on the carbon steel surface was determined using XPS analysis with a K alpha Thermo Scientific Spectrometer on two different samples treated in the same conditions. The specimens were irradiated with a Al-K α radiation ($h\nu = 1486.6$ eV) from a monochromatized source and the X-ray spot was approximately 400 μm in size. Angle-resolved measurements were made at a take-off angle $\Theta = 90^\circ$ (e.g. normal to the sample surface). The pass energy for the surveys was fixed at 160 eV and at 40 eV for high resolution spectra. The spectrometer energy calibration was made using the Au 4f 7/2 (83.9 ± 0.1 eV) and Cu 2p 3/2 (932.8 ± 0.1 eV) photoelectron lines. XPS spectra were recorded in direct N(Ec). Background signal was removed using Shirley method. The binding energy scale was established by referencing the C 1s value of adventitious carbon (284.9 ± 0.1 eV). The photoelectron peaks were analysed by

Gaussian/Lorentzian ($G/L = 30$) peak fitting. Flood gun was also applied for avoiding charge effects.

3.3. Electrochemical measurements

The electrochemical cell used was a conventional three-electrode cell with a saturated sulfate reference electrode and a platinum grid as counter electrode. The working electrode consisted of the carbon steel. The rotation rate was fixed at 500 rpm. Electrochemical impedance measurements were performed using a Solartron 1286 electrochemical interface connected to a Solartron 1250 frequency response analyzer. Impedance diagrams were obtained under potentiostatic regulation at the corrosion potential (E_{corr}) in the frequency range of 65 kHz to 10 mHz with 8 points per decade, using a 15 mV_{rms} sinusoidal voltage. Impedance data beyond 6.5 kHz were not taking into account due to experimental artifacts, which origin have been described by Tran et al. [30]. The validity of the EIS was checked with Kramers-Kronig transform using the Lin-KK tool [31–33]. Data modeling was carried out using a non-commercial software developed at the LISE CNRS (Paris), based on a simplex method.

4. Results and discussion

4.1. Morphology and hydrophobicity of the surface film

Fig. 1 shows the sample surface after the treatment at 80 °C with and without ODA. Without ODA, corrosion products with the shape of hydrodynamic pattern are observed (Fig. 1a). In the presence of ODA, the carbon steel surface is not attacked but covered with a film (Fig. 1b). White clusters with dimensions between 0.1-5 μm are clearly observed all over the electrode surface (Fig. 1b). Raman spectroscopy analysis (results not shown) have revealed that the clusters are made of bulk ODA. The whole carbon steel surface is assumed to be covered with a thin layer of ODA.

Contact angle measurements were performed on the bare carbon steel surface and on the ODA treated sample. The results are shown in Fig. 2. For the bare steel, the surface presented a hydrophilic character with a contact angle of $39^\circ \pm 5^\circ$ (Fig. 2a). After treatment with ODA, the measured contact angle (Fig. 2b), is $93^\circ \pm 2^\circ$ showing that the surface lost its hydrophilic character, which is a well-known effect of ODA adsorption [1]. The contact angles, are identical all over the surface, indicating that the hydrophobicity of the film was constant whatever the form of ODA (thin film or aggregates).

4.2. XPS analysis

Fig. 3 shows the surveys spectra for the carbon steel surface before (Fig. 3a) and after the ODA treatment (Fig. 3b). They were obtained on four different locations on two samples. On Fig. 3b, the Fe, O, C and N signals are observed and the spectra are superimposed showing a homogeneous coverage of the film and a good reproducibility of the deposition process. Nitrogen peak is not observed on Fig. 3a, and in contrast, the intense peaks of N and C on Fig. 3b are associated to the presence of the ODA film. Fig. 4 displays the high resolution spectra of C 1s, Fe 2p_{3/2}, N 1s and O 1s. The binding energies for the different signals are summarised in Table 2 as well as the chemical composition of the surface (in at. %), calculated from the peak area.

