



UNIVERSIDADE DE LISBOA
INSTITUTO SUPERIOR TÉCNICO

**Study of corrosion at cut edges and at micro-defects on
organic-coated electrogalvanized steel by Electrochemical Impedance
Spectroscopy and Scanning Electrochemical Techniques**

Andreia Isabel Granadeiro Cercas Marques

Supervisor: Doctor Alda Maria Pereira Simões

**Thesis approved in public session to obtain the PhD Degree in
Materials Engineering**

Jury final classification: Pass with Distinction

Jury

Chairperson: Chairman of the IST Scientific Board

Members of the Committee:

Doctor Christopher Michael Ashton Brett

Doctor Alda Maria Pereira Simões

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"One may well ask, why in the world would you want to make such a small electrode?"

R. M. Wightman, Microvoltammetric electrodes, Anal.Chem. 53 (1981) 1125-1134

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
ac	Alternating current
AFM	Atomic force microscopy
CCD	Charged-coupled device
CE	Counter electrode
CNLS	Complex nonlinear least squares data-fitting
CPE	Constant-phase-element
dc	Direct current
EDS	Energy dispersion spectroscopy
EEC	Equivalent electrical circuit
EG	Electrogalvanized
EI	Electrochemical interface
EIS	Electrochemical impedance spectroscopy
FEM	Finite element method
FcMeOH/ FcMeOH ⁺	Ferrocenemethanol/ Ferrocenium-methanol
FEG-SEM	Field emission gun - Scanning electron microscope
FFT	Fast Fourier Transform
FIB	Focused ion beam
FRA	Frequency response analyser
FTIR	Fourier transform infrared
FWMH	Full width at medium height
HER	Hydrogen evolution reaction
hf	High frequency
IS	Impedance spectroscopy
ISME	ion-selective microelectrode
LBL	Layer-by-layer
LEIS	Localized electrochemical impedance spectroscopy
lf	Low frequency
LDH	Layered double-hydroxides
mf	Medium frequency
ORR	Oxygen reduction reaction
PAH	Polyelectrolyte
PC	Personal computer
RC	Resistor/Capacitor
RG	Ratio between the radius of the glass sheath and of the platinum disk of an UME
REF	Reference electrode
SCE	Saturated calomel electrode
SKP	scanning Kelvin probe
pH-SME	pH sensing microelectrode

SRET	scanning reference electrode technique
SHE	Standard hydrogen electrode
SECM	Scanning electrochemical microscope/y
SIET	Scanning ion-selective electrode technique
SVET	Scanning vibrating electrode technique
UME	Ultramicroelectrode
WE	Working electrode
ZRP	Zinc-rich paint

Publications

As first author

- (i) A. G. Marques, A. M. Simões, EIS and SVET assessment of corrosion resistance of thin Zn-55% Al-rich primers: Effect of immersion and of controlled deformation, *Electrochimica Acta*, 148 (2014) 153-163
- (ii) A. G. Marques, J. Izquierdo, R. M. Souto, A. M. Simões, SECM imaging of the cut edge corrosion of galvanized steel as a function of pH, *Electrochimica Acta*, 153 (2015) 238-245
- (iii) A.G. Marques, M. Taryba, A. S. Panão, S. Lamaka, A.M. Simões, Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in nearly neutral chloride solutions, *Corrosion Science*, 104 (2016) 123-131

Others

- (i) R.M. Souto, J.J. Santana, A.G. Marques, A.M. Simões, Local electrochemical impedance spectroscopy investigation of corrosion inhibitor films on copper, *ECS Transactions*, 41 (2012) 227-235
- (ii) S.A.S. Dias, A. Marques, S. V. Lamaka, A. Simões, T. C. Diamantino, M. G. S. Ferreira, The role of Ce(III)-enriched zeolites on the corrosion protection of AA2014-T3, *Electrochimica Acta*, 112 (2013) 549-556
- (iii) J. Mondal, A. Marques, L. Aarik, J. Kozlova, A. Simões, V. Sammelselg, Development of a thin ceramic-graphene nanolaminate coating for corrosion protection of stainless steel, *Corrosion Science*, *In Press*, Corrected Proof available online 14 January 2016

Oral Presentations

- (i) A. G. Marques, J. Izquierdo, R. M. Souto, A. M. Simões, SECM and SVET study of the cut edge corrosion on galvanized steel, EUROCORR 2013, 1-5 September 2013, Estoril, Portugal
- (ii) A. Marques, A. M. Simões, Aplicação de técnicas electroquímicas com resolução espacial ao estudo da corrosão do aço galvanizado, 6^{as} Jornadas de Corrosão e Protecção de Materiais, 10 Novembro 2011, Lisboa, Portugal
- (iii) A. Marques, A. M. Simões, Application of the Scanning Electrochemical Microscope to study the corrosion mechanism in thin organic coatings with defects, XII Iberic Meeting of Electrochemistry & XVI Meeting of the Portuguese Electrochemical Society, 8-11 September 2010, Lisboa, Portugal
- (iv) A. G. Marques, M. Taryba, A. S. Panão, S. Lamaka, A. M. Simões, Evaluation of iron-zinc corrosion as a function of pH, 11th International Symposium on Electrochemical Methods in Corrosion Research, 24-29 May 2015, Tróia, Portugal

Posters

- (i) A. Marques, J. B. Jorcin, A. M. Simões, Modelling corrosion behaviour of conductive coatings based on EIS, SVET and LEIS experiments, 2^{as} Jornadas de Electroquímica e Inovação, 11 February, 2011, Faro, Portugal
- (ii) A. Marques, A. M. Simões, Modelling of corrosion mechanisms in thin conductive coatings and self-repair kinetics at induced micro-defects, 8th International Symposium on Electrochemical Impedance Spectroscopy, 6-11 June 2010, Carvoeiro, Portugal

Collaboration on projects

Prediction of the kinetics of self-repair of forming-induced defects on thin functional primers for advanced automotive applications (KINSREP). Project carried out with a financial grant of the Research Programme of the Research Fund for Coal and Steel (under contract RFSR-CT-2008-00028)

1. General introduction

The prohibition of chromium containing coatings by the E.U. in 2007 [1] has led to important research and developments aiming at new formulations capable of extending the lifetime of painted structures [2]. One major issue in terms of durability is the loss of adhesion starting either from scratches resulting from handling or from microscopic defects induced by forming operations, especially in the automotive industry [3, 4].

Corrosion resistance in the automotive industry has been greatly increased by the use of galvanized steel. This method of corrosion protection is mainly related to the control of “perforating corrosion” which is assured by the sacrificial corrosion of the zinc layer applied on steel. Another issue is that of “cosmetic corrosion”, which basically consists of delamination of the coating starting from cracks or scratches [5, 6]. Although not affecting the structural integrity of the car or object it leads to loss of gloss and to customer complaints and for this issue improved solutions are still under quest [7-9].

Many trials have been attempted to develop “smart coatings” using encapsulated inhibitors in an organic film. The aim is to attain a controlled or “intelligent” release of inhibitor that would better satisfy the industry and be more environmentally friendly, as in the case of the inhibitor release being triggered by local pH variations, i.e., when there is an active defect. Although a great number of authors [10-18] have claimed the development of smart self-healing coatings, many questions remain on the efficiency of these systems, as well as on the substrates they can be used upon, the load and type of inhibitor for encapsulation, the inhibition mechanism and the pH domain.

More recently, the development of localized electrochemical techniques has brought new light into the issue of localized corrosion phenomena [19-24]. Those techniques are so far limited to fundamental research and a few simple systems [25-32]. Further, even some global techniques, like the Electrochemical Impedance Spectroscopy (EIS), which has been extremely useful for painted systems, has been applied mainly to barrier coatings [33, 34], but its use on thin weldable coatings having forming induced defects is very limited [35-45].

1.1 Motivation and objectives

The research presented in this dissertation was partially funded by a project from the Research Programme of the Research Fund for Coal and Steel, having as theme the *Prediction of the kinetics of self-repair of forming-induced defects on thin functional primers for advanced automotive applications (KINSREP)*. Within the aims of this project, the dissertation focused at gaining fundamental understanding of the mechanisms of corrosion on weldable primers for the automotive industry using classical and advanced surface-resolved techniques. During the research, the need to explore the application of surface-resolved techniques to simpler systems was identified and thus the topic diverged from the initial theme and focused on the electrochemical techniques rather than on the materials.

In summary, the objectives of this dissertation are:

- Characterization of a thin weldable primer containing large Zn-55Al particles, applied on electrogalvanized steel substrate;
- The development of a physical model for monitoring the effect of water penetration and of forming-induced defects in this primer;
- To gain fundamental knowledge on the physico-chemical processes of corrosion on zinc-coated steel;
- To evaluate the suitability of scanning microprobe electrochemical techniques to study self-healing and localized corrosion phenomenon.

1.2 Organization of the chapters

Chapter 2 is an introductory section containing fundamental concepts of corrosion and working principles of the electrochemical techniques used within the aim of the research.

The experimental section is written as a compilation of four original research papers (not all published work). Chapter 3 -*EIS and SVET assessment of corrosion resistance of thin Zn-55% Al-rich primers: Effect of immersion and of controlled deformation*, deals with the application of electrochemical tools to the study of organic coatings. EIS and SVET are used to characterize a weldable primer containing Zn-55Al particles and a model is proposed considering the effect of water penetration in intact coatings and in deformed coatings. Chapters 4, 5 and 6 deal with the

use of various scanning microprobe techniques for characterization of cut edges and analogous systems. On Chapter 4- *SECM imaging of the cut edge corrosion of galvanized steel as a function of pH*, SECM and SVET are used to monitor corrosion at a coil coated cut edge in chloride solutions of pH2, pH5 and pH10. The study of an analogous model system with enlarged dimensions, is presented on Chapter 5 (pH5) – *Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in nearly neutral chloride solutions* and on Chapter 6 (pH2 and 10) - *Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in non-neutral chloride solutions*.

Finally, the general discussion of the results, concerning the aims of this research is presented on Chapter 7, suggestions for future work in Chapter 8 and the main conclusions are summarized on Chapter 9.

2. Background theory and technique description

This introductory chapter is a review of fundamental theory (sections 2.1 and 2.2) which has the purpose to contextualize the reader of the basic concepts behind corrosion monitoring and corrosion protection strategies (section 2.3). Further, it introduces the working principles of the electrochemical techniques (sections 2.4 to 2.6) used to perform the studies presented in the experimental chapters. A review of the state of the art relevant for the purpose of the research is presented within each of the experimental chapters.

2.1 Corrosion ^{46, 47, 48}

Corrosion may be defined as the loss of properties or structural integrity of a material due to chemical interaction with the surrounding environment. This is a general description of a problem usually associated with rusting. Chemical corrosion occurs because materials tend to their thermodynamically stable state which for most metals consists of their oxides, carbonates, sulphides or others, with the exception of noble metals like gold, platinum and silver, which are stable in their metallic forms. The metals are extracted from ores after supplying a large amount of energy. It is their natural tendency to go back to the low energy state by recombining with the elements present in the environment. Nevertheless, the term “corrosion” applies to a variety of materials including ceramics and polymers and to a variety of environments like atmospheric, aqueous and high temperature. A more general term when referring to polymers and ceramics might be “degradation”. Corrosion or degradation is usually undesirable as it leads to costly repairs or replacement of structures, buildings or machines or even bio-compatible prosthetics. In some cases it may not lead to severe structural damage but rather aesthetic issues, which also require costly repairs. Corrosion may also be desirable; for example, weathering steel, also known as COR-TEN [49] is popular for outdoor sculptures as it forms a stable rust or patina layer that avoids the need of painting. In 1998, the U.S.A National Association of Corrosion Engineers (NACE) released a Corrosion Costs Study in which, just in the U.S., the direct losses due to corrosion represented annually c.a. 3.1% of the gross national product (GNP). These direct costs include things as materials and man hours necessary for replacement or repair. Indirect costs such as lost of production, waste production and environmental damage are estimated to be equally relevant, thus elevating the total costs due to corrosion to approximately 6% of the GNP of industrialized countries. In a more recent study,

started in 2013, the values of 1998 were extrapolated to 2013 based on inflation and the costs of total corrosion almost doubled [50, 51]. These numbers alone are reason enough to motivate the development of corrosion science and protection methods.

2.2 Electrochemical theory of corrosion

Corrosion is essentially the exchange of electrons between half-reactions, i.e. an anodic reaction supplies electrons by oxidation and a cathodic reaction consumes the electrons by reduction. Electrochemical cells generate electrical energy due to electrochemical reactions. Thermodynamics gives an indication of the tendency of electrode reactions to occur, whereas electrode kinetics addresses the rates of such reactions [47].

Thermodynamics ^{19, 52}

There is a critical cell potential to exceed before current can flow in an electrochemical circuit; this is called the electrical potential energy. This energy is determined by the thermodynamic equilibrium of all the components of the cell. If the anodic and cathodic reactions represent forward and backward rates of the same reaction, e.g. zinc immersed in a deaerated solution containing zinc ions, a zero current can be obtained under the condition of reaction equilibrium. A zero current is observed if the forward and backward rates for the reaction are equal [19].



If a current density i_a is assigned to the forward reaction and a current i_c is assigned to the backward reaction, the net current density will be given by:

$$i = i_a + i_c \quad \text{Eq. 2.2}$$

where $i_a < 0$ and $i_c > 0$ and in equilibrium $i_a = i_c$ and $i = 0$. The potential at which the current for a single electrochemical reaction is equal to zero is termed the equilibrium potential E . The

equilibrium potential can be determined from the free-energy change associated to the electrochemical reaction:

$$\Delta G = -nFE \quad \text{Eq. 2.3}$$

where n is the number of electrons transferred and F the Faraday constant. When all species have unitary activity the equation can be written $\Delta G^0 = -nFE^0$ and E^0 is referred as the standard electrode potential [52]. The equilibrium potential E can thus be expressed by the Nernst equation in terms of the chemical activity of the reactants and products involved in the reaction [19]:

$$E = E^0 + 2.3 \frac{RT}{nF} \log \frac{a_{ox}}{a_{red}} \quad \text{Eq. 2.4}$$

where E^0 is the standard electrode potential, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and a_{ox} , a_{red} are the activities of the oxidized (or reactants) and reduced (products) species respectively. The standard electrode potential corresponds to the cell potential at which the activities of the ionic species are unitary and the standard hydrogen electrode is the anode. The E^0 values for common electrodes are tabulated in the electrochemical series [52].

The potential of the electrode (E) is always referred to the potential of a reference electrode, which is placed at some distance from its surface. The electrode potential has two components. One is the interfacial potential, which is the potential difference between the potential of the metal and the potential of the electrolyte immediately adjacent to the metal, i.e. just outside the double layer, including the diffuse region of charge and the inner Helmholtz plane and the other component is the ohmic drop [19].

If the anodic and cathodic reactions represent forward and backward rates of different reactions, e.g. zinc current immersed in an oxygenated solution, the zero current condition arises through a balancing of different reactions:



The potential at which the net current for multiple electrochemical reactions is equal to zero is termed the mixed potential or, in the case of metal dissolution, the corrosion potential. The corrosion potential cannot be determined simply by thermodynamic concepts as the free-energy. Kinetics and mass-transport laws must be applied to calculate values for the mixed or corrosion potential [19]. The mixed potential can be measured experimentally in most practical situations of transition metals or alloy electrodes immersed in aqueous electrolytes.

Pourbaix diagrams ^{47, 53, 54}

The Pourbaix diagrams identify for each element, the phases that have the lowest Gibbs free energy, i.e. which are stable, for various values of pH and electrode potential. In this way it is possible to determine which reactions are spontaneous and thus will participate in the corrosion process. The domains of stability of each phase are indicated by plotting the reversible potential for the corresponding reaction, given by the Nernst equation, as a function of pH. The conditions for which the diagrams were calculated are [52]:

- electrodes are immersed in pure water, at 25°C and at atmospheric pressure;
- reversible potentials are referred to the standard hydrogen electrode;
- the lines labelled with numbers inside a circle indicate a specific reaction;
- the individual lines labelled as 0, – 2, – 4, and – 6 indicate the values for the activity of the ion to which they refer, i.e., 10^0 , 10^{-2} , 10^{-4} and 10^{-6} ;
- a metal is considered to be actively corroding if the equilibrium activity of a soluble ion derived from it exceeds 10^{-6} ;
- dashed lines indicate that all the species in the reaction are dissolved.

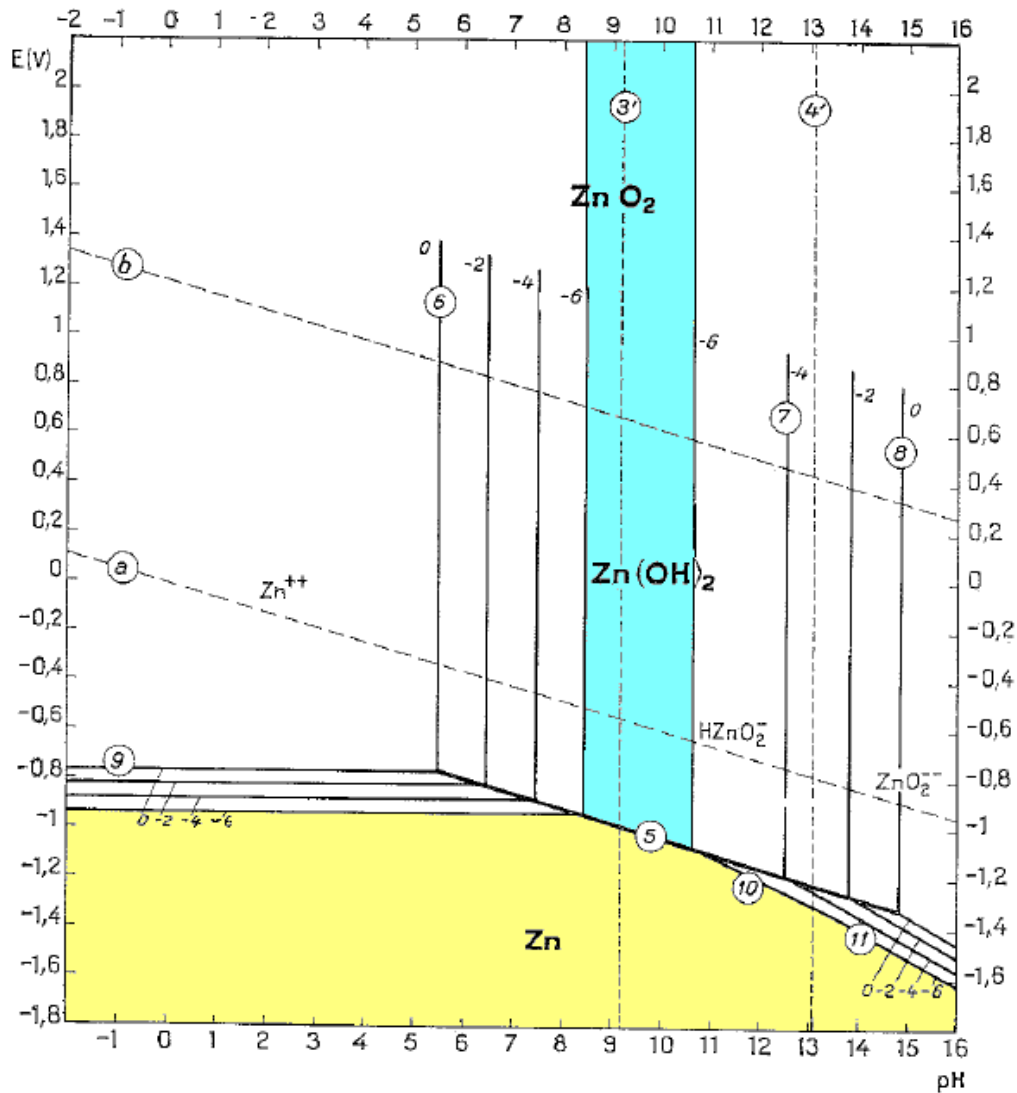


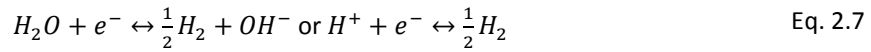
Figure 2.1. Pourbaix diagram (E vs. pH) for the zinc-water system [54].