The N 1s spectrum displayed two peaks at 399.5 eV and 401 eV which were identified as NH₂ [34–37] and NH³⁺ [17,38] respectively. The bonding energy difference between NH₂ and NH³⁺ (1.6 eV) is in agreement with previous studies [38]. The same value of binding energies have been reported for NH₂ in the case of metallic Ag and Pd substrates: CH₃NH₂/Pd[34], CH₃CH₂NH₂/Ag [35], NH₂(C₆H₄)O(C₆H₄)NH₂/Ag [36] and graphene oxide (GO) substrate: ODA/GO [37]. The C 1s spectrum displayed three peaks, the first one at 285 eV corresponds to the aliphatic bonding C-C of the ODA molecule [37]. The one at 286.1 eV is linked to a mixture of C-O and C-N bondings [39]. The peak at 288.3 eV is characteristic of C-N bonds in amides and O=C-O bonds [37] which are probably originated from surface pollution. The Fe 2p spectrum shows the presence of metallic iron (706.3 eV) and oxidized iron (beyond 708.0 eV). An oxide film was assumed to be formed at the carbon steel surface after the polishing step. Thus ODA adsorbed on a thin iron oxide/hydroxide layer, probably Fe₂O₃ or FeOOH formed in the aerated test solution, and not directly on the bare carbon steel surface. Finally, the O 1s peak, located in a binding energy range from 529.7

eV to 532.4 eV, is mainly attributed to O²⁻ in the form of iron oxides [39], iron hydroxides OH [40] and surface pollution.

The $\frac{[N\ 1s]}{[C-C]}$ ratio, calculated from Table 3, after the deconvolution of the C 1s spectrum was about 0.042 which was smaller than the expected theoretical value of 0.055. The presence of carbonated pollution on the surface may influence the measured ratio by increasing the C-C contribution.

From the XPS analysis, it can be seen that both the signal from the organic film and from the substrate were observed. This indicates that the film thickness ranges between 2 nm (thickness of an ODA monolayer) and about 10 nm. This thickness value is due to the short inelastic mean free path, λ , of electrons in condensed materials (about 3 nm). The major part of the signal is contained in a depth of 3λ [41], and therefore cannot exceed 10 nm. However, it is important to mention that a spontaneous height reduction, known as “ripening” occurs when ODA self-assembled layers are in contact with air [18,38,39]. Besides, weakly adsorbed multilayers that are stable when immersed in the electrolyte may be damaged during the removal from the solution [16].

4.3. EIS measurements

4.3.1. Graphical method

Impedance spectra of the treated and untreated carbon steel electrodes are presented in Fig. 5. The Nyquist diagram of the carbon steel after the ODA treatment (Fig. 5a) shows two depressed capacitive loops. The first loop at high frequencies, between 10^1 and 10^4 Hz, can be linked to the presence of the ODA film, as clearly seen on the phase angle (Fig. 5c). The second capacitive loop can be attributed to the process occurring at the metal/film interface. It was checked that the second loop was little dependent of the electrode rotation rate

(diagrams not shown). First, the impedance data analysis focussed on the high frequency time-constant obtained for the treated ODA sample in order to extract the ODA film thickness.

Fig. 6 displays the impedance diagram in Bode coordinates corrected from the ohmic drop of the carbon steel treated with ODA. It highlights a plateau at high frequency on the phase diagram, characteristic of a pure CPE behaviour, at a phase angle of -68 degrees. The calculated CPE parameter $\alpha_f = 68/90 = 0.75$.

In order to estimate the film thickness, the complex-capacitance plots were obtained from the corrected impedance data using Eq. 4. Fig. 7 presents the complex-capacitance plot corresponding to the curves presented in Fig. 6. The extrapolation of the high-frequency data to the real axis does not allow an accurate determination of the capacitance. However, it is possible to estimate a capacitance value (C_f) between 0.1-0.2 $\mu\text{F cm}^{-2}$. Once the film capacitance is known, the film thickness can be obtained from Eq. 5. The permittivity of the ODA film is not known. However, in the literature, permittivity values of self-assembled surfactants were reported and the values were ranging from 2 to 3 [42–47]. A value of 2.7, found for bulk ODA [47], was used in Eq. 4 to calculate the film thickness. Due to the uncertainty on the film capacitance determination, the calculated ODA film thickness varied from 12 to 22 nm.

The high frequency time constant highlight a non-ideal behaviour that can be described using a CPE (Q_f, α_f). The parameters α_f and Q_f were graphically determined (Fig. 8). Fig. 8a shows that the absolute value of the $\text{dlog}(-Z_j)/\text{dlog}(f)$ slope, α_f , is 0.75, in agreement with the value determined with Fig. 6. Knowing α_f value, it is possible to determine the CPE coefficient value Q_f from Eq. 2. The horizontal asymptote provides the value for the CPE coefficient $Q_f = 4.14 \mu\text{F cm}^{-2} \text{ s}^{(\alpha-1)}$ for the high frequency time constant

(Fig. 8b). Values of α_f of about 0.75 are linked to normal distributions of time constants which is expected in the case of the presence of a dielectric film at the surface [48]. Finally, ρ_δ could be framed with the graphically determined values of δ , Q_f and α_f by using Eq. 7. Finally, ρ_0 was calculated using Eq. 9 with the characteristic frequency visible at the maximum of the imaginary part of the impedance visible Fig. 8a, results are presented in Table 4.

4.3.2. Power-law resistivity of film impedance

The high-frequency part of the diagram (6.5 kHz to 65 Hz) was regressed to the model (Eq. 7). The best fitted curves is shown as dotted line in Fig. 7. A good fitting is achieved with a general sum of the deviations between experimental and calculated spectra $\chi^2 = 0.36$. The regression procedure provided numerical values of the adjustable parameters α_f , ρ_0 , ρ_δ , ε_f relevant to the ODA film. These values are reported in Table 3 and compared to the graphically extracted parameters. A good agreement is obtained between the regressed parameters and the values graphically determined. The film thickness obtained from the model is equal to 16 nm and the permittivity value is close to the one found in literature.

The values of ρ_0 , ρ_δ and α_f obtained from the analysis of the high frequency part of the impedance diagram were used to calculate the in-depth profile of the steel/film/electrolyte system (Eq. 6). The result is shown in Fig. 9. A high resistivity area is observed ($\rho_0 = 1 \times 10^{10} \Omega \text{ cm}$) close to the metal/film interface in the first 2 nm, that corresponds to the thickness of a close-packed ODA monolayer considering a tilt angle of the ODA aliphatic chains of roughly 15° [38]. Beyond about 2 nm, the resistivity decreases rapidly to reach a minimum value of ρ_δ of $1.6 \times 10^6 \Omega \text{ cm}$ at the film/electrolyte interface. This result may indicate a strong interaction between the first layer of ODA in contact with the carbon steel surface. The additional layers would be less compact due to weaker interactions.

The ODA film formed on the carbon steel surface is compact and insulating. However, the low impedance values after treatment indicates the presence of porosity in the ODA film, leading to charge transfer processes at the bottom of the pores, described by the second capacitive loop. The CPE behaviour of the carbon steel electrode corresponds to surface variation of time constant in accordance with a double-layer model. The electric double-layer is located at the end of the through porosity of the ODA film, on the conductive accessible electrode surface.

4.3.3. Low frequency behaviour

The CPE_{dl} parameters, Q_{dl} and α_{dl}, the electrolyte resistance R_e and the charge transfer resistance R_t for the bare carbon steel sample were graphically determined. In the case of the treated ODA sample, the CPE_{dl} parameters could not be graphically determined due to the strongly depressed aspect of the second capacitive loop. The latter was fitted with a R//CPE circuit allowing a proper determination of the low frequency CPE parameters. The parameters R_e, R_t, Q_{dl}, and α_{dl} are reported in Table 5. A value of α_{dl} = 0.44 is obtained for the treated sample. From the CPE parameters, the effective capacitance can be calculated considering a distribution of the charge transfer resistances on the electrode surface. The effective capacitance of the electrical double-layer for the treated ODA sample and the bare carbon steel were calculated using the following Brug formula :

$$C_{eff} = Q_{dl}^{\frac{1}{\alpha}} \left(\frac{1}{R_e} + \frac{1}{R_t} \right)^{(\alpha-1)/\alpha}$$

with Q_{dl} the pseudo-capacitance of the electric double-layer, R_e the electrolyte resistance and R_t the charge transfer resistance. The effective capacitances were 100 μF cm⁻² and 12 μF cm⁻² for the bare carbon steel and the ODA treated carbon steel, respectively. The effective

capacitance of the bare carbon steel electrode is in the order of magnitude of double-layer capacitance ($\approx 50 \mu\text{F}\cdot\text{cm}^{-2}$) [25].