There are three types of lines on Pourbaix diagrams; horizontal lines describe reactions that are dependent only on potential; vertical lines describe reactions that are dependent only on pH; and lines with a slope correspond to reactions that depend on both potential and pH. An arbitrary potential and pH define a point in the diagram that provides information regarding the behaviour of the material in its domain of [47]:

- immunity, in which the metal is the stable species and is immune to corrosion;
- corrosion, in which the stable species is a soluble ion and the metal is expected to corrode;
- passivity, in which the stable species is an insoluble solid that may protect the metal. An oxide species in contact with an aqueous solution, in principle does not allow corrosion to proceed if it forms a continuous and highly adherent

layer. Thus, thin layers of oxides and hydroxides ($\text{Zn}(\text{OH})_2$, Fe_2O_3 , Fe_3O_4) on the metal surface are usually highly protective under this condition [54].

In aqueous solution, the most common reduction reactions are the oxygen reduction reaction (ORR) and the reduction of water, known as hydrogen evolution reaction (HER). For this reason, all Pourbaix diagrams contain the dashed lines that bound the regions of stability for water, known as the reversible hydrogen (“a”) and reversible oxygen (“b”) lines. The Nernst equations for oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) are simplified due to their dependence only on pH. Reduction of water can only occur at potentials more negative than line “a,” below which conditions the hydrogen evolution reaction (HER) is favoured [54]:



$$E^0 = -0.0591\text{pH} \quad \text{Eq. 2.8}$$

Similarly, oxygen can be reduced only at potentials below the line “b,” conditions for which the oxygen reduction reaction (ORR) is favoured:



$$E^0 = 1.228 - 0.0591\text{pH} \quad \text{Eq. 2.10}$$

Pourbaix diagrams however have significant limitations. They are limited to pure metals, thus excluding alloys; further, overlaying the diagrams for the individual elements allows drawing only limited conclusions. For example, passivity of pure iron in acid is not predicted from E -pH diagrams but is observed experimentally and can be explained by kinetics. Further, chloride ions present in solution usually attack oxide or hydroxide layers, diminishing their protective power and the passivity they impose on the metal [53]. As an example, the influence of pH on the corrosion of zinc has recently been discussed in detail by Thomas et al [55]. It was demonstrated that, in acidic solutions ($\text{pH} < 3$), active dissolution of the metal occurs under kinetic control of the cathodic reaction (predominantly hydrogen evolution, HER). However, according to Figure 2.1 the electromotive force for ORR on zinc is higher. In practice, the concentration of dissolved oxygen in acidic solutions is very low and has little influence on corrosion kinetics. In less acidic environments (namely for pH in the range 4-5) a domain of pseudo-passivity was observed, although it was not clear whether this effect was caused by the

shift in the cathodic reaction from the hydrogen evolution reaction to oxygen electrode reaction (ORR) or by the formation of surface oxides. For self corroding zinc in pH 4-5, precipitation of zinc oxides is not supported by thermodynamic calculations (Pourbaix diagram). However, scanning electron micrographs showed the appearance of nodules of zinc oxides in this pH range [55]. Zinc oxides and hydroxides can form for pH above 7 but they are not stable and dissolve due to metal hydrolysis which occurs for pH values up to 10 [55]. Stable, protective zinc oxides are only formed when the local solution pH is greater than 11 [55]. Although surface oxides formed in weak alkaline conditions do not effectively passivate the substrate they may act as a barrier to the OH^- ions, thus protecting the metal to a certain extent [56].

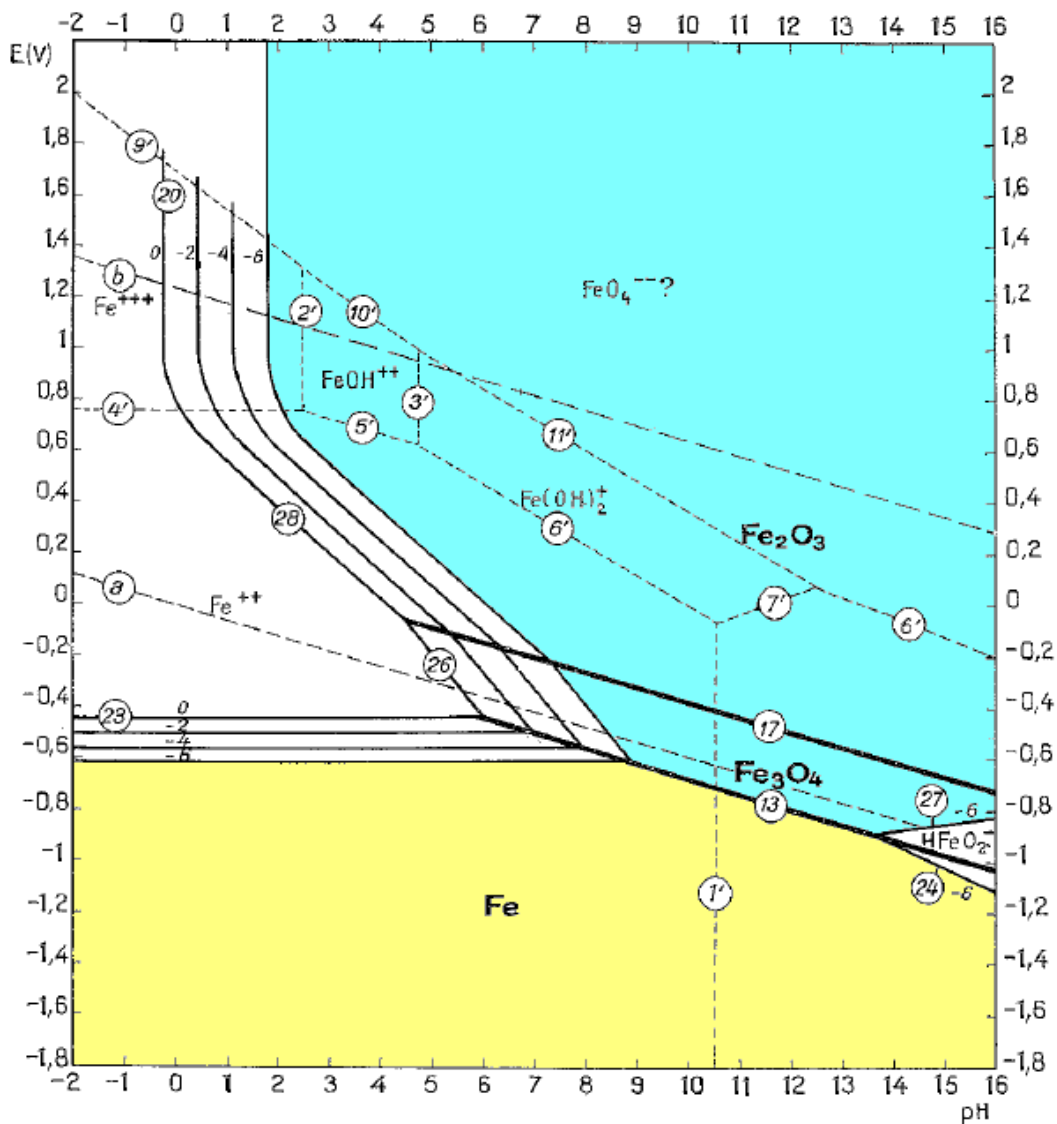


Figure 2.2. Pourbaix diagram (E vs. pH) for the iron-water system [54].

According to the Pourbaix diagram, the region of immunity of iron extends over a wide range of pH and potential values. If iron is left alone immersed in water containing naturally dissolved oxygen of pH 6.5, it will only corrode (Eq. 2.11 and Eq. 2.12) with a potential more positive than -0.617 V vs. SHE. This reversible potential corresponds to the horizontal line 23 under the mark -6 and defines the upper limit for the region of immunity of iron. On the surface of iron, both water (Eq. 2.9) and oxygen (Eq. 2.7) can be reduced as the reversible potential is below lines “a” and “b” [54]:



$$E^0 = -0.440 + 0.0295 \log(a_{Fe^{2+}}) \quad \text{Eq. 2.12}$$

Kinetics

An electrochemical reaction, or half-cell reaction, can be defined as a reaction in which electrons are explicitly reagents or products. The region of kinetic control of electrochemical reactions is characterized by current densities that are exponential functions of potential. The influence of potential on the current density, for a single reversible reaction is provided by the Butler-Volmer equation [19]:

$$i = i_0 \left\{ \exp \left(\frac{(1 - \alpha)nF}{RT} \eta \right) - \exp \left(\frac{\alpha nF}{RT} \eta \right) \right\} \quad \text{Eq. 2.13}$$

where $i_0 = i_a = -i_c$, at E^0 is the exchange current density, η is the overpotential, i.e. the shift from the equilibrium potential ($\eta = E - E^0$) corresponding to an equilibrium potential when $\eta = 0$ and the net current is equal to zero ($i = 0$). The symmetry factor α is the fraction of the surface presenting an overpotential that promotes the cathodic reaction. In a narrow range of potential near the zero-current potential (low overpotentials), the current density can be described as being a linear function of potential. At more positive and more negative potentials (high overpotentials), the Butler-Volmer equation can be simplified giving rise to the Tafel equations [19]:

$$i_a = i_0 \exp \left(\frac{(1 - \alpha)nF}{RT} \eta \right) = i_0 \exp(b_a \eta) \quad \text{Eq. 2.14}$$

$$i_c = -i_0 \exp\left(-\frac{\alpha n F}{RT} \eta\right) = -i_0 \exp(-b_c \eta) \quad \text{Eq. 2.15}$$

These equations can alternatively be resolved for the overpotential as a linear function of the current:

$$\eta = \frac{1}{b_a} \ln i_0 + \frac{1}{b_a} \ln i_a = a_a + b_a \ln i_a \quad \text{Eq. 2.16}$$

$$\eta = \frac{1}{b_c} \ln i_0 + \frac{1}{b_c} \ln i_c = a_c + b_c \ln i_c \quad \text{Eq. 2.17}$$

where, the plots of η vs. $\ln i$ intercept on $\ln|i_0|$ with a Tafel slope of b_a for the anodic branch and $-b_c$ for the cathodic branch.

Mass-transport

Mass transfer is the movement of species within the solution occurring either from differences in electrical (migration) or chemical potential (diffusion) at two locations or from the convective movement of the solution. If the reacting species diffuse through the electrolyte towards the surface of the electrode at which the reaction takes place at a slower rate than the one at which they are being consumed, then the reaction is said to be under mass-transport control. Considering that the total current associated to the cathodic process is generated only by migration and diffusion, then:

- the Butler-Volmer equation can describe the flow of species under the influence of a potential gradient. The exchange current density (i_0) is proportional to the concentration of the reacting species at the interface ($c_i(0)$) with a power to the stoichiometric coefficient (s_i). The proportionality constant is m_0 , the mass-transfer coefficient. The current density produced by migration of the species in the bulk electrolyte, with $s_i = 1$, is [19]:

$$i_c = -m_0 n F c_i(0)^{s_i} \exp(-b_c \eta_s) \quad \text{Eq. 2.18}$$

- Fick's laws can describe the flux of species under the influence of a concentration gradient [52].

$$i = -nFD_i \frac{dc_i}{dy}_{y=0} \quad \text{Eq. 2.19}$$

Considering that the concentration gradient has a linear distribution in the direction y and there is a stagnant layer (Nernst diffusion layer) of the reacting species with a finite thickness δ_i , Eq. 2.19 becomes [57]:

$$i = -nFD_i \frac{c_i(\infty) - c_i(0)}{\delta_i} \quad \text{Eq. 2.20}$$

or expressed in terms of overpotential:

$$\eta = b_c \ln \frac{i_c}{i_0} + \frac{RT}{nF} \ln \left(1 - \frac{i_c}{i_L} \right) \quad \text{Eq. 2.21}$$

In most corrosion situations, electrochemical reactions occur under this activation-concentration condition.

Evans diagram

In an Evans diagram, either current or current density is plotted against potential. Current density representation is only possible if the ratio of anodic to cathodic area is taken as unity. These polarization diagrams can be quite useful for describing or explaining parallel corrosion processes. Any electrochemical reaction can be algebraically divided into separate oxidation and reduction reactions with null net current, (Eq. 2.14 and Eq. 2.15). In order to draw an Evans diagram it is necessary to have information concerning the activation overpotential and the possible interference of mass transport (concentration overpotential) for each corrosion process involved. The current density can be described by a linear function of overpotential in a narrow range of potentials near the corrosion potential. Under these conditions an Evans plot is linear and the process is said to be under activation control. This means that a small overpotential (activation energy) is enough to produce a shift of the electrode reaction in the forward (anodic) or backward (cathodic) direction. However, if the current density is further increased there may be a deviation from linearity. For an activation controlled process, each reaction can be described by a straight line, with positive Tafel slope for the anodic processes and negative Tafel slope for the cathodic process [48]. As an example, the diagram in Figure 2.3

represents the corrosion of iron in deaerated solution. The four lines represented, correspond to the half-cell reaction of a corroding iron in deaerated acidic medium. The exchange currents densities and the reversible potential for each of the half-cell reactions are indicated as $i_{0\text{H}^+/\text{H}_2}$, $i_{0\text{Fe}/\text{Fe}^{2+}}$ and $E_{\text{H}^+/\text{H}_2}$, $E_{\text{Fe}/\text{Fe}^{2+}}$, respectively. The lines corresponding to hydrogen oxidation and metal reduction can be ignored for spontaneous conditions because they occur only at very high and very low overpotentials, respectively [52]. The curves corresponding to the above reactions intercept at the corrosion potential (E_{corr}) and the corresponding current is called the corrosion current, (i_{corr}). At the corrosion potential, the main anodic and cathodic reactions are two different reactions and the corrosion rate is equal to the total anodic and cathodic rates of corrosion. The corrosion current represents the contribution of both anode and cathode to polarization, hence, it represents a mixed potential [52].

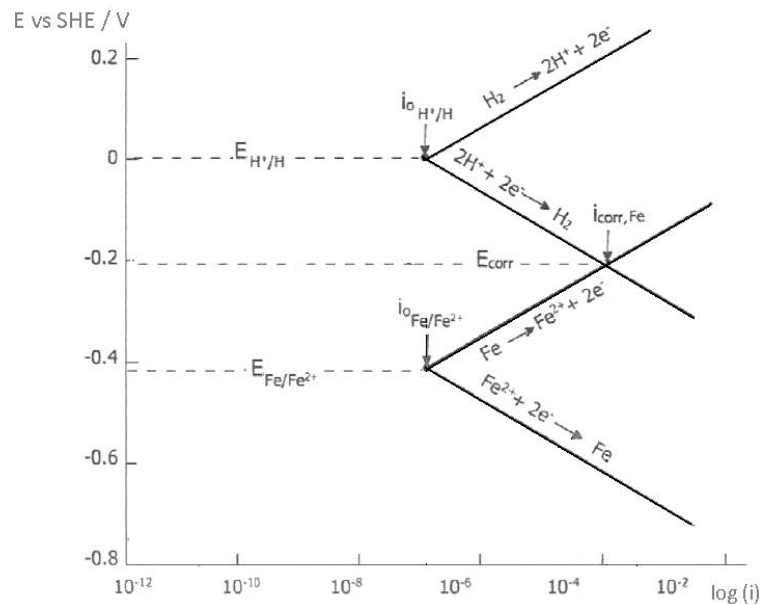


Figure 2.3. Evans diagram for iron in deaerated solution [52].

Metal anions formed at the metal surface require some time to cross the diffusion-layer and reach the bulk electrolyte. On the other hand, oxygen takes time to diffuse from the bulk solution in the direction of the metal surface. By increasing the current density, the rate of generation of anions becomes very high at higher current densities and crossing the double-layer becomes increasingly difficult. Anions build up on the outer part of the double-layer and exert a repulsive force on the anions just formed, blocking the further progress of anodic dissolution. The repulsive forces do not allow further oxidation and release of anions and the process becomes self-limited. The current at this point is called limiting current (i_L) as it becomes

independent of potential [52]. The limited solubility of oxygen in water often causes the cathodic reagent (commonly, oxygen) to fall in short supply. The species from bulk solution are unable to diffuse across the double-layer to replace the species that have been reduced. The process then occurs under concentration polarization, Figure 2.4 a, describes the corrosion of iron in nearly neutral aerated solution. Two cathodic reactions are possible, oxygen reduction reaction and hydrogen evolution. The total cathodic current corresponding to the sum of the currents of the hydrogen reaction and oxygen reduction has to be balanced by the single anodic reaction. The intercept where the opposing currents are balanced occurs at E_{corr} and in this case, the corrosion current is the sum of two components, activation polarization (Eq. 2.18) and concentration polarization (Eq. 2.20) [52]. The overpotential can be calculated by Eq. 2.21 and the process is said to be under mixed control. In Figure 2.4 b, the solution is stirred which has an effect similar to an increased concentration of dissolved oxygen, thus increasing the build up of charge at the double-layer. The limiting current (Eq. 2.20) increases and the contribution of the activation polarization becomes negligible. The mass transport on the ORR cathodic reaction becomes rate controlling.

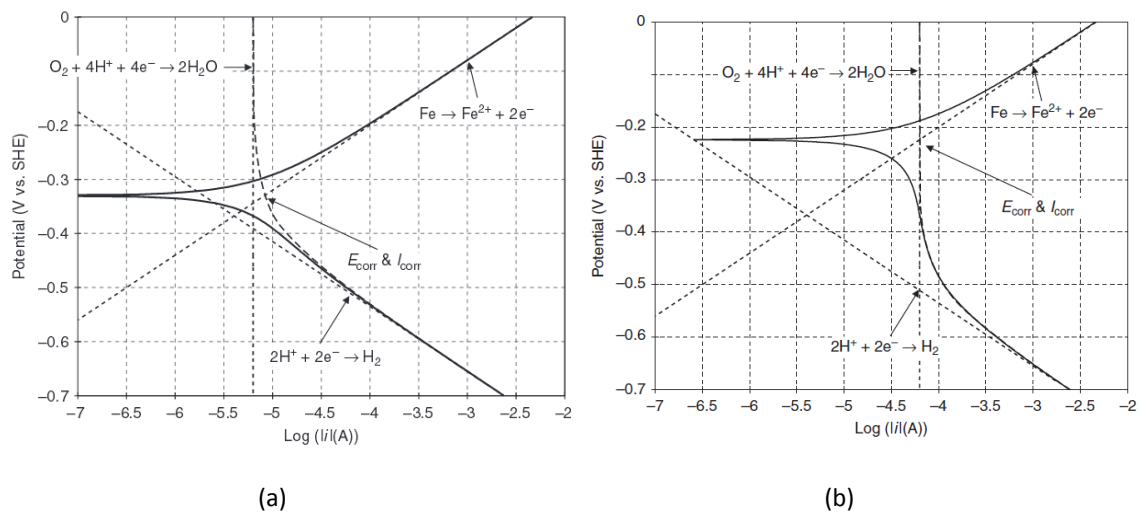


Figure 2.4. Polarization behaviour of iron in nearly neutral aerated solution under (a) stagnant and (b) in stirring conditions [48].