The ratio of effective capacitances for the bare carbon steel and the treated sample, gives an insight about the accessible surface at the bottom of the through-pores of ODA film. A value of 12 % is obtained. R_t values were used to calculate the inhibitive efficiency (IE) according to the following equation :

$$IE\% = \frac{R_t^{inh} - R_t^0}{R_t^{inh}} \times 100$$

With $R_t^{inh} = 11720 \Omega \text{ cm}^2$, the charge transfer resistance of the ODA treated sample and $R_t^0 = 1175 \Omega \text{ cm}^2$ the charge transfer resistance of the bare carbon steel. The efficiency was 90 %, in accordance with the effective capacitance ratio.

We have shown first that the high frequency CPE behaviour of the treated sample can be successfully described by a power-law resistivity model linked to resistivity gradient due to the distribution of non-through pores in the ODA layer. On the other hand, the low frequency CPE was attributed to the electric double-layer at the bottom of the pores. The impedance of the through-pores is usually represented by a resistance R_{pore} , associated to the electrolyte resistance in the porosity. Finally, regarding the previous observations, the EEC commonly used for organic coatings (Fig. 10), appears appropriate to describe the electrochemical behaviour of the ODA treated carbon steel. The experimental diagram is in good accordance with the fitted data ($\chi^2 = 0.32$).

5. Conclusions

In this study, optical observations, drop angle measurements and XPS analysis were performed to highlight the formation of a thin, hydrophobic, ODA film at the surface of carbon steel electrode covered by a native, thin oxide layer, as shown from XPS analysis. The

film was scattered with small ODA clusters of various sizes and its thickness in dry and vacuum conditions was estimated from XPS analysis between 2 and 10 nm.

The analysis presented was based on the use of the power-law model to describe the non-ideal behaviour of the system and to extract quantitative parameters such as the permittivity of the film and its thickness. All the regressed parameters are in accordance with graphically estimated values. The thickness of the film was 16 nm, in the same order of magnitude of the thickness estimated by XPS analysis. From these results, an in-depth profile of resistivity was calculated, it highlighted a narrow part of high resistivity corresponding to the thickness of the first layer of ODA in contact with the carbon steel and an exponential decrease above. From the low frequency part of the impedance diagrams, it was shown that approximately 10 % of the carbon steel surface was accessible to the electrolyte, in agreement with 90 % of efficiency calculated from the charge transfer resistance.

This work, based both on a graphical and a model study, gave new insights and methodologies for the *in situ* analysis of organic thin films at conducting surfaces for the determination of physical parameters of the film, namely the thickness and the permittivity, that are usually difficult to access by other techniques.

The whole procedure of deposition and study by EIS have been performed with another carbon steel grade (100C6). The same aspect of impedance diagrams was obtained showing that ODA covers also other grades of carbon steel thus protecting the surface against corrosion. Similar regression procedure with the power-law model in the high frequency domain have shown very close results in term of thickness of the ODA film, permittivity, and resistivity at interfaces meaning that this procedure is reproducible for analysing ODA thin films on carbon steel electrodes.

Table 1: Chemical composition of the P275 carbon steel (EN10028-3).

Element (wt%)	C	Si	Mn	Cr	Mo	Ni	Cu	Fe
P275 NL1	0.16	0.4	0.5-1.5	0.3	0.08	0.5	0.3	Bal.

Table 2: Deposition parameters for the formation of the ODA film.

ODA concentration	100 mg.kg ⁻¹
Temperature	80 °C
Rotation rate	500 rpm
pH _{25 °C}	10
Time	30 min

Tableau 3: Chemical composition of the treated ODA carbon steel surface obtained by XPS analysis.

Components	Binding Energy (eV)	FWHM ^a	At. %
C 1s C-C, C-H	285 [37]	1.1	47
C 1s C-N/C-O	286.1 [39]	1.6	3.7
C 1s O-C=O	288.3 [37]	1.5	1.6
O 1s (Fe oxides, OH)	529.7 - 532.4 [39,40]	1.2	32.5
N 1s NH ₂	399.5 [34-37]	1.6	1.6
N 1s NH ₃ ⁺	401.1 [17,38,39]	2	0.4
Fe 2p _{3/2} Oxides	708.0 [49]	-	7.6
Fe 2p _{3/2} Metal	706.3 [40]	1.8	5.6
Total			100
N/C ratio			0.042

^a : Full Width at Half Maximum

Table 4: Estimated parameters and regressed parameters obtained with the power-law model.