It is usual to classify corrosion into wet corrosion and dry corrosion as the resulting mechanism, kinetics and by-products are very different. Wet corrosion is of particular interest as it accounts for the largest parcel of the prevention, control and repair costs [51]. Wet corrosion involves electrolytes and is driven by electrochemical reactions occurring at the solid-liquid interface. In the simplest case, a corroding system implies two spontaneous coupled

reactions. One is the reaction by which aggressive or oxidizing species in the solution remove electrons from a metal; the other reaction occurs at the surface of the metal to counterbalance the excess of positively charged atoms in the solid phase. This transfer of charge imposes an electric potential between the metal surface and the electrolyte. When dissimilar metals are immersed in the same electrolyte they will acquire different electric potentials forming a galvanic cell. The tendency will be to reach for equilibrium and the driving force to reach that equilibrium, the electromotive force, will be given by the difference between the electrode potentials in open circuit. When the metals are in physical contact or connected by an electron conductor, electrons will flow from the anode to the cathode. The oxidation reaction occurs at the anode, i.e. at the metal atoms lose their electrons and pass into the solution in the form of cations. The electrons released at the anode are conducted through the metal or contact to the cathode and are consumed in the cathodic reactions, which in natural environments is often oxygen reduction and hydrogen evolution [47].

The rate and extent of corrosion depend on many factors, such as the nature of the metals themselves and the environment. Quite often the conditions in the environment change with time during the onset of corrosion, e.g. the concentration of chloride and oxygen may vary the pH. For example, solution evaporation increases the conductivity and thus facilitates the circulation of charge accelerating corrosion. In the presence of chloride ions this phenomenon becomes particularly undesirable. Concerning the metal, the potential that it acquires in a certain environment indicates its thermodynamic tendency to corrode; the more negative the potential, the greater is the tendency to corrode. The relative areas of the anode and cathode are also a determining factor. When the cathodic area is larger than the anodic, the demand for electrons will result in increased metal dissolution rate at the anodic regions thus accelerating corrosion. Under certain conditions, metal cations recombine with anions from the environment and form corrosion products. If the corrosion product is soluble in the corroding medium, the corrosion of the metal will proceed. On the other hand, if the corrosion product is insoluble, it will precipitate on the surface of the cathode and may hinder or even suppress corrosion by inhibiting the cathodic reaction. When it comes to the environment, temperature, pH, chloride and oxygen concentration are the main factors affecting the corrosion process. The increase in thermal energy causes an increase in the rate of corrosion because it accelerates the reactions and the rate of diffusion of ions. The effect of pH is more complex as it may conduct the metal into a domain of corrosion, immunity or passivity. The possibility of corrosion with respect to pH of the solution and the electrode potential of the metal can be correlated with the help of a Pourbaix diagram.

2.3 Corrosion Protection Strategies ^{47, 48}

To-date the most effective coatings known are still those that contain chromate based components. Chromium can easily be converted to its hexavalent form (Cr^{6+}), which is a threat to nature and human health. Chromium containing coatings were banned from Europe in 2007 and nowadays can only be used in aircraft production “when no other scientifically verifiable replacement can be found in a safety related function” [1]. This type of protection is thus not a valid option anymore. In some situations corrosion can be avoided by the adequate selection of the metal for a specific purpose. For example, with the use of noble metals (platinum, gold) or metals and alloys that possess the ability to spontaneously form a passive layer on its surface; this is the case of aluminium, stainless steel, nickel and titanium. Sometimes, these options are not cost effective and an alternative protection method is required. In the impressed current cathodic protection method, a current generated by a power supply is applied to the metal that needs to be protected converting the corroding metal from anode to cathode. Therefore, an anode (usually made of graphite) is intentionally added to the system providing anodic current and protecting the structure. A similar method takes advantage of the fact that dissimilar metals present different reactivity levels in the same environment and thus it is possible to establish a hierarchy between them. Metals with less tendency to react are said to be noble and metals with more tendency to react are less noble. In sacrificial protection, an active anode is coupled to a structure with the aim of shifting the anodic reaction from the metal structure to the sacrificial anode. This method is used for the protection of ships, in which plates of zinc or magnesium are hung around the hull of the ship to work as anodes and protect the ship structure [46]. This is also the main principle behind galvanized steel or zinc-rich primers applied on steel; while there are zinc atoms capable of transferring electrons to the aggressive species in the environment, steel remains protected. Zinc protects steel from corrosion by sacrificial anodic dissolution but also it is also generally accepted that the formation of a passive layer of zinc corrosion products causes moderate inhibition of the cathodic reaction [5,52,58]. Quite often, this sacrificial protection is combined with the application of a protective coating of organic nature. The organic layer acts as a physical barrier blocking the access of the corrosive medium to the substrate. However, a single pore or scratch can provide a route to penetration of the electrolyte and aggressive species. Once corrosion starts, the polymeric layer cannot stop it from advancing on zinc [59-61]. The examples above, have considered three main types of protective coatings, namely, metallic, with electrogalvanized steel an example; inorganic, e.g. chromates; and finally organic, usually paints. Besides protection from aggressive environments, such

coatings may also give decorative appearance. Metallic coatings are mostly applied on steel because they are cheaper than paints and are commonly used in materials for construction or domestic appliances. These are usually imparted by hot dipping or electroplating. In the process of hot dipping, the metal to be coated or substrate is dipped in a molten bath of the coating metal and the coating thickness is determined by the duration of the immersion, the withdrawal rate and the thickness of the substrate. Hot-dip coating produces thick, non-uniform coatings with excellent adhesion as the coating metal forms an alloy with the substrate. Hot-dipping can be performed using zinc or zinc alloys (aluminium, magnesium) as a coating material for steel. An alternative method for hot-dip coating is electrodeposition, in which the coating metal is applied on the substrate by means of electrolysis. In this process, the substrate metal which is to receive the coating is made cathodic in a suitable electrolyte bath containing a solution of the salt of the metal to be electrodeposited and additional reagents to favour the formation of a smooth, dense and coherent coating. The concentration of the salt solution is maintained by the addition of the metal salt at regular intervals or by the use of a continuously dissolving anode. The coating is usually thin, with a shiny appearance and the adhesion to the substrate depends on the conditioning of the surface prior to electroplating. Classic organic coatings are inert polymeric barriers applied to the surface of a metal with the double purpose of protecting it from corrosion and provide a decorative effect. Paints are the main organic coatings and consist in a suspension of solid pigments in a fluid medium. After drying, the result should be a continuous and adherent film that offers corrosion resistance [48].

Self-healing coatings ⁶²

A recent trend in corrosion protection consists in combining classical organic coatings with active agents, giving origin to smart or self-healing coatings. Corrosion protection is commonly classified as passive protection or active protection. Passive protection is achieved by creation of a physical barrier preventing contact of the metal with the corrosive environment; self-healing is an active corrosion protection method which aims at a decrease of the corrosion rate when the main barrier is damaged by controlled release of a corrosion inhibitor to the environment [63]. These active agents are called corrosion inhibitors and can be added directly to the polymeric matrix, adsorbed on porous particles or can additionally be encapsulated. They can be incorporated in all the components of a coating system like the pre-treatment, primer and top-coat [64]. There are several types of corrosion inhibitors, they can be organic, inorganic and provide different mechanisms of protection. A class of inhibitors reacts with the cations

released during corrosion to produce insoluble precipitates which adsorb on the anode forming a protective film and reducing corrosion. These are known as anodic inhibitors and include molybdates and phosphates. Cathodic inhibitors interfere with the cathodic reaction usually by adsorbing on the cathodic regions or by reducing the oxygen dissolved in solution [64-67].

The direct introduction of inhibitor components into protective coatings often leads to the deactivation of the corrosion inhibitor and physico-chemical degradation of the polymer matrix [67]. To overcome this, recent research has focused on the strategy of entrapping the active agent in microscopic carrier particles, preventing its direct interaction with the coating matrix while creating passive host-active guest system [64]. The carriers should have good compatibility with all the polymeric matrix compounds, should not form agglomerates or lumps and should be completely covered. Good carriers therefore have a small size with a large surface area allowing them to keep the active agent in a trapped state while distributing themselves uniformly in the matrix. Further, the inhibitor release should only be triggered upon the beginning of the corrosion process. There are currently many encapsulation strategies that respect these requirements, including the use of oxide nanoparticles, ion-exchange pigments and polyelectrolyte layers. Oxide nanoparticles have a large loading capacity because of the large surface area. Usually for this purpose, mesoporous oxides are preferred, i.e., when the pore size is between 2-50 nm, Figure 2.5.

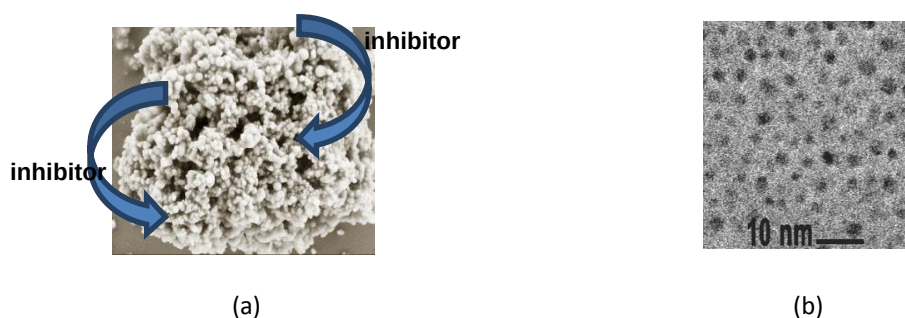


Figure 2.5. Mesoporous nano-particles as carriers for corrosion inhibitors; (a) schematic of inhibitor entrapment on pores and (b) micrograph revealing the distribution of the nanosized oxide particles on a polymeric matrix [69].

Mesoporous oxide nanoparticles offer the advantages of being commercially available and of allowing the adsorption of inhibitor by simple immersion in solution or by ion-exchange mechanism. Additionally, the simple introduction of oxide nanoparticles in the polymeric matrix enhances barrier properties [68].

Layered double hydroxides (LDH) are anion-exchange pigments that can be used as inhibitor carriers forming a host-guest structure. A positively charged host (Al-Zn, Al-Mg or Al-Mg) hydroxide layer is separated from an identical layer by a gallery of anions and polar

molecules like water [67], as presented in Figure 2.6. The anions between the hydroxide layers can be corrosion inhibitors.

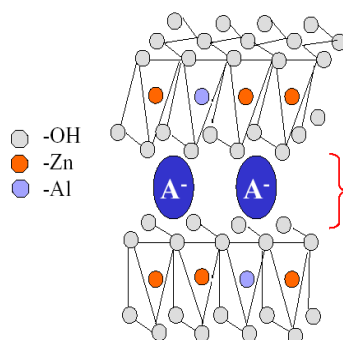


Figure 2.6. Schematics of a Zn-Al LDH: anions (A^-) and polar molecules can be trapped inside the gallery [67].

In contact with an aggressive environment containing anions (Cl^-) the ion exchange reaction will occur; the inhibitor anions are released to the electrolyte while the chloride becomes entrapped in the gallery. Not only an active agent is released to hinder corrosion activity, but also electrolyte aggressiveness will be reduced. A Halloysite is a naturally occurring ion-exchange mineral with a size varying between 0.15-15 μm in length and an inner diameter of 10-150 nm. For a pH range 3-8, electrostatic forces make the mineral to bend over itself forming a nanotube with positive charge inside and negative charge outside. The positive charge inside allows the loading with negatively charged inhibitors. Because the structure is pH sensitive, the release of the inhibitor will occur only during the onset of the cathodic reaction [64, 68]. The controlled release of inhibitor presents an advantage towards the LDH.

In the systems previously described there is a simple adsorption of the inhibitor on the external or internal surfaces of the carriers, which eventually may not ensure the blocking of interaction between polymeric matrix and inhibitor, the spontaneous leaching of the inhibitor, the controlled release and the permeability of the carrier to small ions or molecules. The release of the inhibitor should happen only when triggered for example by changes in the local pH that occur during the onset of corrosion. This can be achieved by creating a polyelectrolyte shell around the carrier through a layer-by-layer (LBL) approach. Polyelectrolytes are macromolecules with a large number of functional groups that are charged or can be charged. They are essentially block-copolymers that depending on the functional groups, can behave as cations, anions, or even both. The shell of the resulting polyelectrolyte capsule is semi permeable and sensitive to a variety of physical and chemical conditions of the surrounding media. Usually the shell is permeable for $pH < 3$ allowing their loading and at neutral pH they are impermeable, closing their structure and entrapping the inhibitor; as the pH becomes more alkaline the inhibitor is slowly released

from inside the particles, Figure 2.7. The procedure consists on assembling alternately, layer-by-layer, oppositely charged polyelectrolytes on a template surface (mesoporous oxides, halloysites, LDH). By repeating the cycle a multilayer shell can be obtained [64, 67, 70, 71].

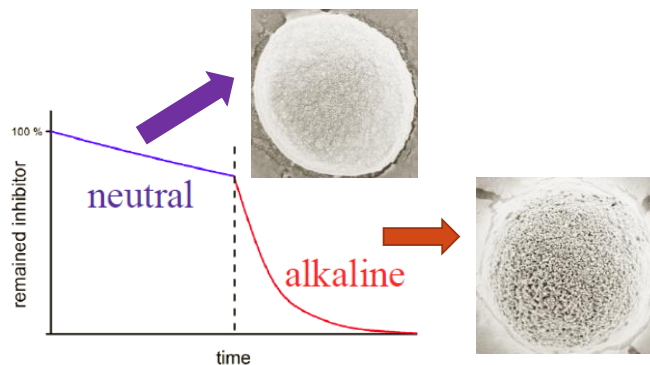


Figure 2.7. A mesoporous particle covered with polyelectrolyte layers entraps the inhibitor at neutral pH. When the corrosion starts hydroxyl groups are formed increasing the pH. The polyelectrolyte becomes permeable releasing the inhibitor [71].

2.4 Electrochemical Impedance Spectroscopy (EIS)

The development of what is known today as impedance started with the work of Oliver Heaviside in the 1870's. Heaviside was an electrical engineer, mathematician and physicist, contemporary of Albert Einstein and Schrodinger and considered one of the most brilliant scientists of his time. This scientist was responsible for introducing several concepts in electrical engineering, like capacitance, impedance and inductance [72]. However, the first measurement of the dielectric constants of an aqueous electrolyte was only performed in 1984 by Nernst [72].

Impedance spectroscopy is an analytical technique that can be applied to characterize the electric properties of various materials, e.g. solid and liquid electrolytes on batteries and fuel cells, ceramics, metals, free-standing polymers, protective paint films applied on substrates and also biological tissue [72, 73]. Variations in physical, chemical and electrochemical properties of these materials produce interfaces with non-uniform charge distribution (polarization). Each interface will polarize in a unique way when subjected to an external electrical stimulus. The rate at which a polarized region will change when an ac signal is applied is characteristic of the type of interface [74]. A great advantage of EIS is that it can be used both as an advanced method to obtain kinetic and mechanistic knowledge of electrochemical process and as an empirical quality control tool. The main advantage is that it offers a method of predicting the corrosion behaviour of organic coatings in a few minutes without the need of performing time and

resource consuming accelerated tests. The development of software that automatically controls the input potential signal and analyses the output current contributed to make the technique available for more people. Further, it takes little sample preparation, modern equipment and software are simple to handle and measurements require only a few minutes. A mathematical model or an electrical equivalent circuit (EEC) can be used to estimate properties of the materials under study such as corrosion rate, diffusion constant, dielectric constant, capacitance, resistivity and defect area [74]. The main disadvantage of the technique is related to ambiguity in interpretation, namely when using electrical equivalent circuits. Quite often, more than one circuit configuration having the same equivalent impedance can be fitted to the experimental data. Experience and knowledge of the physics of the system and a critical analysis of the results is required to obtain reliable conclusions [72]. Other issue is that quite often simple electrical elements are not sufficient to describe the response of real systems. Electrochemical interfaces usually have heterogeneous properties causing the impedance response to spread over a range of frequencies. For that reason, distributed elements, which have no electrical equivalent, are defined specifically for EIS [74].

Principles ^{57, 73, 74, 77-80}

Ohm's Law states that the current (I) passing through two points of a metallic wire is directly proportional to the potential difference (V) between those points. The proportionality constant is the resistance (R), given by Eq. 2.22.

$$R = \frac{V}{I} \quad \text{Eq. 2.22}$$

The resistance is valid for direct current (dc) circuits only, i.e. in the case of unidirectional flow of current produced by a battery source. Impedance (Z) is an equivalent to resistance for alternating current (ac) circuits and it is a transfer function, i.e. it determines the relationship between the signal applied to the system under study and the corresponding response, Eq. 2.23. Typically, experiments are carried out in the potentiostatic mode. In this mode the applied signal is a small amplitude sine wave potential, $V(t)$ and the response is an alternating sine wave current, $I(t)$.

$$Z(t) = \frac{V(t)}{I(t)} \equiv \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} \quad \text{Eq. 2.23}$$

In the equation, V_0 and I_0 are the amplitudes of the sine waves of potential and current, $\omega=2\pi f$ is the angular frequency of the wave and f is the frequency in Hz. When a system in equilibrium is perturbed, it will require some time to find a new equilibrium state. This is known as the relaxation time (τ) and is responsible for the phase-shift (θ) between the applied potential and the current response.

Possible graphical representations of the sine waves in the time domain are presented in Figure 2.8.

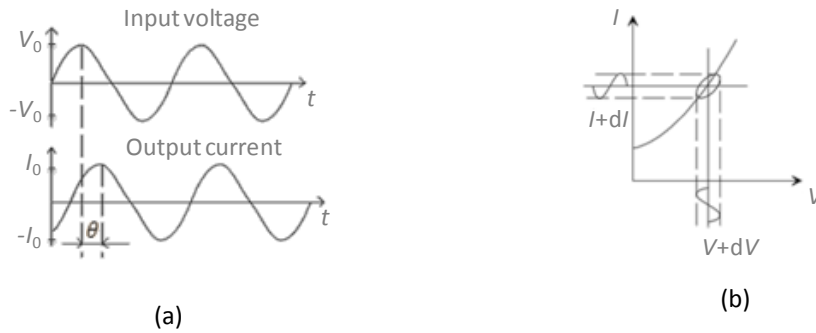


Figure 2.8. Graphical representation of the sine waves corresponding to (a) the applied potential and the current measured and (b) the Lissajous figure [81].

According to Eq. 2.23 it is possible to state that the impedance of a system, at a fixed frequency is fully characterized by two components: a resistive component, corresponding to the ratio between the amplitudes of the excitation and output waves V_0/I_0 , known as the impedance modulus Z_0 or $|Z|$; and a reactive component, corresponding to the time gap between both signals, the phase-shift θ .

Interpretation and manipulation of impedance data in the time domain is not convenient due to the trigonometric relationships. Modern equipments are equipped with software that uses the Fourier transformation to convert data into the frequency domain. Complex impedance $Z(\omega)$ is a mathematical transfer function that performs this Fourier transformation:

$$Z(\omega) = \int_0^{\infty} Z(t)e^{-j\omega t} \cdot dt = \int_0^{\infty} Z(t)[\cos(\omega t) + j \sin(\omega t)] \cdot dt \quad \text{Eq. 2.24}$$

where $j = (-1)^{1/2} = e^{j\pi/2}$.

For each increment or frequency, the complex impedance solution of the integral is thus treated as a complex number, which is time invariant:

$$Z(\omega) = |Z|(\cos \omega + j \sin \omega) = Z'(\text{resistive}) + jZ''(\text{reactive}) \quad \text{Eq. 2.25}$$

where $|Z| = \sqrt{(Z')^2 + (Z'')^2}$, $\theta = \tan^{-1} \left(\frac{Z''}{Z'} \right)$, $Z' = |Z| \cos \theta$ and $Z'' = |Z| \sin \theta$, in rectangular coordinates. If the real Z' and imaginary Z'' components are plotted in a Cartesian plane, the Argand diagram, each frequency will be represented by a vector of magnitude $|Z|$ and angle θ , Figure 2.9. The impedance expression can be further simplified and expressed in polar coordinates as given by Eq. 2.26:

$$Z(\omega) = |Z|e^{j\theta} \quad \text{Eq. 2.26}$$

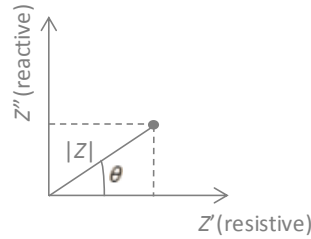


Figure 2.9. Representation of complex impedance.

Transformation to the frequency domain thus allows determining the relationship between current and potential as a simple Ohm's law. However, in order for this mathematical operation to be valid, the integral increments should be very small i.e. the system must be stationary or quasi-stationary. For example, complex impedance should not be used for analysis of pitting corrosion [77]. The constraints to respect while performing complex impedance analysis are:

- Linearity: the response of the system to a sine wave should be a sine wave with the same frequency, and different amplitude and phase; the impedance should not be dependent on the amplitude of the applied signal;
- Stability: upon removal of the perturbation, the system should return to its initial state; therefore, impedance should not be a destructive technique;
- Causality: the measured response results only as consequence of the applied perturbation to the system;

- Continuity: the impedance must be finite, physical systems cannot contain singularities in the evolution of their properties, i.e. for each frequency there should be a single response.

Compliance with the constraints can be tested using integral transform techniques, namely the Kramers-Kronig (K-K) transforms, which are independent of the physical processes involved. The K-K transforms provide imaginary- to-real axis transformations and the real-to-imaginary axis transformations [74]. Whenever allowed by the instrumentation and measuring software, the linearity of a system can be confirmed by observing the Lissajous figures at each frequency. A linear response should result in an ellipse centred on the origin and symmetric to both axes or a straight line if the response is resistive. Distortions are a sign of non-linearity and to solve this issue, either the amplitude of the excitation signal can be reduced or the frequency range under study may need to be adjusted [73, 76].

Three other complex quantities can be derived from complex impedance, namely admittance (Y) -Eq. 2.27, complex modulus (M) -Eq. 2.28- and permittivity also called complex dielectric constant (ε) -Eq. 2.29. These quantities can be subdivided into two sets (Z, M) and (Y, ε) [74]; impedance and complex modulus are preferred when the system is intrinsically conductive whereas admittance and the complex dielectric constant are preferred in the non conducting case as it emphasizes values at high frequencies [73].

$$Y = Z^{-1} = Y' + iY'' \quad \text{Eq. 2.27}$$

$$M = j\omega C_0 Z = M' + M'' \quad \text{Eq. 2.28}$$

$$\varepsilon = M^{-1} = Y(j\omega C_0)^{-1} = \varepsilon' - i\varepsilon'' \quad \text{Eq. 2.29}$$

Where $C_0 = \varepsilon_0 \frac{A}{l}$ is the vacuum capacitance of the empty measuring cell with an area A and separation l between the capacitor plates; and ε_0 is the permittivity of vacuum ($8.854 \times 10^{-14} \text{ Fcm}^{-1}$) [74]. Admittance is the inverse of impedance and is sometimes called complex conductance. The real component Y' is more commonly known as the conductivity σ .

Circuit Elements ^{73, 74, 77, 79-83}

It is natural to establish an analogy between electrochemical impedance and electrical impedance. Each of the elements used represent a particular physical phenomena. Certain components are identical to their electrical counterparts, like the resistor, the capacitor and the

inductor. Other components are specific to the electrochemical processes as the Warburg impedance and the constant-phase-element (CPE).

The impedance of a resistor has only a real component and its response is a constant number R , irrespective of frequency and in phase with the applied signal ($\theta = 0$):

$$Z_R = \frac{V_0}{I_0} = R \quad \text{Eq. 2.30}$$

A capacitor is defined as an element composed of two parallel conducting plates separated by a dielectric material which is able to store electrical charge $-Q$. The capacitance C is the proportionality constant between the stored charge and the potential difference established between the two plates $-V(t)$, Eq. 2.31.

$$C = \frac{Q}{V(t)} \quad \text{Eq. 2.31}$$

$$Z_c = \frac{V(t)}{I(t)} = \frac{V(t)}{C \frac{dV(t)}{dt}} = \frac{\sin(\omega t)}{C \omega \sin(\omega t + \frac{\pi}{2})} = \frac{e^{j\omega t}}{C \omega e^{j(\omega t + \frac{\pi}{2})}} = \frac{1}{jC\omega} \quad \text{Eq. 2.32}$$

where $\cos(\omega t) = \sin(\omega t + \frac{\pi}{2})$, meaning that the voltage lags the current and the phase shift for the impedance is $-\frac{\pi}{2}$. The impedance of a capacitor has only an imaginary component which is dependent on the frequency.

Another important definition is the capacitance of a parallel plate capacitor:

$$C = \frac{\epsilon \epsilon_0 A}{d} \quad \text{Eq. 2.33}$$

where, d is the separation between the plates and A is their area, ϵ is the dielectric constant or relative permittivity of the material between the plates and $\epsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ is the vacuum permittivity.

The inductor is less commonly found, especially when dealing with organic coatings. Similarly to the capacitance, it only has an imaginary component:

$$Z_L = \frac{L \frac{dI(t)}{dt}}{I(t)} = \frac{L \omega I_0 \cos(\theta')}{I_0 \sin(\theta')} = \frac{L \omega \sin(\theta' + \frac{\pi}{2})}{\sin(\theta')} = \frac{L \omega e^{j(\theta' + \frac{\pi}{2})}}{e^{j\theta'}} = L \omega j \quad \text{Eq. 2.34}$$

where, $\theta' = \omega t + \theta$ and $e^{j\frac{\pi}{2}} = j$, therefore it is the current that lags the voltage and the phase shift for the impedance is $\frac{\pi}{2}$.

Passive elements describe well the impedance of charge-transfer by electrons across solids. Nevertheless, in electrochemical systems the flow of current is also possible by mass transfer. Resistors, capacitors and inductors cannot be used to describe systems under diffusion control, i.e. when the kinetics of charge transfer is faster than the mass transport of species in the solution. The Warburg impedance is used to describe this situation, often found in stagnant electrolytes where natural convection is absent. After sufficient time, with constant flux, the concentration profile near the electrode will be stationary for a semi-infinite distance. Assuming that the redox process of the electroactive species is reversible, the mass transfer impedance or semi-infinite Warburg impedance [74] is given by Eq. 2.35:

$$Z_W = \frac{\sigma}{\omega^{1/2}} - \frac{\sigma}{\omega^{1/2}} j \quad \text{Eq. 2.35}$$

where σ is the Warburg or mass transfer coefficient given by:

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left[\frac{1}{\sqrt{D_{\text{ox}}} C_{\text{ox}}(0)} + \frac{1}{\sqrt{D_{\text{red}}} C_{\text{red}}(0)} \right] \quad \text{Eq. 2.36}$$

The diffusion coefficient of the oxidized and reduced form of the electroactive species are D_{ox} and D_{red} , respectively; and $C_{\text{ox}}(0)$ and $C_{\text{red}}(0)$ are the surface concentrations [77].

Diffusion is usually modelled by the introduction of the Warburg element in series with the charge transfer resistance. For increasing values of σ , i.e. as the diffusion process becomes slower, a diffusion tail develops at the low frequency end of the semi-circle. When σ is significantly larger than R_{ct} the semi-circular shape is distorted and is prolonged by a diffusion tail having a slope of 45° ($|Z'| = |Z''|$) [82, 83]. The diffusion layer may also have a finite thickness which is produced when the variation of the concentration of the active species follows the Nernst model. The impedance is then given by:

$$Z_W(\omega) = R_d \frac{\tanh\left(\sqrt{j\omega} \frac{\delta_n^2}{D}\right)}{\sqrt{j\omega} \frac{\delta_n^2}{D}} \quad \text{Eq. 2.37}$$

where R_d is the diffusion resistance and δ_n the thickness of the diffusion layer in the Nernst model. When $\omega \rightarrow 0$ the impedance tends to a particular value termed the polarization resistance, R_p . In fact the slope of $dE(t)/dI(t)$ around the corrosion potential is R_p .

The constant phase element (CPE) is another distributed impedance element often found in electrochemical systems. The response of the CPE combines resistive and reactive elements to model the response of real systems which, in practice, are interfaces with defects and pores having dissimilar reactivities and an averaged response which is dispersed in frequency [74,79]. An empirical relationship for such behaviour is depicted in Eq. 2.38 [84]. When represented graphically, the CPE's correspond to a depressed semi-circle whose centre is located below the real axis in the Nyquist plot and to an inclined line with a phase-shift under 90° in the Bode plot [74,83].

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad \text{Eq. 2.38}$$

where Y_0 [F s^{n-1}] and n are empirical constants with no physical meaning when considered individually. According to this definition [84], the response of the CPE can be equivalent to that of a resistance ($0 < n < 0.2$), a capacitor ($0.8 < n < 1$) or to semi-infinite diffusion ($n = 0.5$) [77]. In the case of $n \sim 1$, there is an empirical relationship between the imaginary component of the CPE and the impedance of a pure capacitor for a fixed frequency [85]:

$$C = \frac{Y_0 \omega^{n-1}}{\sin\left(n \frac{\pi}{2}\right)} \quad \text{Eq. 2.39}$$

Interpretation ^{73, 76, 77, 83}

When a solid is immersed in an electrolyte it will assume a potential which depends on the nature of the material and the electrolyte itself. There will be a build up of charged species at the interface, the double-layer, thus creating a potential gradient. In the absence of a Faradic reaction, i.e. for a blocking electrode, the concentration of species is uniform in the bulk solution and the impedance of the interface corresponds to the Ohmic drop which is described as the resistance of the electrolyte and the double-layer capacitance:

$$Z(\omega) = R_s + \frac{1}{Z_{\text{Cdl}}} \quad \text{Eq. 2.40}$$

The application of a sine wave potential causes the charge and discharge of the double-layer, which behaves as a capacitor. The response generates a current which depends on the frequency of the perturbation, Eq. 2.32 or Eq. 2.38.

If a Faradic process develops, there are two possibilities; the reaction kinetics is controlled either by the charge transfer or by diffusion. In the case of charge transfer control, the Faradic contribution of the current is independent of the frequency:

$$Z_{R_{ct}}(\omega) = R_{ct} \quad \text{Eq. 2.41}$$

In the case where the kinetics is controlled by diffusion, it is necessary to take into account the current associated with the relaxation processes of the active elements inside the diffusion layer, i.e. the Warburg impedance Eq. 2.35 and Eq. 2.37.

The way these elements are placed is important to calculate the impedance of a system and to create an analog equivalent electrical circuit. The order of the elements should follow the physical logic of the system, with consecutive process placed in series while simultaneous processes are placed in parallel. The simplest EEC refers to the behaviour of blocking electrodes. This circuit is composed by the impedance of the electrolyte Z_{R_s} placed in series with the impedance of the double-layer Z_{dl} or Z_{CPE} when the behaviour is not ideal. When there is a Faradic reaction, the model is more complex. If it is not controlled by diffusion, it can be described by the circuit in Figure 2.10, in which R_{ct} is the charge transfer resistance in parallel with the double layer capacitance C_{dl} . The mathematical expression to the impedance of such circuit is determined by Kirchhoff's laws, Eq. 2.42. In case of diffusion control, it is necessary to add a Warburg element (Z_w) in series to the charge transfer impedance, giving rise to the Randles circuit in Figure 2.11.

$$Z = R_s + \frac{1}{1/R_{ct} + j\omega C} \quad \text{Eq. 2.42}$$

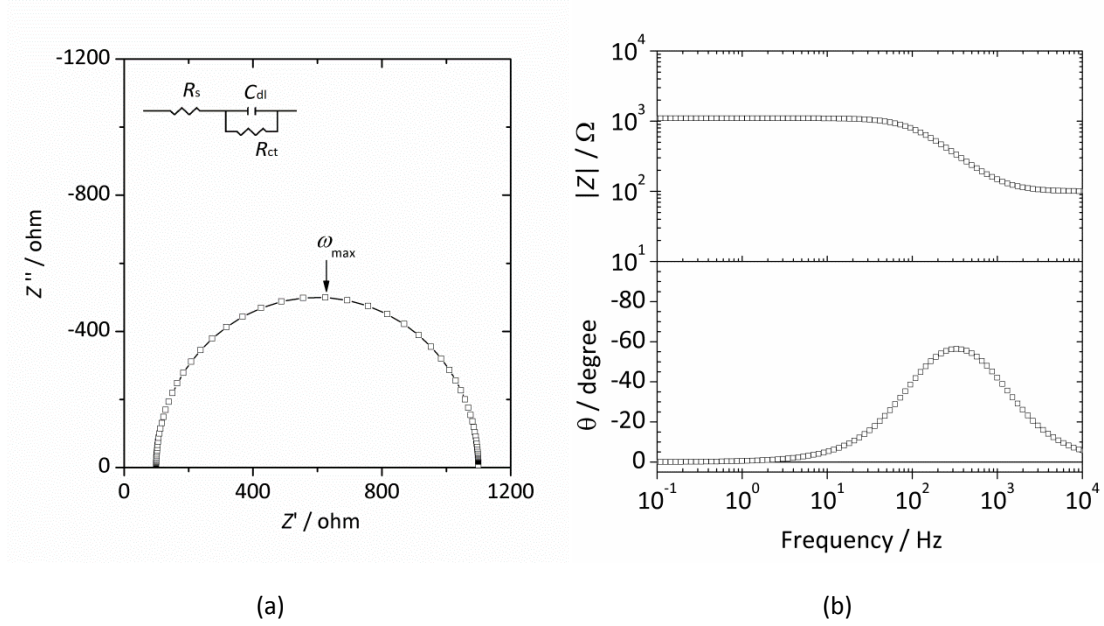


Figure 2.10. Impedance spectra for a non-specified metal with $R_s = 100 \Omega$, $R_{ct} = 1000 \Omega$ and $C_{dl} = 1 \times 10^{-5} \text{ F}$.

Therefore any electrochemical process can generally be characterized by a resistance and a capacitor [83]. In the frequency domain, different RC elements can be identified by their relaxation time or time constant (τ) given by Eq. 2.43, with RC measured at the frequency of the maximum loss, ω_{max} in the complex plane plots [74, 78, 82].

$$\tau = RC = \frac{1}{\omega_{max}} \quad \text{Eq. 2.43}$$

Fast processes, corresponding to low τ values, occur at high frequencies whereas slow processes, with high τ , occur at low frequencies. The order of magnitude of the capacitance values enables a correlation between the observed electrical properties and the various regions within the system. Typically, a capacitance of $10^{-4} \text{ F cm}^{-2}$ will correspond to Faradic reactions, a capacitance of 10^{-7} - $10^{-5} \text{ F cm}^{-2}$ to phenomenon at the sample-electrode interface and both may be studied at lower frequencies; whereas a capacitance of $10^{-12} \text{ F cm}^{-2}$ will correspond to the bulk response of a material and maybe studied at higher frequencies [78, 82]. The responses of these different processes can spread out through 12 orders of magnitude in the frequency range. Interfacial processes can be observed at frequencies as low as 10 μHz whereas a bulk response of the electrode can be observed up to 50 MHz. Therefore, by sweeping the frequency of the applied ac potential it becomes possible to separate the kinetics of the different processes in a single experiment. Similarly to other spectroscopy techniques (visible, Fourier transform

infrared (FTIR), Raman and others), certain phenomena will typically respond at specific frequencies, allowing the sample under study to be characterized. The main difficulty associated with ac measurements arises over the interpretation of the data collected. Impedance is a complex variable and therefore it has no physical meaning unless the physical nature of the test system and its conducting behaviour are taken into account.

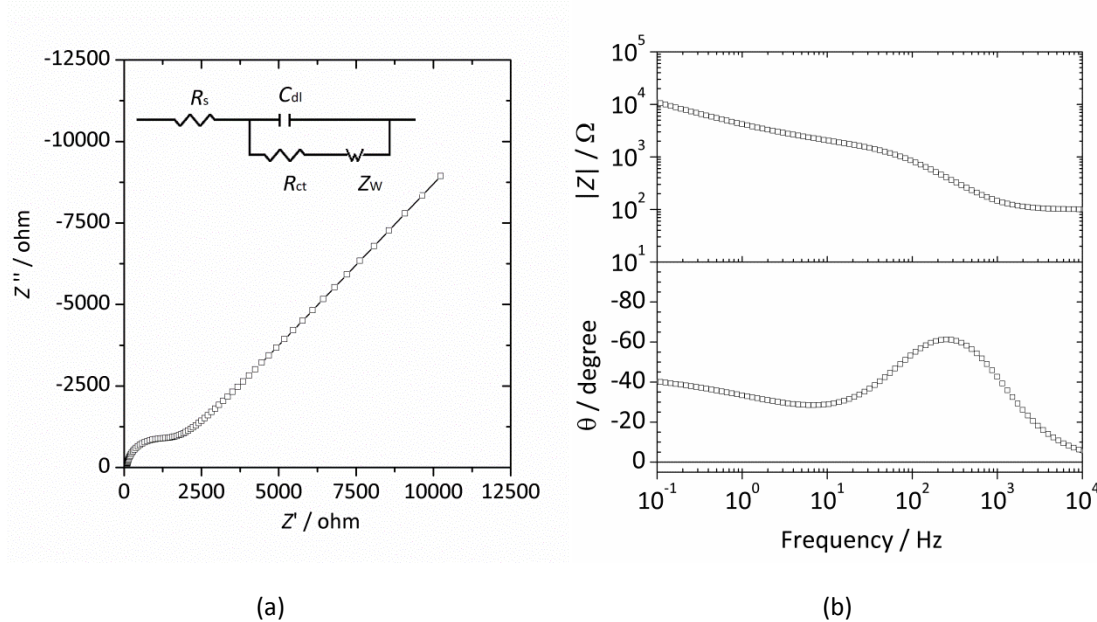


Figure 2.11. Impedance spectra for a non-specified metal with $R_s = 100 \Omega$, $R_{ct} = 1000 \Omega$ and $C_{dl} = 1 \times 10^{-5} \text{ F}$ and a generic Warburg impedance with finite-thickness diffusion layer.