	ε	ρ_0 (Ω cm)	ρ_δ (Ω cm)	α_f	δ (nm)	R_e (Ω cm ²)
<i>Graphically extracted parameters</i>	Literature 2.7 [48]	1×10^{10}	$[1.5 \times 10^6 ; 2.4 \times 10^7]$	0.75	[12 ; 22]	1080
Power-law parameters	2.8	1×10^{10}	1.6×10^6	0.78	16	1080

Table 5: Extracted parameters related from the low frequency capacitive loop of the bare carbon steel and the ODA treated sample.

	R_e (Ω cm ²)	R_t (Ω cm ²)	Q_{dl} (F.cm ⁻² .s ^($\alpha-1$))	α_{dl}	C_{eff} (μ F.cm ⁻²)	IE%
Bare carbon steel	1157	1178	2.48×10^{-4}	0.7	100	90%
Treated ODA sample	1080	11720	1.3×10^{-4}	0.44	12	

References

- [1] I. Betova, M. Bojinov, T. Saario, Film-forming amines in steam / water cycles – structure, properties, and influence on corrosion, VTT. VTT-R-0323 (2014) 1–41.
- [2] C.W. Turner, L. Case, Fouling of nuclear steam generators : fundamental studies, operating experience and remedial measures using chemical additives, AECL Nucl. Rev. 2 (2013) 61–88.
- [3] Technical guidance document: Application of film-forming amines in fossil, combined cycle, and biomass power plants, IAPWS. (2016).
- [4] R. Crovetto, A. Rossi, D. Meskers, C. Pierce, J. Melzer, K. Pearson, State of Knowledge on Film-Forming Amines 2015, EPRI, Palo Alto, CA 2015. 3002003678. (2015).
- [5] K. Sipilä, T. Saario, Effect of octadecylamine on carbon steel corrosion under PWR secondary side conditions, VTT. (2014) 1–16.
- [6] S. Cao, J. Hu, J. Xie, Q. Liang, L. Yin, Research on the film-forming characteristics of octadecylamine at high temperatures, Anti-Corrosion Methods Mater. 60 (2013) 14–19.
- [7] Q.-Q. Liao, G.-D. Zhou, H.-H. Ge, L.-M. Qi, Characterisation of surface film on iron samples treated with octadecylamine, Corros. Eng. Sci. Technol. 42 (2007) 102–105.
- [8] H.-H. Ge, G.-D. Zhou, Q.-Q. Liao, Y.G. Lee, B.H. Loo, A study of anti-corrosion behavior of octadecylamine-treated iron samples, Appl. Surf. Sci. 156 (2000) 39–46.
- [9] R. Wagner, E. Czempik, Preservation of boilers and turbines with the surface active substance octadecylamine (ODA), VGB PowerTech J. 2014 (2014) 2–5.

- [10] E. V Chernyshev, E.N. Veprov, V.A. Petrov, S.L. Bogdanov, T.Y. Levina, T.I. Petrova, V.I. Kashinskii, A.A. Zonov, A.E. Verkhovskii, Increasing the corrosion resistance of equipment due to the use of film-forming amines, *Power Technol. Eng.* 40 (2006) 34–37.
- [11] A. V. Kurshakov, A. V. Ryzhenkov, A.A. Bodrov, O. V. Ryzhenkov, A.A. Patakin, E.F. Chernov, Heat transfer enhancement in steam-turbine condensers with the use of surface-active substances, *Therm. Eng.* 61 (2014) 785–789.
- [12] W. Hater, D. Olivet, N. Rudschützky, The chemistry and properties of organic boiler feedwater additives based on film-forming amines and their use in steam generators, *Powerpl. Chem.* 11 (2009) 90–96.
- [13] F. Mao, C. Dong, D.D. Macdonald, Effect of octadecylamine on the corrosion behavior of Type 316SS in acetate buffer, *Corros. Sci.* 98 (2015) 192–200.
- [14] B.N. Khodyrev, A.L. Krichevtsov, A.A. Sokolyuk, Studying the processes relating to oxidation of organic substances contained in the coolant of thermal and nuclear power stations, *Therm. Eng.* 57 (2010) 553–559.
- [15] R.F.M. Lobo, M.A. Pereira-Da-Silva, M. Raposo, R.M. Faria, O.N. Oliveira, In situ thickness measurements of ultra-thin multilayer polymer films by atomic force microscopy, *Nanotechnology.* 10 (1999) 389–393.
- [16] S. Campen, J.H. Green, G.D. Lamb, H.A. Spikes, In situ study of model organic friction modifiers using liquid cell AFM: Self-assembly of octadecylamine, *Tribol. Lett.* 58 (2015).