Impedance data can be presented in various forms, the most common being either the complex plane, i.e. imaginary vs. real component (Z'' vs. Z'), known as the Nyquist diagram and the spectroscopic plot, i.e. the impedance modulus and the phase angle as a function of frequency ($\log |Z|$ / $\log \theta$ vs. $\log \omega$), known as Bode plot. Presentation in three dimensional plots, with $\log \omega$ perpendicular to the complex plane is less common [82]. The Nyquist and Bode representations of the same result can be considered complementary because each shows a particular aspect of the diagram. The Nyquist diagram has the disadvantage of not indicating frequency response directly, but the number of loops and their shape indicate the number and nature of the physical processes present. For this representation it is necessary to use isotropic axes, otherwise the diagrams will be deformed. The Bode plot offers a more complete vision of the frequency domain but has the disadvantage of reduced resolution inherent to logarithmic plots.

The simple observation of the shape of the Nyquist and Bode plots therefore allows the identification of the number of process present and their physical nature, i.e. the presence of resistive-capacitive effects, interface reactions or diffusion. Detailed analysis can confirm the

presence of these processes and provide the values of such quantities as capacitance, resistivity, dielectric constant, corrosion rate and diffusion coefficient. The tools used to interpret impedance data fall into two classes: analogs or physical models [57]. A detailed physico-chemical model is always preferred to an analog but in most situations phenomena occur at a microscopic level that are not easy to describe by a detailed model. Simpler models are thus recommended, often expressed as equivalent circuits. Analogs are ambiguous because an equivalent circuit that contains three or more elements may be arranged in various combinations but still yield the same overall impedance response; there is no unique analog for a particular test system. Usually the EEC analog is chosen based on the following rules [74]:

- Intuition as to what kind of circuit elements are expected to be present in the system under study and whether they are connected in series or parallel;
- Examination of the experimental data to decide whether the response is consistent with the proposed circuit;
- Critical interpretation of the values obtained for electrical elements in order to check how reasonable they are and their independence.

A hierarchical ladder-network connection is usually the most adequate choice for a homogeneous material. When using this circuit, bulk charging and conduction effects take place before interfacial reaction/ adsorption ones as they would in the real system [72].

Complex Nonlinear Least Squares Data-Fitting ⁷²

The most practical method to perform quantitative analysis from EIS is to fit the experimental data to an equivalent electrical circuit. Commercial software based on Complex Nonlinear Least Squares Data-Fitting (CNLS) is used to estimate the electrical parameters and their standard deviations.

The standard deviation provides an indication of which elements have predominant responses on the global response and those which are useless or at least not well determined from the data [57]. CNLS fits minimize the weighted sum of squares (S) of the real and imaginary residuals. A residual is the difference between a data value at a given frequency and the corresponding value calculated from the model. A good match between the data and the model implies that the residuals are randomly distributed around zero for all the tested frequency range [76, 77]. The user must provide appropriate estimates of the parameters to introduce in the model in order for the software to converge rapidly to the solution. Therefore, it is useful to have some knowledge about the system under study.

Instrumentation ^{73, 77, 81}

For aqueous electrochemistry, the electrodes are immersed in a liquid electrolyte and a three-electrode configuration is the most common. The electrode under investigation is called the working electrode (WE) and the electrode necessary to close the electrical circuit is the counter electrode (CE), Figure 2.12. The counter electrode is commonly made of platinum having sufficient surface area such that the counter reaction of the half cell occurring at the working electrode occurs without perturbing the system, i.e. must not be diffusion limited. A reference electrode (RE) is required to determine the potential across the electrochemical interface. The choice of the reference electrode is based on the nature of the electrolyte and the material under study. In the presence of chloride ions it is convenient to use the saturated calomel reference (SCE). A four-electrode cell is used to analyze processes occurring within the electrolyte, between two electrodes separated by a membrane. This kind of a cell is usually used to study ion transport through the membrane [81]. Vacuum, a neutral atmosphere such as argon, an oxidizing atmosphere and thermostatic baths can also be used by closing the cell in a cage. Further, electric field generated by electrical devices placed near the cell or the electrical line installation may contribute to noise in the system. For this purpose, the use of a Faraday cage and avoiding measurements at line frequency is often advised.

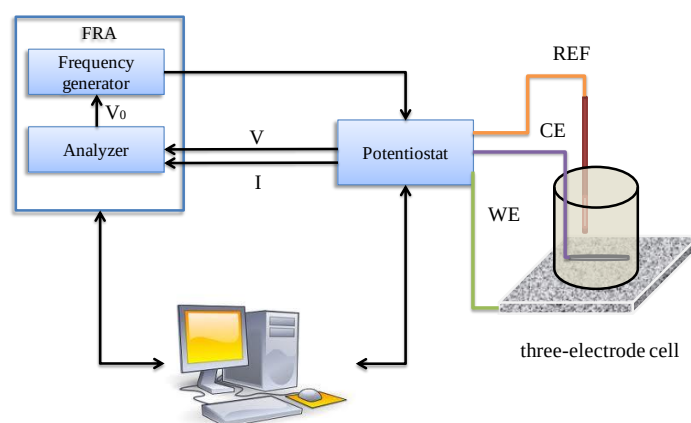


Figure 2.12. Diagram showing the modern apparatus for an IS experiment in the potentiostatic mode.

Experiments can be performed under galvanostatic control, mainly for battery research or under potentiostatic control which is preferred in electrochemical studies. The potentiostat which can also be called an electrochemical interface (EI) measures and controls the potential

difference between the WE and the REF. In order to maintain this potential difference constant, current must pass through the CE. The potentiostat has a set of inner resistances with a current range sufficient to be able to measure the response of a wide range of samples. A very high inner resistance would result in noisy measurements; and an inner resistance lower than the sample resistance, would result in an overload. Modern equipments have a numerical algorithm that estimates the resistance at each frequency and performs automatic selection of the inner resistance of the potentiostat optimising the signal-to-noise ratio.

Usually, a single-frequency voltage is applied to the working electrode and the phase shift and amplitude of the resulting current at that frequency are measured while the real and imaginary part of impedance is computed automatically using fast Fourier transform (FFT) analysis. Lock-in amplifiers and FRA's are used to measure automatically the amplitudes of the input and output signals and the phase angle and are reliable in the frequency ranges of about 0.01 Hz to 10^5 Hz. The frequency range is limited by instrumentation at the high frequency range and due to non-linear behaviour of the system at the low frequency range. Lock-in amplifiers are the most economic alternative to provide the impedance response of a system, but they are slower and less versatile than the FRA. The FRA is thus the most important instrument in impedance spectroscopy. It allows potentiostatic control of the cell, incorporates automatic frequency sweeps and automatic control of the magnitude of the applied ac signal with an accuracy of 0.1% [74]. For each frequency, time-dependent potential and current are converted in a complex number by FFT algorithms. The numerical error associated to such transformation might be minimized by increasing the number of integration iterations, i.e. by providing the equipment a longer time to perform the calculations or by increasing the number of integration cycles. The FRA usually allows auto-integration, i.e. the possibility to select automatically the method that more rapidly converges to the solution. This option is termed short integration. In this dissertation, experiments were performed using a Femtostat FAS1 system (Gamry Instruments, PA, USA) which extracts the graphical parameters of the resulting Lissajous figures to plot the impedance spectra. The range of frequencies for measurement was between 10 kHz and 0.01 Hz, with 9 points per decade, with amplitude of 10mV, which was found to be a good compromise between the information obtained, time of experiment and linearity.

Electrochemical characterization of organic coatings^{77, 78}

Organic coatings protect the underlying substrate by acting as a physical barrier for water, oxygen and aggressive ions. Besides determination of physical and chemical properties of the organic layer, it is also important to determine the rate of penetration of electrolyte through the coating and the condition of the metal underneath. The first non-visual test for coating degradation was introduced in 1936 by Burns and Haring and consisted in measuring the open circuit potential over time and [86]. The principle is quite simple: a freely corroding coated sample immersed in an aggressive electrolyte will show a shift in potential towards more positive values when passivated. On the other hand, if the potential reveals a decreasing shift, the sample is active. The technique proved to be very useful to study the influence of substrate surface condition, number and thickness of organic layers and the influence of coating composition on the rate of coating breakdown. Later works using this technique revealed many inconsistent phenomena and it was concluded that potential curves could not fully explain the behaviour of coatings [87, 88]. Electrochemical impedance spectroscopy on the other hand, is recognized as a tool for the detection of breakdown of coated systems [89, 90] and offers a viable alternative to accelerated corrosion tests, widely used in the automotive industry, which are time consuming. Further, accelerated tests do not reveal the failure of the material until the coating is degraded since corrosion occurs under the paint film and it is often hidden [87, 91] whereas EIS is a non destructive technique,

The simplest EEC for a corroding bare metal is the circuit in Figure 2.10. This circuit can also be used to describe the behaviour of an intact organic coating applied on a metallic substrate. In that case, the resistance corresponds to the resistance offered by the coating pores to the passage of ions in series with the charge transfer at the bottom of the pore (R_p) and the capacitance is a measure of the dielectric properties of the coating (C_c). In the case of a barrier coating having a very resistive behaviour, the impedance of the capacitance predominates over the total impedance of the system. For a barrier coating, a typical capacitance would be 10^{-10} to 10^{-12} Fcm⁻² and for a double-layer capacitance associated to bare metal exposed, a typical value would be 10^{-5} Fcm⁻² [91].

The corrosion current density (i_{corr}), a measure of corrosion kinetics, can be calculated from the Faradaic resistance (R_{ct}) normalized by the area of the sample exposed to the electrolyte using the Stern-Geary relationship [92], Eq. 2.44.

$$R_{ct} = \frac{\frac{b_a b_c}{2.3(b_a + b_c)}}{i_{corr}} = \frac{B}{i_{corr}} \quad \text{Eq. 2.44}$$

where b_a and b_c are the anodic and cathodic Tafel constants, respectively, that can be obtained either from linear polarization plots (in the activation region) or from data found in the literature whenever possible.

The most popular method to determine the breakdown of an organic coating, based on EIS, consists in measuring the capacitance in the earlier stages of immersion and following its evolution, as the changes in capacity can be associated to the water uptake as found by Brasher and Kingsbury [93]. A linear relationship between the reciprocal of capacitance and the weight of dry film reveals that the capacitance of the coating is governed by the nature of the film at the moment of immersion. The pores in the coating fill with water which distributes along columns perpendicularly to the surface, instead of forming a uniform front. Assuming that the capacitance of the polymer is not affected by the solution, the permittivity of adsorbed water is constant and equal to 80 and the capacitance changes are proportional to permittivity changes, then:

$$X_v = \frac{100 \times \log(C_c/C_{c,0})}{\log 80} \quad \text{Eq. 2.45}$$

where, X_v is the volume fraction of water expressed in the percentage by volume of water taken up, C_c and $C_{c,0}$ are the measured capacitances at time t , and extrapolated to $t = 0$ (dry coating), respectively.

The water-uptake models have some limitations as a method of predicting coating breakdown, namely, the incorporation of corrosion inhibitive pigments in the polymer modifies the mechanism of water uptake in the organic coating. A simple equation like Eq. 2.45 cannot be used to predict the breakdown of a doped primer.

When a coating is intact the impedance spectra shows a single time constant with a wide capacitive slope and a phase angle close to 90° . As time elapses, the coating becomes degraded and permeable to the passage of water and oxygen molecules and ions. Inevitably there will be corrosion and delamination (loss of adhesion) at the interface with the metal. The coated system will then be described by a combination of circuit elements accounting for the intact coating and the Faradic process at the metal interface. The breakdown of a coating can thus be determined by an alternative method, the breakpoint frequency f_b method [94], Eq. 2.46. It is possible to determine the delaminated area from the frequency corresponding to the transition from the

capacitive slope to the resistive plateau. However, it can only be used when the time constants are well separated, which is not always the case in real systems. Further, small defects inherent to the coating cannot be detected by this method.

$$\frac{1}{R_{ct}} = j\omega C_c \leftrightarrow \frac{A_d}{\rho d} = 2\pi f_b \frac{\varepsilon \varepsilon_0}{d} A \quad \text{Eq. 2.46}$$

where, A_d is the defect or delaminated area, A is the total specimen area, ρ is the intrinsic coating resistivity and d the coating thickness.

Hirayama and Haruyama [95] have developed an extended breakpoint frequency method to evaluate the delamination of polymer coated metals which already have defects. The ionic current is concentrated on the defect region and thus the active surface area $A_{\text{pore}}/A_{\text{total}}$, which increases with immersion time will influence the values of R_p , C_{dl} and R_{ct} while the coating layer capacitance remains fairly constant throughout immersion. Unless the pores become extremely large, water uptake can be neglected even for long exposure times because the coating's dielectric constant will only change slightly. It may happen that the pore resistance starts to decrease as signal of clogging due to the accumulation of corrosion products [91]. The impedance of a coating with a defect will be given by the following:

$$Z = R_s + \frac{1}{j\omega C_c + \frac{1}{R_p + j\omega C_{dl} + \frac{1}{R_{ct}}}} \quad \text{Eq. 2.47}$$

where, Hirayama and Haruyama [95] found the following relationships to be reproducible when describing delamination of barrier coatings:

$$R_p = \frac{R_p^0}{A_d} = \frac{\rho d}{A_d} \quad \text{Eq. 2.48}$$

$$R_{ct} = \frac{R_{ct}^0}{A_d} \quad \text{Eq. 2.49}$$

$$C_{dl} = C_{dl}^0 A_d \quad \text{Eq. 2.50}$$

$$C_c = C_c^0 A = \frac{\varepsilon \varepsilon_0}{d} A \quad \text{Eq. 2.51}$$

where ρ is the resistivity of the electrolyte inside the pore; d is the coating thickness; A_d is the defect or delaminated area; A is the geometrical area and R_p, R_p^0 are the pore and charge transfer R_{ct}, R_{ct}^0 resistances and C_c, C_c^0 are the coating capacitances for an arbitrary and the first instant of immersion, respectively.

2.5 Localized impedance spectroscopy (LEIS) ^{96, 97}

Conventional EIS provides information on the averaged electrochemical parameters of a surface or material. Local electrochemical processes occurring at micro-regions such as pinholes, cracks and blisters can be detected on EIS spectra under certain conditions, i.e. depending on the relative impedances of the micro-heterogeneities and their areas, as demonstrated by Hirayama and Harayama [95], but cannot be geometrically located. Localized electrochemical impedance spectroscopy (LEIS) has been developed to overcome this limitation [97]. The working principle of LEIS is similar to that of EIS, in the sense that a small sine wave perturbation is applied to a working electrode or sample and the resulting current is measured in order to calculate the impedance. However, in LEIS the current is measured in the solution. There are two important factors controlling the resolution of the technique, the probe size and the probe-to-sample distance [98].

The first measurements of localized electrochemical impedance spectroscopy were carried out in 80's by Isaacs et al [97] which successfully mapped various heterogeneous samples using different bi-probe geometries. These studies did not generate quantitative information further they used a thin layer cell geometry which influences the distribution of current density in solution relatively to a full immersion condition. More than ten years later, the LEIS was officially introduced by Lillard et al who applied LEIS, as a quantitative local technique to the study of aluminium and aluminium/molybdenum systems [99] and later to the study of organic coatings [100].

Principles ^{73, 96, 99}

It is possible to define various transfer functions by applying and measuring different signals as a function of frequency. The most evident consists on the application of a sine wave

potential to the system under study and measuring the corresponding sine wave current flowing from it. This transfer function corresponds to complex impedance measured in conventional EIS:

$$Z(\omega) = \frac{\Delta E_{glob}(\omega)}{\Delta I_{glob}(\omega)} \quad \text{Eq. 2.52}$$

where $\Delta I_{glob}(\omega)$ is the sine wave current measured across the sample as a response to the application of a sine wave potential $\Delta E_{glob}(\omega)$ signal.

A logic definition of local electrochemical impedance would then be the transfer function proposed by Bayet et al [101] and later by Huang et al. [102], named the local interfacial impedance (z_0).

$$z_0(\omega) = \frac{\Delta E_{loc}(\omega)}{\Delta I_{loc}(\omega)} \quad \text{Eq. 2.53}$$

This impedance consists on measuring the local current density with a bi-probe and the local potential drop measured across the double-layer, i.e. as if the reference electrode was placed just outside the double-layer (Eq. 2.53).

The definition of local impedance that became more popularly known as localized electrochemical impedance, corresponding to the definition used through this dissertation, was also introduced by Huang et al [102] and is defined as:

$$z(\omega) = \frac{\Delta E_{glob}(\omega)}{\Delta I_{loc}(\omega)} \quad \text{Eq. 2.54}$$

where, $\Delta I_{loc}(\omega)$ is the current measured in solution. This approach can be achieved with the use of a dual microelectrode or bi-probe for sensing the local ac potential gradient (ΔV_{loc}) which then allows the determination of the local current (I_{loc}) from the following:

$$I_{loc} = \Delta V_{loc} \frac{k}{d} \quad \text{Eq. 2.55}$$

where d is the distance between the electrodes of the bi-probe and k is the conductivity of the electrolyte, which is assumed as constant between the two measurement points [99].

A local Ohmic impedance (z_e) was also defined by Huang et al [102]. The local Ohmic impedance is determined by measuring a local ac current (I_{loc}) and a potential drop from the outer region of the diffusive double layer to the reference electrode. In practice, z_e cannot be measured directly and it corresponds to the difference between the local impedance and the

local interfacial impedance. According to this definition, the local Ohmic impedance is a complex number.

$$z(\omega) = z_0(\omega) + z_e(\omega) \quad \text{Eq. 2.56}$$

Modes of operation^{96,99}

It is possible to perform local electrochemical impedance spectroscopy in a cartographic or mapping mode and in a spectroscopic mode. The mapping mode consists in scanning the surface along a plane parallel to the surface of the working electrode at a fixed frequency. The maps can represent the module of impedance or admittance or the phase angle as a function of the position xy of the bi-probe. In most cases the admittance representation is preferred because it enhances the regions which are source of current, i.e. defects, which is generally the information searched. In the spectroscopic mode the bi-probe is placed at a fixed position and a full spectrum is obtained for a frequency range like in conventinal EIS experiment.

The influence of the potential field ⁹⁶

A desirable condition for making measurements is that the potential varies linearly above the sample, Eq. 2.55. Only under close to ideal conditions is it true that the electric field in solution is uniform between the probe tips and thus the current density in solution is a direct measure of the potential field generated by the sample. In practice, the ac potential gradient in solution above an electrode is influenced by many parameters and the current irradiating from a sample spreads over the electrolyte contributing to reduce the spatial resolution [98]. For this reason and contrary to what is recommended in EIS, the measurements should be made at a small distance of the surface of the system under study in the region where the potential field is less likely to be distorted.