- [17] J. Oviedo, M.A. San-Miguel, J.A. Heredia-Guerrero, J.J. Benítez, Electrostatic induced molecular tilting in self-assembled monolayers of n -octadecylamine on mica, *J. Phys. Chem. C.* 116 (2012) 7099–7105.
- [18] K.G. Patil, V. Santhanam, S.K. Biswas, K.G. Ayappa, Combined atomic force microscopy and modeling study of the evolution of octadecylamine films on a mica surface, *J. Phys. Chem. C.* 114 (2010) 3549–3559.
- [19] T. Barrès, B. Tribollet, O. Stephan, H. Montigaud, M. Boinet, Y. Cohin, Characterization of the porosity of silicon nitride thin layers by Electrochemical Impedance Spectroscopy, *Electrochim. Acta.* 227 (2017) 1–6.
- [20] N. Srisuwan, N. Ochoa, N. Pébère, B. Tribollet, Variation of carbon steel corrosion rate with flow conditions in the presence of an inhibitive formulation, *Corros. Sci.* 50 (2008) 1245–1250.
- [21] W. Kuang, J.A. Mathews, D.D. Macdonald, The effect of Anodamine on the corrosion behavior of 1018 mild steel in deionized water:I. Immersion and polarization tests, *Electrochim. Acta.* 127 (2014) 79–85.
- [22] W. Kuang, J.A. Mathews, M.L. Taylor, D.D. Macdonald, The effect of Anodamine on the corrosion behavior of 1018 mild steel in deionized water: II. Electrochemical Impedance Analysis, *Electrochim. Acta.* 136 (2014) 493–503.
- [23] H. Otmacic Curkovic, E. Stupnisek-Lisac, H. Takenouti, The influence of pH value on the efficiency of imidazole based corrosion inhibitors of copper, *Corros. Sci.* 52 (2010) 398–405.
- [24] M. Benoit, C. Bataillon, B. Gwinner, F. Miserque, M.E. Orazem, C.M. Sánchez-sánchez, B. Tribollet, V. Vivier, Comparison of different methods for measuring the

- passive film thickness on metals, *Electrochim. Acta.* 201 (2016) 340–347.
- [25] S. Chakri, I. Frateur, M.E. Orazem, E.M.M. Sutter, T.T.M. Tran, B. Tribollet, V. Vivier, Improved EIS Analysis of the Electrochemical Behaviour of Carbon Steel in Alkaline Solution, *Electrochim. Acta.* 246 (2017) 924–930.
- [26] M.E. Orazem, N. Pébère, B. Tribollet, Enhanced Graphical Representation of Electrochemical Impedance Data, *J. Electrochem. Soc.* 153 (2006) B129.
- [27] A.S. Nguyen, N. Causse, M. Musiani, M.E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Determination of water uptake in organic coatings deposited on 2024 aluminium alloy: Comparison between impedance measurements and gravimetry, *Prog. Org. Coatings.* 112 (2017) 93–100.
- [28] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Constant-Phase-Element Behavior Caused by Resistivity Distributions in Films. I: Theory, *J. Electrochem. Soc.* 157 (2010) C452.
- [29] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Constant-Phase-Element Behavior Caused by Resistivity Distributions in Films. II: Applications, *J. Electrochem. Soc.* 157 (2010) C458.
- [30] A.T. Tran, F. Huet, K. Ngo, P. Rousseau, Artefacts in electrochemical impedance measurement in electrolytic solutions due to the reference electrode, *Electrochim. Acta.* 56 (2011) 8034–8039.
- [31] B.A. Boukamp, A Linear Kronig-Kramers Transform Test for Immittance Data Validation, *J. Electrochem. Soc.* 142 (1995) 1885.
- [32] M. Schönleber, D. Klotz, E. Ivers-Tiffée, A Method for Improving the Robustness of