This irregular distribution of current was studied by Newman [103] and later by Isaacs et al [98] who observed that the current distribution becomes infinite at the edge of an ideally disk-shaped blocking electrode, Figure 2.13. As a consequence, the local impedance is highest at the centre of the electrode and lowest at the periphery. Further, the local impedance will also depend on the distance of the surface at which the measurement is made.

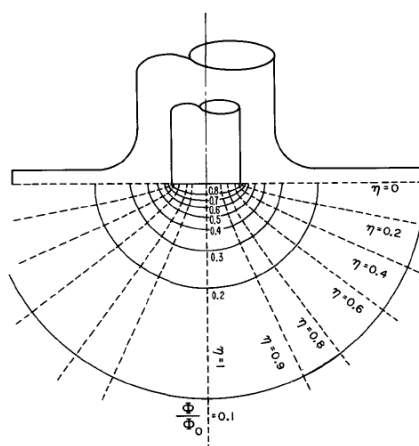


Figure 2.13 Distribution of potential and current fields above a disk shaped electrode. The continuous lines correspond to the iso-potentials while the dashed lines correspond to the current [103].

The distribution of the potential field leads to two important features which are unique to localized electrochemical impedance spectroscopy. The first one is related to the constant-phase-element (CPE) behaviour whereas the second feature is related to the local Ohmic impedance.

The CPE may arise due to variations of the properties of the system under study in the electrode surface plane (two-dimensional distribution) or in the direction normal to the interface under study (three-dimensional distribution). Variations in roughness or porosity of the surface layers may cause 3D distribution, whereas in the absence of Faradic reaction, the presence of grain boundaries, regions of different conductivity or a simple variation of the probe position will cause a 2D distribution. It should be possible to distinguish between 2D and 3D distributions by use of local electrochemical impedance spectroscopy (LEIS). In the case of a 3D distribution, both the local and the global spectrum will reveal CPE behaviour with the same exponent n . In the case of a 2D distribution the local impedance diagram should not reveal a CPE behaviour [104].

The local Ohmic impedance is a complex number that corresponds to the difference between the local and the local interfacial impedances. It presents a real part at very high and very low frequencies but closer to the high frequency limit it may present inductive features varying with the radial position of the probe above the disk-shaped electrode. Huang et al have performed numerical simulations of LEIS spectra for disk-shaped electrodes having blocking, ideally polarisable and Faradic behaviour [102, 105, 106] and observed a distinctive behaviour at the high frequency end when comparing the local and conventional impedance diagrams. For local impedance spectroscopy, the shape of the local spectra at high frequencies depends

strongly on the position of the bi-probe along the radius; an inductive loop is measured at the centre of the disk whereas a capacitive loop is measured at the edge of the disk. Therefore, the real and the imaginary parts of local ohmic impedance dependent both on the conductivity of the electrolyte and on the radius of the sample electrode.

The following equation provides a method to calculate the characteristic frequency (f) for inception of geometry-induced distortions to the impedance [102]:

$$f = \frac{1}{2\pi} \left(\frac{\kappa}{Q_0 r_0} \right)^{1/n} \quad \text{Eq. 2.57}$$

where κ is the conductivity of the electrolyte and r_0 is the radius of the disk shaped sample. When $n = 1$, Q_0 is the capacitance of interface and when $n \neq 1$, Q_0 is the frequency-independent parameter of the CPE. This frequency can also be expressed in terms of an adimensional parameter K [102]:

$$K = \frac{Q_0 \omega r_0}{\kappa} \text{ or } K = \frac{Q_0 \omega^n r_0}{\kappa} \text{ in the presence of a CPE} \quad \text{Eq. 2.58}$$

where ω is the angular frequency.

Instrumentation ⁹⁶

There are different approaches allowing the measurements of localized electrochemical impedance. Regardless the differences, they are all based on the same principle, the measurement of potential difference between two points in the vicinity of a sample surface which allows an indirect measurement of the local current distribution in the electrolyte.

Modification of a Scanning Vibrating Electrode Technique (SVET)

The first experimental assembly for measuring localized impedance using the SVET was described by Bayet et al [108]. For measurement of localized electrochemical impedance it is necessary that the probe only vibrates in the vertical direction. The potential difference measured between the two electrodes of the vibrating probe on the points corresponding to maximum and minimum amplitude of the vibrating is ΔV_{loc} in Eq. 2.55. Because this type of

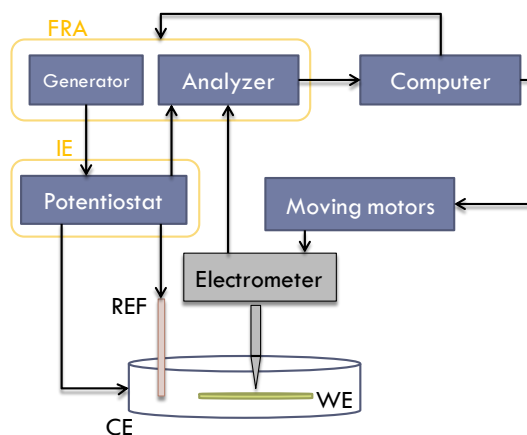
probe can easily be placed at a close distance to the working electrode surface (30-50 μm), the potential measured at the point closer to the surface is taken as a pseudo-reference and thus a localized interfacial impedance (z_0) can be measured. This type of assembly allows a resolution in the order of a few tens of micrometer. However, there are many disadvantages, namely, the vibration of the tip produces stirring of solution which can modify the concentration profiles in the vicinity of the electrode or drag corrosion products and change the current distribution. Further, it is necessary to calibrate the current considering the conductivity of the electrolyte, the frequency and amplitude of vibration [109].

Three-electrode assembly^{96, 73, 110}

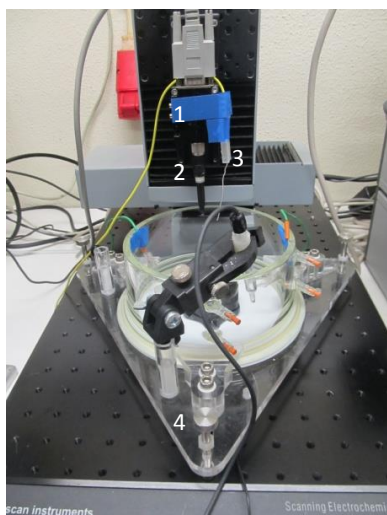
The preferred LEIS assembly consists in an electrochemical cell having working, reference and counter electrodes. The working electrode is the one under study and the reference electrode allows the dc potential of the system to be measured. A bi-probe which is attached to a 3D positioning system is used to measure the local current. The use of a bi-probe presents some advantages over the vibrating probe as there is little influence of convection and stirring because the tip is placed at a higher distance from the surface and it only moves in a plane parallel to it, such that the measurement is below the plane of the movement. Further, with this assembly the tip does not need calibration. This assembly was first reported in the literature by Baril et al [111, 112] who applied LEIS to the study of the corrosion mechanisms in magnesium alloys.

The Uniscan instrument, model M370 includes two sample holders, the TriCell [113] and the $\mu\text{TriCell}$ [114], the electrometer which holds the bi-probe, the 3D positioning system and a vibration stabilization table. The $\mu\text{TriCell}$ allows a reduced volume of electrolyte while the TriCell is more versatile as it allows various sample configurations and therefore it was chosen to perform the experiments discussed in the current dissertation. The electrodes are connected to a potentiostat also called an electrochemical interface (EI), which allows the control and measurement of the potential and current flowing in the cell. The electrochemical interface (EI) used for this dissertation was a Solartron SI 1286 (Solartron Analytical) [115]. This interface is on its turn connected to the Frequency Response Analyser (FRA) which generates the sine wave potential with the desired amplitude and frequencies and allows extracting the real and imaginary parts of impedance. A FRA Solartron 1250 (Solartron Analytical) [116] was used for the measurements. A third element, which is an electrometer is necessary to measure the potential

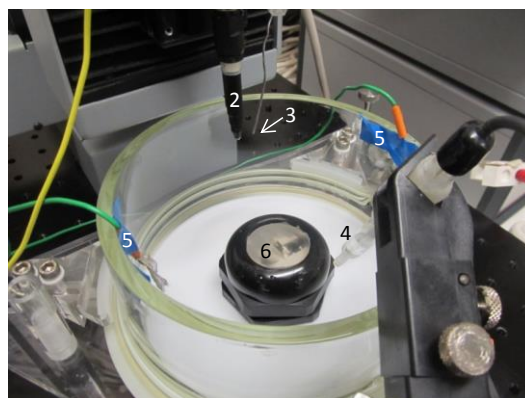
difference between the two electrodes of the bi-probe and to filtrate, amplify and transform this value to be analysed by the FRA, Figure 2.14 a.



(a)



(b)



(c)

Figure 2.14. Experimental apparatus for LEIS experiments: (a) schematics of instruments and connections, (b) photograph of the scan head, cell and anti-vibration table and (c) detail of the electrochemical cell. 1. Electrometer, 2. Bi-probe, 3. High-frequency bypass for reference electrode, 4. Reference electrode, 5. Counter-electrodes, 6. Working electrode.

In a study from Jorcin [96] using similar equipment and the modified bi-probe, it was concluded that the spatial resolution is optimized for a conductivity of 10^{-4} Scm^{-1} corresponding to a concentration of 10^{-3} M of NaCl. Such low conductivity arises a problem since it results in high impedance systems. Most potentiostats cannot measure the resulting impedances at high frequencies and therefore the maximum advised frequency for LEIS is 10 kHz. On the other hand, the reduced scale of the working electrode and the small potential differences generated by them lead to small currents which make the transformation into the Fourier domain very hard

to converge and produce high instability for measurements at frequencies lower than 0.1 Hz. The range of frequencies for measurement was therefore between 10 kHz and 0.1 Hz, with 7 points per decade and 10 mV amplitude, which was found to be a good compromise between the information obtained, time of experiment and linearity. Further, at high frequencies the reference electrode may present high impedance and contribute to attenuate the signal or even produce a phase-shift. In principle, the frequency range used for the experiments is lower than the frequency at which this produces artefacts in the measurements. In any case, the introduction of low impedance reference element formed by a platinum wire in series with a 220 μF capacitor, was performed as recommended by electrode and instrumentation manufacturers [117] and Jorcin [96]. This element was placed in the proximity of the bi-probe and short-circuited with the reference electrode, Figure 2.14 b.

The electrochemical interface and the FRA are usually controlled by a computer equipped with dedicated software that records and displays the experimental data. Commercial software LEIS M370, from Uniscan Instruments, was used for controlling both the hardware and recording the data. In most diagrams it was necessary to remove the point at 50 Hz and its multiples corresponding to the frequency of the power line.

The scan motor has the maximum range of 70 mm in all directions with 8 nm resolution which is accomplished by inchworm motors and a maximum scan speed of 2 mm s^{-1} . The bi-probe is connected to the electrometer which is directly mounted to the z-stage while the electrochemical cell is stationary. The positioning of the bi-probe relatively to the working electrode in the vertical direction is made by visual observation. Nevertheless, reproducibly of the results concerning the same type of sample in the electrolyte is good as the bi-electrode is placed as close to the surface as possible. The TriCell is mounted on an adjustable tilting platform allowing the substrate surface to be levelled which is essential to avoid crashing of the tip, Figure 2.14 c. The TriCell allows a resin disk of 25 mm diameter to be fixed at its centre allowing the working electrode to be embedded in this disk. The surface to be analyzed was grinded with silicon carbide paper to expose the fresh, flat test surface. When the working electrode presented plate geometry, it was mounted on the holder simply by gluing it to the resin disk and insulating the exposed edges with a lacquer. The electrical connection to the potentiostat was made by the rear of the mount by inserting a low resistance metal rod in the resin disk which also made contact with the sample. Silver epoxy paint was used in the contact interface in order to improve the quality of this connection. Ideally, the CE should ensure symmetrical distribution of the current flow across the cell and therefore it should consist on a cylinder or ring shape electrode. In practice, it is quite expensive to have a noble metal with sufficient area for this

purpose and thus the counter electrode consists in a platinum mesh divided in two sections which have approximately the same area and are placed at opposite sides of the sample.

The bi-probe

The bi-probe is a key element as it allows the measurement of the local current generated in solution by the sample and greatly determines the resolution of the technique. The LEIS probe may present various geometrical configurations which allow the measurement of the horizontal and vertical components of the potential field in solution. The bi-probe used for the experiments discussed in this thesis is commercialized by Uniscan Instruments [107] and was further modified in the laboratory. The commercial bi-electrode consists in a conical plastic case which protects the wires and electrical connections from the environment. A sharpened platinum wire with $\sim 10\ \mu\text{m}$ diameter protrudes from the bottom of the cone while other platinum wire leaves the body of the case at a distance of $\sim 3\ \text{mm}$ from the bottom of the cone, wraps around it and closes with a knot around itself forming a ring, Figure 2.15 a. This configuration presented several problems, namely the knot in the ring and the sharp wire at the bottom introduced artefacts. The probe was then modified following the good results obtained by previous work from Jorcin [96]. The modifications consisted in cutting the knot while trying to keep the length of wire necessary to close the ring around the conical cap and grinding carefully the bottom wire electrode to a disk shape, Figure 2.14 b.

The bi-probe is therefore made of two platinum electrodes separated by a distance d normal to the surface of the sample. Using the conductivity of the electrolyte and the distance d , the local current can be obtained by applying Ohm's law to the potential difference measured at the bi-probe according to Eq. 2.55. It is important to notice that even after the knot is cut, the ring is never perfectly parallel to the surface of the working electrode. Further, it does not measure the local current in all (x,y,z) directions. This issue is common to every probe geometrical configuration. Therefore, the global impedance cannot be obtained by simply integrating the local impedance and the potential gradient measured with the bi-probe provides only an approximation of the real potential gradient formed in the solution by the sample.

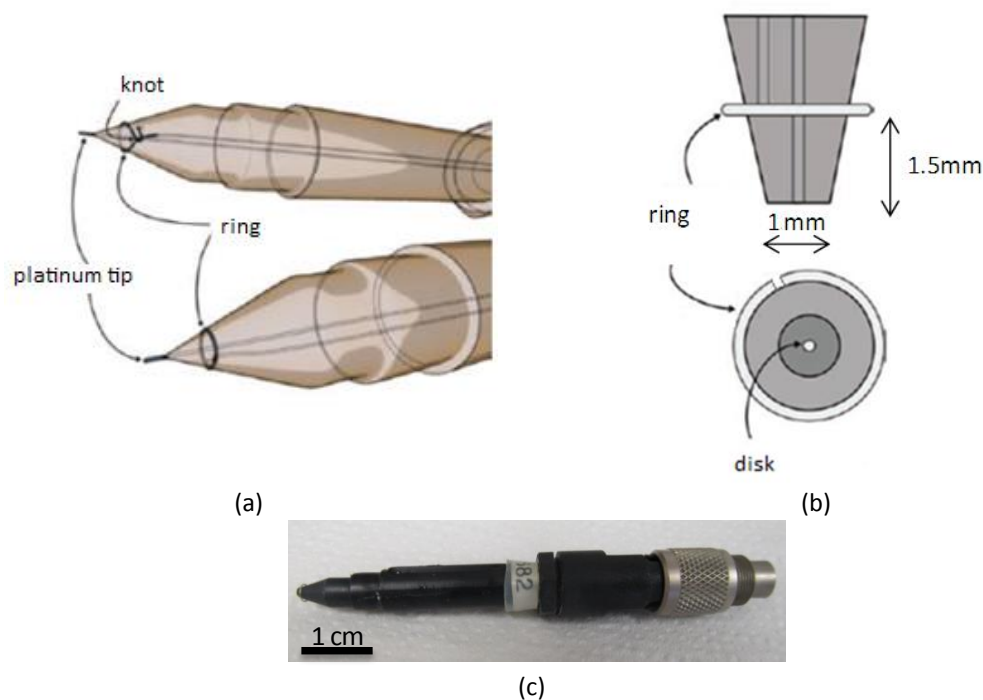


Figure 2.15. Schematics of (a) the original bi-probe and (b) after the modifications proposed by Jorcin [96] and (c) picture of the commercial bi-probe after the modifications.

The determination of spatial resolution in LEIS is not straightforward as it depends not only on the geometry and dimensions of the bi-probe but also on the potential distribution generated by the immersed sample. Newman [103] proposed a mode of estimating the resolution considering a disk shape working electrode:

$$R_s = \frac{1}{kr_0} \quad \text{Eq. 2.59}$$

where r_0 is the radius of the surface analyzed, R_s the Ohmic resistance measured at high frequencies and k the conductivity of the electrolyte. According to this equation, the studies performed in 1mM sodium chloride solution of $k \sim 2 \mu\text{Scm}^{-1}$ have a resolution of the order of 1mm^2 .

2.6 Scanning Electrochemical Microscopy (SECM)

The development of Scanning Electrochemical Microscopy (SECM) started in the early 1980's by the work of Dayton and Ewing [118, 119, 120] which proposed the application of carbon fibre stationary microelectrodes for *in vivo* electrochemistry. Other types of

microelectrodes, e.g. made of tungsten or having other geometries, were described in the literature by the same time [121, 122]. In a pioneer work, Bard et al [123] reported an experimental apparatus for studying substrates immersed in solution in which a microelectrode was mounted on a tripod with piezoelectric elements to move it into the desired position. Tunnelling and faradic currents were measured simultaneously while scanning the electrode over a conductive surface with lateral resolution in the micrometer range. Simultaneously, Engstrom et al [124] used carbon fibre and platinum microelectrodes to perform measurements within the diffusion layer of an immersed heterogeneous substrate. A scan in a plane parallel to the substrate surface was also performed and successfully detected active spots and their dimensions. In a later work, Engstrom et al [125] used the carbon fibre microelectrodes to perform high resolution concentration profiles in the vicinity of a macroelectrode. Chemical species produced at the macroelectrode were obtained with spatial resolution in the micrometer range and time resolution in the millisecond range.

The application of scanning microelectrodes to perform electrochemistry within the diffusion layer of a macroelectrode, was officially defined as the Scanning Electrochemical Microscopy (SECM) technique by Bard et al in a reference paper [126]:

“Scanning electrochemical microscopy (SECM) is a technique in which the current that flows through a very small electrode tip (generally an ultramicroelectrode with a tip diameter of 10 μm or less) near a conductive, semiconductive, or insulating substrate immersed in solution is used to characterize processes and structural features at the substrate as the tip is moved near the surface. The tip can be moved normal to the surface (the z direction) to probe the diffusion layer, or the tip can be scanned at constant z across the surface (the x and y directions). The tip and substrate are part of an electrochemical cell that usually also contains other (e.g., auxiliary and reference) electrodes. The device for carrying out such studies involves means of moving the tip with a resolution down to the $\text{\AA}$ region, for example, by means of piezoelectric elements or stepping motors driving differential springs, and is called a scanning electrochemical microscope. The abbreviation SECM is used interchangeably for both the technique or the instrument.”

SECM is therefore based on the electrochemistry of ultramicroelectrodes (UMEs), which are usually disks made of platinum, having a diameter ranging from 0.1 to 25 μm and embedded in an insulating sheath [127]. The UME current is Faradic and flows by redox processes occurring at the tip and/or at the substrate. The kinetics is controlled by the electron transfer rate at the solid-liquid interfaces and by the mass transfer in the bulk solution [126]. The current at the tip

is usually limited by diffusion because of the small area available for reaction [128]. The typical electrochemical cell requires at least one working electrode (WE), i.e. the tip, a reference electrode (RE) and a counter electrode (CE). All electrodes are connected to a potentiostat and immersed in the same solution such that the electrical circuit is closed [127]. It is possible to use two potentiostats and in this option a second working electrode, the sample under study is biased. The solution necessarily contains a redox species in a concentration c and diffusion coefficient D and an inert supporting electrolyte. When a voltage is applied to the tip, the redox species will be either reduced or oxidized at its surface, generating a current flow which is directly proportional to its concentration [126]:

$$I_{\text{lim}} = 4nFDca \quad \text{Eq. 2.60}$$

in which F is the Faraday constant ($F = 9.648 \times 10^4 \text{ C mol}^{-1}$ [129]), n is the number of electrons involved in the electrochemical reaction and a is the tip radius.

There are several methods and modes of operation of the SECM and some require specific instrumentation as a bi-potentiostat for the substrate-generation/tip-collection method or a feedback system for tip positioning in *constant-distance* imaging. The most commonly used SECM method is amperometry, due to its simplicity and possibility to extract both qualitative and analytical data from the experiments. The amperometric method itself can have various modes of operation, namely the *feedback mode* and the *shielding or competition mode*. Some examples of potentiometric methods will be provided in the applications section of this chapter.

Principles

The *feedback mode* was the first amperometric method to be described by Bard et al [126, 130] and is of particular interest because the substrate does not need to be biased, which is convenient to study freely corroding metals or insulating materials. A potential is applied to the tip for the oxidation or reduction of a redox species present in solution. The reaction occurring at the tip generates a current which depends on the nature of the substrate and the tip-to-substrate distance [126].

The redox species, usually termed the *mediator*, ideally undergoes a reversible one-electron transfer and both the oxidized and the reduced forms should be stable in the electrolyte. The most popular mediators used in aqueous electrolytes are presented in Table 2.1. The *mediator*

is chosen according to the substrate under study, pH and possible side reactions. Any of the presented mediators is suitable to study corroding iron. The oxidation of the mediator would occur with simultaneous reduction of ferric ion into ferrous ion, thus decreasing the feedback current.

Table 2.1. Commonly used redox mediators [128]

Mediator name	Redox half reaction	Standard Potential / V vs. SCE
Potassium ferrocyanide $K_4[Fe(CN)_6] \cdot 3H_2O$	$Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$	0.116
Ferrocenemethanol $C_{11}H_{12}FeO$	$FcMeOH/FcMeOH^+$	0.196
Hexaammineruthenium(III) chloride $Ru(NH_3)_6Cl_3$	$Ru(NH_3)_6^{2+}/Ru(NH_3)_6^{3+}$	0.636
Ferrous ion Fe^{2+}	Fe^{2+}/Fe^{3+}	0.826

Fick's laws provide the concentration variation of the redox species diffusing between a disk (the UME) and a plane (the substrate). From the relationship established in Eq. 2.60, the tip current (I_{lim}) can be predicted both in space and time. Considering the geometry of the system in cylindrical coordinates (r, ϕ, z) , the tip current changes along the coordinates in the directions radial (r) and normal (z) to the UME surface, whereas it is independent of the angle ϕ because of the symmetry of the tip [128]. Further, assuming the diffusion coefficient of the reduced and oxidized forms of the redox mediator are identical (D) and a steady-state ($\frac{\partial C}{\partial T} = 0$) is achieved in less than one second ($\sim \frac{a^2}{D}$) [128], Fick's second law is reduced to [128]:

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R} \frac{\partial C}{\partial R} \quad \text{Eq. 2.61}$$

where, the equation was reduced to dimensionless units using the following relationships $R = \frac{r}{a}$, $Z = \frac{z}{a}$, $C = \frac{c}{c_0}$ and $T = \frac{tD}{a^2}$. The solution to Eq. 2.61 requires solving two-dimensional differential equations, usually by numerical methods. Analytical approximations of the diffusion problem are available for relatively simple and well defined electrochemical systems, e.g. a disk UME approaching a flat, infinite substrate of uniform reactivity [130-134]. General expressions are provided for other tip geometries and various parameters, namely the tip current as a function of normalized distance between tip and substrate [135-139]. For more complicated geometries and processes, e.g. non-steady state conditions or liquid-liquid interfaces, generally analytical solutions are not available.

When operating in the *feedback mode*, a voltammogram is made with the tip placed in bulk solution containing the *mediator*, Figure 2.16. A potential corresponding to steady reduction or

oxidation of the redox species is then applied to the tip in order to obtain a constant current at the UME, that is, the limiting current (I_{lim}).

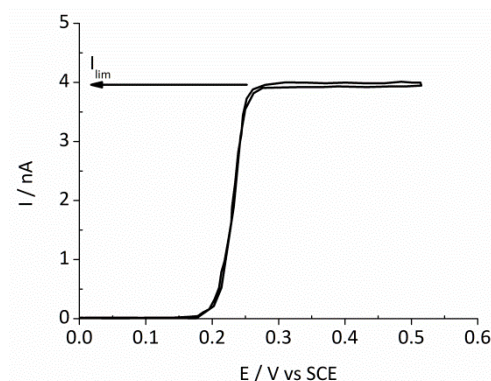


Figure 2.16. Ideal voltammogram for a SECM tip in bulk solution.

The *approach curve* is a plot of the tip current against the distance to the substrate and provides information about the nature of the substrate and the range of working distances for imaging. Theoretical *approach curves* derived from solutions of Eq. 2.61 are usually provided in a dimensionless form, i.e. representing a normalized tip current ($I = I_z / I_{lim}$) vs. a normalized tip-substrate distance ($L = Z/a$) [128]. Far away from the substrate surface, the diffusion layer is hemispherical as there is no restriction from closely placed surfaces and the solution for the diffusion equation is the tip current approximated by Eq. 2.60 [126]. The redox species is consumed at the tip reaction and is quickly renewed as it is widely available in the bulk solution. Because the tip surface is very small it is assumed the variation in the redox species bulk concentration is negligible.

When the tip is brought to the vicinity of any surface, the diffusion of the *mediator* to the UME is restricted and its concentration under the tip decreases as the access to bulk solution is limited by geometrical constriction. The tip current will be lower than I_{lim} , with decreasing values as the tip approaches the substrate and eventually reaching zero if it does touch the surface, Figure 2.17. This decrease in current while it approaches the substrate surface is called *negative feedback* [126]. However, the *approach curve* is different when the tip approaches a conductive surface. While the diffusion of the redox species to the platinum disk is blocked, the substrate may regenerate the species reacted at the tip increasing its concentration. As a consequence the tip current increases relatively to I_{lim} , while it approaches the substrate surface. This variation is called *positive feedback* [126], Figure 2.17.

A *positive feedback* current is obtained when the substrate is at a potential which is sufficiently anodic to regenerate the *mediator* [141]. The open circuit potential of a freely

corroding metal is not an equilibrium potential and thus may change during the time of the experiment. It is therefore important to know if the potential of the substrate is stable and keeps sufficiently anodic to regenerate the mediator.

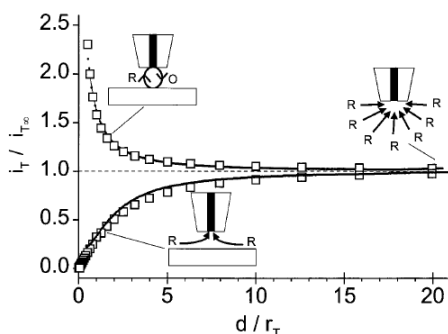


Figure 2.17. Normalized current as a function of normalized UME–substrate distance and schematic representation of the diffusion at the UME. Schematics from reference [140].

Imaging or mapping is performed by scanning the tip laterally over the substrate [142]. If the redox reaction at the substrate occurs under diffusion limited conditions, the rate of regeneration of the mediator is uniform along the substrate and the tip current reflects the conductive or insulating nature of the substrate. In this case, the *mass transport rate* is approximately the ratio of diffusion coefficient of the redox species and the distance between the tip and the surface ($m_0 \sim D/d$). As the tip-to-substrate distance influences the current, the presence of topographic features complicates interpretation of results. Further, if the mediator reaction at the substrate is not occurring under diffusion limited conditions, imaging would reflect different reaction rates of the mediator on the substrate surface. Regions having higher electron transfer rate will result in larger tip currents. The study of reaction rates requires that the substrate is biased to various potentials and then either imaging or *approach curves* to various points of the surface are performed and fitted to numerical models in order to extract the kinetic parameters [128].

A conductive substrate can in some cases reveal *positive feedback* or *negative feedback*; the first case occurs when the electron transfer rate at the substrate is diffusion-limited or at least is very high and the latter occurs if the electron transfer rate is finite and small. Diffusion limitation at the tip occurs in most of the experiments as a consequence of the substrate having an infinite area when compared to that of the UME [128]. When conducting experiments on unbiased substrates, it is necessary to take into account that the relative concentrations of the oxidized and reduced form of the mediator influence the substrate potential. Under the tip, the concentration of the oxidized/reduced form will be higher than in the remaining surface, thus a

concentration cell will be established. In most cases, the substrate surface is infinite when compared to the tip surface and electrons will then flow from the large surface of the substrate to the small portion under the tip. If the electron transfer rate at the solid-liquid interface is fast, the limiting step for mediator regeneration will be mass transport and the reaction will be diffusion limited with positive feedback response. In some cases, the electron transfer rate at the solid-liquid interface may be so slow that even if there is good electron supply to the region under the tip, the surface may behave as insulating and result in *negative feedback* [141].

The feedback mode can also be used to determine heterogeneous electron transfer rates at substrates that consist of conductive regions embedded in an insulating matrix and vice versa, as long as the surface is flat [143]. However, performing a kinetic study on a substrate which is electrochemically heterogeneous and has topographic features is very complicated as in a *constant-height* experiment; the current may be a convolution of surface reactions and topography of the substrate. A *constant-distance* experiment ensures the probe to substrate distance is the same throughout the scan and the tip current results only from the electrochemical response of the interface. Although there are different technologies for operating in *constant-distance*, there are a number of problems associated with this kind of experiment, namely tip crashing with the sample when it has both conductive and insulating regions [144-147]. Therefore, in practice, this type of experiment is not commonly used [140].

An alternative operating mode, which does not require biasing the substrate, is the *shielding or competitive mode*. In this mode, the same redox reaction occurs both at the tip and at the substrate, e.g. the oxygen reduction reaction. A scan over the substrate can identify regions where the reaction occurs; typically the tip is much smaller than the substrate and therefore the current will decrease over regions where the redox species is being consumed (depleted) while it is constant over inactive regions [128, 148]. In the *competitive mode*, the substrate potential must be cathodic enough to deplete the mediator (e.g. oxygen). Under these conditions, the tip current is zero as the redox mediator is being consumed under limited diffusion conditions both at the tip and at the substrate [149].

Amperometric tips

The tip size and geometry strongly determine the resolution of the technique [126]. It determines the working-distance, i.e. the distance between the tip and the substrate in a vertical plane; the step-size; the geometrical or lateral resolution and the acquisition-time. The smaller the tip is, the smaller will be the working-distance and step-size necessary to obtain adequate resolution. Consequently, the geometrical resolution will be improved while sacrificing the acquisition-time. On the other hand, the size of the tip should be chosen considering the area of the substrate to scan, its roughness and the scale of the corrosion process itself. Further, the current distribution also has a role concerning the resolution of the technique [126].

The amperometric tips, consist of metal wires embedded in glass and having a disk-shaped reactive surface, Figure 2.18. With the adequate equipment and some practice it is relatively easy to produce tips. A high purity metal or alloy as platinum, platinum-iridium, gold, silver and even stainless steel, with diameters typically ranging from 1 to 25 μm , is inserted in a borosilicate glass capillary and is sealed at one end. Sealing is performed by heating the capillary with a proper heating coil and stretching it to form a needle like shape while the glass melts around the metal wire and is often carried out using a pipette puller. The capillary is then carefully cut just below the tip. After inspection under the microscope confirms there are no air bubbles around the wire, the tip is polished until the cross section of the wire is exposed. A copper wire is inserted through the open side of the capillary along with silver paint to make electrical connection to the thin noble metal working as an UME. Commercial tips are prepared in a more careful way, for example using vacuum to remove impurities or moist from inside the glass capillary and polishing the tips with automated machines sharpening the glass to an almost perfect conical shape and reducing the RG ratio between radius of the glass sheath r_g and of the platinum disk- a - to values below 10 [128]. The small RG ratio ensures that the glass does not crash into the substrate if the tip is tilted relatively to the substrate avoiding damage to the tip and the substrate itself.

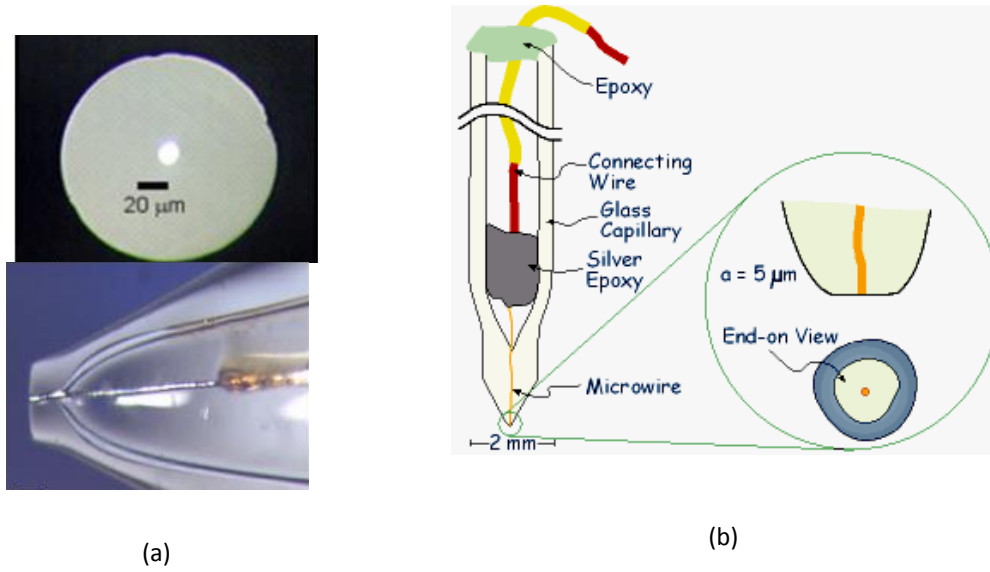


Figure 2.18. Cross section and lateral view of a commercial SECM tip: (a) optical photographs [150] and (b) schematic representation with construction details [128].

Bard et al [130] offer a method for verifying tip calibration, i.e. to check if the tip has the ideal disk geometry and hasn't turned hemispherical due to repetitive polishing. The method consists in fitting the experimental *approach curve* to an expression determined from numerical methods (having an associated error of 2%) [130]:

$$I(L) = \frac{I_{\text{tip}}}{I_{\text{lim}}} = \frac{\pi a}{4d} + 0.901 + 0.099 \exp\left(-0.16 \frac{a}{d}\right) - 0.29 \exp\left(-0.39 \frac{d}{a}\right) \quad \text{Eq. 2.62}$$

where a is the tip radius and I_{tip} the tip current at a distance d from the substrate and the normalized current values ($I_{\text{tip}}/I_{\text{lim}}$) as a function of dimensionless working distance ($L=d/a$), are tabulated for $RG = 10, 100$ and 1000 . The current is essentially independent of RG for a conductive substrate; however this is not true for an insulating substrate. The RG ratio actually influences the *approach-curve* to an insulating surface according to Eq. 2.63, which is valid for $RG < 3$ [130].

$$I(L) = \frac{\frac{2.08}{RG^{0.358}} \left(L - \frac{0.145}{RG} \right) + 1.585}{\frac{2.08}{RG^{0.358}} (L + 0.0023RG) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG} \ln \left(1 + \frac{\pi RG}{2L} \right)} \quad \text{Eq. 2.63}$$

There are simpler expressions for conductive (Eq. 2.64) and insulating substrates (Eq. 2.65) valid to RG values between 1.1 and 10 and $0.04 < L < 10$, with an associated error of just 1% [128, 140]

$$I(L) = A + \frac{B}{L} + C \exp(D/L) \quad \text{Eq. 2.64}$$

$$I(L) = \frac{1}{A + \frac{B}{L} + C \exp(D/L)} + \frac{E \times L}{F + L} \quad \text{Eq. 2.65}$$

where, the values for A, B, C, D, E, F and L are tabulated and can be consulted in reference [128].

Amphlet et al [140, 151] determined that the RG ratio influences the currents even in the case of *positive feedback* and propose their own analytical expressions to describe *approach curves* in the case of *positive* (Eq. 2.66) and *negative feedback* (Eq. 2.67), valid for $L \geq 0.2$ and $2 < RG < 10$. Notice that Eq. 2.66 is equivalent to Eq. 2.64.

$$I(L) = k_1 + \frac{k_2}{L} + k_3 \exp\left(\frac{k_4}{L}\right) \quad \text{Eq. 2. 66}$$

$$I(L) = \frac{1}{\left[k_1 + \frac{k_2}{L} + k_3 \exp\left(\frac{k_4}{L}\right)\right]} \quad \text{Eq. 2.67}$$

where I_{tip} is the tip current at a distance d from the substrate, I_{lim} is the tip current in bulk solution and the constants k_i depend on the RG ratio and are tabulated in reference [151].

It is possible to produce UME with diameters below 1 μm , although they are hard to fabricate and characterize [152]. Often it requires that the commercial wires are sharpened by chemical etching and then coated by some insulating polymer instead of sealing them inside a glass capillary. Small UME's are desirable because they lead to improved resolution [126], the drawback is that their application is limited to small scanning areas and highly flat surfaces since the best resolution is obtained when the tip-to-substrate separation is a tip diameter or less [153]. The original tips provided by Uniscan Instruments [154] had a large RG ($RG = 50$), making it difficult to identify the position of the surface from the approach curves and they easily crashed on the surface. It was thus decided to use tips from Sensolytics [155] with RG of 20, Figure 2.19.



Figure 2.19. Optical photographs of the UME's tip from Uniscan and Sensolytics.

Instrumentation

The basic elements of any SECM are schematized on Figure 2.20 where the positioning system and the potentiostat are the main components. The positioning system allows the tip to be moved along three orthogonal axes. Usually z is the direction normal to the substrate surface and xy is the plane parallel to it. The positioning arms make use of inchworm motors which have piezoelectric actuators to move the tip in a smooth manner with nanometric precision and with minimum hysteresis [142]. The working distance should be around two to four tip radius for best resolution and because any hysteresis of the positioning system could cause the tip to crash on the substrate. Some equipments have the z -motor connected to a feedback system, allowing the distance of the tip-to-substrate to be automatically adjusted to the substrate topography, although this option was not available in the system used. The data acquisition system includes the bipotentiostat, which controls the tip and eventually the substrate potential, an amplifier for the tip current and a computer. Specific software is used to control the positioning system, acquire and display data. The substrate holder is usually fixed to a vibration isolation table and has a levelling system to avoid any tilting of the surface.