- linear Kramers-Kronig Validity Tests, *Electrochim. Acta.* 131 (2014) 20–27.
- [33] Lin-KK tool, (n.d.) <http://www.iwe.kit.edu/Lin-KK.php>.
- [34] J.J. Chen, N. Winograd, The adsorption and decomposition of methylamine on Pd{111}, *Surf. Sci.* 326 (1995) 285–300.
- [35] D.M. Thornburg, R.J. Madix, Cleavage of NH bonds by active oxygen on Ag(110). II. Selective oxidation of ethylamine to acetonitrile, *Surf. Sci.* 226 (1990) 61–76.
- [36] M. Grunze, R.N. Lamb, Adhesion of vapour phase deposited ultra-thin film polyimide films on polycrystalline silver, *Surf. Sci.* 204 (1988) 183–212.
- [37] N. Alzate-Carvajal, E. V. Basiuk, V. Meza-Laguna, I. Puente-Lee, M.H. Farías, N. Bogdanchikova, V.A. Basiuk, Solvent-free one-step covalent functionalization of graphene oxide and nanodiamond with amines, *RSC Adv.* 6 (2016) 113596–113610.
- [38] J.J. Benítez, M.A. San-Miguel, S. Domínguez-Meister, J.A. Heredia-Guerrero, M. Salmeron, Structure and chemical state of octadecylamine self-assembled monolayers on mica, *J. Phys. Chem. C.* 115 (2011) 19716–19723.
- [39] O. Olivares-Xometl, N. V. Likhanova, R. Martínez-Palou, M.A. Domínguez-Aguilar, Electrochemistry and XPS study of an imidazoline as corrosion inhibitor of mild steel in an acidic environment, *Mater. Corros.* 60 (2009) 14–21.
- [40] T. Yamashita, P. Hayes, Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials, *Appl. Surf. Sci.* 254 (2008) 2441–2449.
- [41] D. Briggs, M.P. Seah, *Practical Surface Analysis*, 2nd Editio, John Wiley & Sons, 1993.

- [42] M.A. Rampi, O.J.A. Schueller, G.M. Whitesides, Alkanethiol self-assembled monolayers as the dielectric of capacitors with nanoscale thickness, *Appl. Phys. Lett.* 72 (1998) 1781–1783.
- [43] F.S. Damos, R.C.S. Luz, L.T. Kubota, Determination of thickness, dielectric constant of thiol films, and kinetics of adsorption using surface plasmon resonance, *Langmuir*. 21 (2005) 602–609.
- [44] F. Gala, G. Zollo, Dielectric Properties of Self-Assembled Monolayer Coatings on a (111) Silicon Surface, *J. Phys. Chem. C*. 119 (2015) 7264–7274.
- [45] J.J. Benitez, O.R. De La Fuente, I. Díez-Préz, F. Sanz, M. Salmeron, Dielectric properties of self-assembled layers of octadecylamine on mica in dry and humid environments, *J. Chem. Phys.* 123 (2005) 1–6.
- [46] C.E.D. Chidsey, D.N. Loiacono, Chemical Functionality in Self -Assembled Monolayers: Structural and Electrochemical Properties, *Langmuir*. 6 (1990) 682–691.
- [47] D.R. Lide, *CRC Handbook of chemistry and physics*, 84th edition, 2003.
- [48] Y. Ben Amor, E.M.M. Sutter, H. Takenouti, M.E. Orazem, B. Tribollet, Interpretation of Electrochemical Impedance for Corrosion of a Coated Silver Film in Terms of a Pore-in-Pore Model, *J. Electrochem. Soc.* 161 (2014) 573–579.
- [49] A.P. Grosvenor, B.A. Kobe, M.C. Biesinger, N.S. McIntyre, Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds, *Surf. Interface Anal.* 36 (2004) 1564–1574.