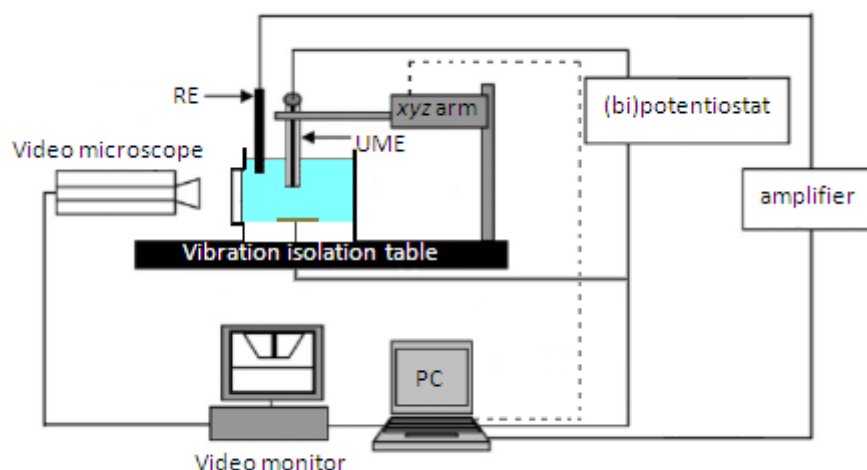


Figure 2.20. Schematic representation of instrumentation needed for SECM, adapted from reference [150].

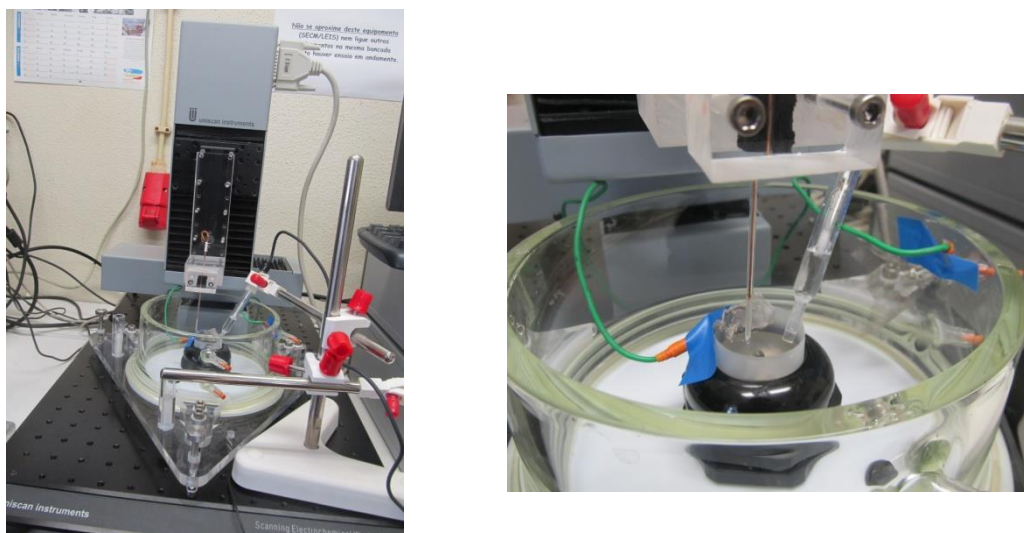
A commercial scanning electrochemical microscope, model SECM370 (Uniscan Instruments) [110] was used to perform the work presented in the current dissertation, Figure 2.21. This equipment was projected to be an all-in-one solution allowing several scanning electrochemical techniques to operate in a single expandable platform. For example, to change from the SECM technique to the LEIS it is only necessary to replace the tip and tip holder, re-connect the electrodes to the respective potentiostat and select the adequate data acquisition software. In theory, it's possible to perform analysis by different techniques on the same substrate without moving it or the electrolyte. For practical purposes, quite often it is relevant to observe processes occurring shortly after immersion and therefore it is desirable to expose fresh substrates. The Uniscan instrument, includes the electrochemical cell (TriCell [113]), the tip holder, the positioning system, an optical table and a bipotentiostat/galvanostat. The tip holder is directly mounted to the z-stage, while the electrochemical cell is stationary, Figure 2.22. The commercial holder was found to be inadequate as the tip oscillated during the scan; a new holder produced from acrylic plates was developed within the scope of this research producing much better results, Figure 2.22.



Figure 2.21. Picture of Uniscan M370 Electrochemical Workstation: (1) bi-potentiostat PG580R, (2) electronic rack (electronics control unit), (3) xyz scanning head, (4) original tip holder, (5) optical table with anti-vibration system and (6) video microscope.

The bipotentiostat/galvanostat allows voltammetric measurements with tip and substrate potentials up to ± 2 V and a compliance voltage (the voltage applied to the CE) of ± 8 V. The current sensitivity is sub-pico (61 fA) and has a range of 8 decades (1 nA to 10 mA/V). The M370 software runs on Windows and provides all the controls necessary to position the probe and moving it according to a determined step-increment and speed between steps, select the electrochemical experiment (voltammetry, approach curve, linear scan, map...), the experimental parameters and visualize the data in real-time. It also allows creating an automatic sequence of experiments with the tip placed at a constant height.

The TriCell, Figure 2.22 a, is made of glass and has four inlet/outlet purge ports, allowing liquid flow and eventually temperature control of experiments. It can accommodate substrates having a rod-like geometry, plate or any other geometry as long as it can be embedded or glued to a cylinder of 24 mm diameter. It also allows the use of counter electrodes and reference electrodes of standard size. The cell capacity is around 700 mL. For the experiments here presented, the electrolyte volume was reduced by forming a reservoir with adhesive tape rolled around the epoxy disk, Figure 2.22 b.



(a) (b)
Figure 2.22. Picture from the TriCell (a) mounted on the M370 workstation with the adapted tip holder and (b) detail of the adhesive type reservoir.

Other applications

SECM has been successfully used since its early beginning for microfabrication, i.e. etching and deposition [156]. Bard et al [157] described a method that could be used for microdevice fabrication by etching copper using the SECM. The method described requires the SECM to be operated in the feedback mode using a redox mediator, such as phenanthroline or bipyridyl, in a buffered solution. Copper oxidation occurs by reduction of the mediator without the production of hydrogen bubbles at the tip. The width and depth of the dissolved region can be adjusted by varying UME diameter and operating distance; when the tip is placed at a distance of the substrate which is smaller than its diameter, than the dissolved area corresponds to the tip diameter. Other groups have successfully employed the SECM for microfabrication, and surface patterning of metals and polymers as Borgwarth et al [158] and Schuhmann et al [159, 160].

The application of the SECM to the study of biological substrates was presented in the early years of the development of the technique in a series of works from Bard et al dealing with the measurement of topography and photosynthesis of leafs [161] and enzyme reactions [162-164]. More recently, the application of SECM has expanded to areas such as energy [165-167] and many reports on its application in the biology field can be found [150, 168-176].

Scanning electrochemical microscopy is even proposed as a cancer diagnostic tool in the work of Rapino et al [177]. The working principal is related to glutathione (GSH), which is a protein taking part in several cell reactions. Under specific conditions, GSH can be oxidized to glutathione disulfide (GSSG). The redox balance of GSH/GSSG ratio has been found to be altered in cancerigenous lung cells and can be measured by means of SECM. The tip is used to monitor the interaction of an exogenously added redox species (ferrocenemethanol - FcMeOH) with the living cells. Oxidised ferrocenemethanol, *i.e.* FcMeOH^+ , is generated at the microelectrode, diffuses to the living cell, oxidizing GSH while it is reduced back to FcMeOH, causing an increase of the faradic current recorded at the UME. Tumour cells were found to regenerate FcMeOH (*i.e.*, promote electrochemical reduction of FcMeOH^+) more efficiently than normal ones. As the topography contributes in the same extend to both cell types, the differences in the absolute feedback currents measured between transformed and normal cells using FcMeOH, are caused by their different abilities to regenerate the mediator.

Hybrid scanning electrochemical techniques

AFM-SECM

A current trend has been the combination of atomic force microscopy (AFM) with SECM. By integrating a conducting electrode into the AFM probe design, it is possible to obtain both electrochemical and topographical information with spatial resolution in the micrometer range [178, 179]. Various approaches to fabricating SECM–AFM probes have been carried out. The first consists on coating a flattened microwire with an electrophoretic paint and then etching it. The flattened section provides a flexible cantilever (AFM sensor), whereas the etched tip works as an SECM probe. Figure 2.23 a, depicts an SECM–AFM probe which has been fabricated in this way [150].

A second method for the combined use of AFM-SECM employs a conventional AFM probe as a template. Electrochemical capability is built by bottom-up approach by sputtering or evaporating a thin metal film as platinum or gold [150, 180, 181] onto the AFM probe. The body of the probe is insulated, leaving the exposed cantilever as the electrode (typical length 100 – 200 μm , width 20 – 40 μm) [150]. A development of the previous method consists of insulating the entire probe, then shaping and remodelling the original AFM tip using a focused ion beam (FIB), Figure 2.23 b [150, 181, 182]. Ultrahigh-resolution imaging probes have been developed

by attachment of carbon nanotubes to the tip of a metal-coated AFM tip and using these as a template for the deposition of a metal nanowire. The whole probe is insulated and the end of the nanowire is cut by FIB. The resulting electrode, Figure 2.23 c, has well defined disk geometry with typical diameters between 50 and 100 nm [150].

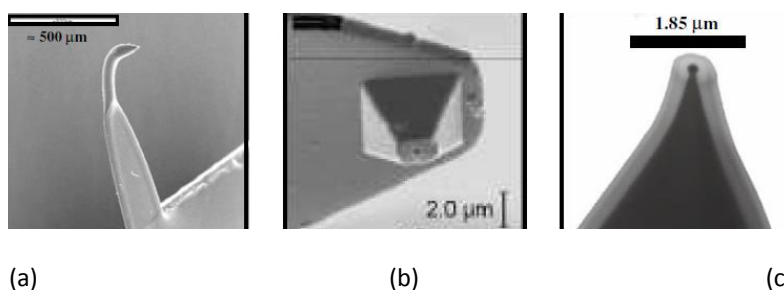


Figure 2.23. Scanning electron micrographs of (a) a typical hand-fabricated SECM-AFM probe, (b) an integrated frame microelectrode and (c) the tip of a nanowire SECM-AFM probe [150].

There are quite a few publications on development of AFM-SECM tips and more fundamental studies including a quantitative description of approach curves for conical AFM-SECM tips [183] and the study of transient effects and advective transport of species [184]. However, the application of this hybrid technique to corrosion science is limited because the topography of the surface changes either due to dissolution of metals or precipitation of corrosion products [185, 186, 187]. Further, the topographical capabilities of the probes are below those of commercial AFM tips.

Alternating current SECM

The alternating current SECM (AC-SECM) was developed to solve the need to obtain deconvoluted images of topography and electrochemical contrast of the substrate in a *constant-distance* rather than in a *constant-height* method. Application of an alternating potential was just a tool to position the tip in the absence of mediator or in a potentiometric experiment [153, 188]. Schuhmann et al [189] and Eitenne et al [190] were the first to actually apply it as a *mediator-free mode* for imaging local variations in surface conductivity for simple systems. In subsequent works, Eckhard et al [191] applied the AC-SECM to image active pits on iron, Diakowski et al [192] and Morkvenaite-Vilkonciene et al [193] to the mapping of topography of living cells and changes of solution composition in the vicinity of the cell, Souto et al to the study of corrosion inhibitor films applied on metals [194] and Jamali et al [195] to mapping of conductive regions of AZ31 magnesium alloy immersed on simulated body fluid solution (SBF).

In this mode of operation, a small amplitude sinusoidal waveform potential is applied to the tip. Similarly to conventional impedance spectroscopy, a lock-in amplifier is used to determine both the magnitude and the phase of the output signal (the tip current) with respect to the applied potential. However, this technique is different from local impedance spectroscopy (LEIS) because the substrate remains unconnected or maintained at a constant potential and producing a dc-current only if it consists of an active sample. The main advantage is that the system operates with the same UME as for conventional SECM and it does not require a redox mediator [196]. Further, it can be used in electrolytes with very high resistivity.

In the case of insulating substrates, the current flows between the tip and the CE and a simple equivalent electrical circuit consisting of the solution resistance (R_s) in series with the tip impedance (C_T), can be used to determine the tip impedance [147]:

$$|Z_T| = \sqrt{|R_s(L)|^2 + (1/j\omega C_T)^2} \quad \text{Eq. 2.68}$$

Since the impedance is inversely proportional to the frequency for a capacitor, the tip current increases with rising perturbation frequency. Beyond a characteristic threshold frequency, the capacitor should no longer contribute to the overall cell impedance and the tip current depends only on the solution resistance. The resistance depends on its turn on the volume of solution between the tip and the substrate. As the tip approaches an insulator, the solution resistance increases because the surface partially blocks some of the pathways for ions to travel between the tip and the CE and therefore it can be used to image topographic features. An analogy between the normalized tip current $I(L)$ and the variation of the resistance (R) with the tip-to-substrate separation (L) is established [188]:

$$I(L) \sim \frac{R_\infty}{R_s(L)} \quad \text{Eq. 2.69}$$

The current magnitude is thus inversely proportional to the solution resistance (R_s) and similarly to the *feedback mode*, electrical insulating samples lead to a “*negative feedback*” because the current decreases with distance [147, 188].

Conductive samples can show *positive* or *negative, feedback* depending on the perturbation frequency as demonstrated by Diakowky et al [197]. In the presence of a conductive substrate, the current can alternatively flow through the conductive solid and the equivalent electrical circuit becomes more complicated; the capacitance of the tip will be in

series with the solution resistance $R_s(d)$ and the substrate impedance. For high frequencies, the current flows from the tip to the substrate resulting in *positive feedback*. In this situation the predominant contribution to the overall cell impedance is the impedance of the substrate and therefore high frequency measurements should be less sensitive to changes in the topography but more sensitive to electrochemical properties. The sum of R_s and the charge transfer resistance at the substrate interface do not show a linear relationship with distance. For low enough frequencies, a small current is produced by the tip which will flow preferably through the solution towards the CE, resulting in *negative feedback* [197].

An experiment with the AC-SECM is time consuming as it usually requires recording full-frequency spectra in a grid of points over a substrate to determine the threshold frequency at which a conductive substrate starts exhibiting positive feedback [198]. This behaviour is not linear as it depends on the nature of the substrate; further, the presence of Faradic reactions complicates the interpretation of AC-SECM [196].

Potentiometric SECM

The potentiometric method is sometimes called scanning ion-selective electrode technique (SIET) because it makes use of ion-selective microelectrodes. The response of these electrodes is Nernstian, i.e. the potential is sensitive to a particular ion concentration, or more accurately, its chemical activity. For this operating method, it is necessary that the electrochemical reactions occur under steady conditions and that the concentration gradient does not change during a scan [199]. Thus, one disadvantage is that the scan rates must be very slow in order not to disturb the concentration gradient [200]. In the amperometric mode, this is not an issue because the diffusion layer is confined to the small volume under the tip, whereas in the potentiometric mode, the diffusion layer is created by the macroelectrode and the tip works as a passive probe [201]. Other issue of the potentiometric probes is their positioning relatively to the substrate surface. Because they are passive probes, their signal cannot be used to measure the tip-to-substrate distance which then has to be carried out with a video microscope. The potentiometric mode is usually used in combination with other methods that are able to provide information regarding the distance of the tip to the substrate.

Potentiometric tips may consist of capillaries filled with ion-exchange membranes [202, 203], which are commercially available or solid electrodes [201, 204, 205]. Glass capillary tips

are very sensitive and fragile and get often damaged during the experiment; iridium-oxide solid electrodes are more robust but are also larger and produce stirring of solution, therefore are used mostly for point measurements rather than for scanning large areas [128].

Probably one of the first papers reporting the use of SECM with a potentiometric tip is the work from Denuault et al [199]. The microelectrodes consisted of (HCl) anodized silver wires, sheathed in glass capillaries. The potentiometric tips measured successfully at discrete points, a flux of silver anions producing during deposition and stripping of a silver macroelectrode and the flux of chloride ions permeating through a polyaniline film. In a later work, Bard et al [201] presented a pH sensitive antimony-filled capillary electrode and the theory associated with the potentiometric mode. The pH profiles in the vicinity of platinum, silver iodine and enzyme substrates were successfully measured with micrometric resolution using these electrodes. One disadvantage of the antimony electrode relatively to the Ag/AgCl is that it is sensitive to the presence of redox couples in solution, namely O_2/OH^- . This property actually allows the tip to be operated in the amperometric mode for tip positioning and then switched to potentiometric mode for ion sensitivity. A steady current is obtained for the electrode in bulk solution, corresponding to oxygen reduction, whereas a negative feedback is obtained during an approach curve, allowing the tip-to-substrate distance to be determined [201]. In another work, Bard et al [206] offered a different approach to solve the positioning problem associated with potentiometric tips. A double barrel capillary with Ag/AgCl electrodes placed on each channel of the capillary is used, in which one is filled with a reference solution and the other with an ion selective membrane. The distance is determined using the side filled with a reference solution, taking into account the distance dependence of the solution resistance rather than the blocking of the oxygen reduction reaction.

Currently, the most employed setup consists in coupling the glass capillary ion selective microelectrode with the scanning vibrating electrode technique (SVET), that measures ionic currents [128, 207, 208, 209].

2.7 Complementary techniques

Scanning Vibrating Electrode Technique (SVET) ^{109,210}

The technique known today as Scanning Vibrating Electrode Technique (SVET) found its first application in the study of biological tissue. Isaacs, the same scientist who developed the LEIS, introduced the SVET to the study of corrosion during the 1980's [211, 212].

The SVET uses a vibrating probe to measure the potential difference between the two points between which it vibrates. The probe is usually a sphere shaped ultramicroelectrode made of platinum having 20 μm diameter. The vibration amplitude is around 30 μm and is sufficiently small not to strongly perturb the concentration gradients in solution. In the SVET the sample is left to corrode freely and unlike in the LEIS and the SECM, it is not connected to a potentiostat and there is no counter electrode. The immersed sample is therefore a closed system and in the case it is inert or inactive, the probe will only detect electrical noise. If the sample is active, the electric charge produced by ions arising or being consumed at the surface will cause a concentration gradient generating an electrical field in the solution which can be measured by the probe. Oxidation of a metal at the anodic sites produces cations which diffuse towards the bulk of the solution and thus generate positive current density values. In the cathodic regions, either the generation of hydroxyl ions (in alkaline medium) or the consumption of protons (in acidic medium) leads to a downward flow of anions and to the occurrence of negative current densities in the electrolyte. Accurately all charged species in solution produce a current flow but the species involved in the redox reactions are responsible for the largest part of the response in the vicinity of the sample. The vibration of the tip in this potential field generates an ac signal with the same frequency as the vibration of the probe [213]. In this way, frequencies different from this vibration are filtered by a lock-in amplifier reducing the background noise and allowing very small currents to be detected. The vibration of the probe is usually produced in different directions and can have different amplitudes thus allowing various information to be extracted. The direction of the vectorial sum of the current density vectors normal and parallel to the surface indicate the ionic flow direction. Usually, only the vertical component of vibration is presented as it provides the best correlation with the position of anodes (current sources) and cathodes (current sinks).

The microelectrode electrical potential recorded at the extremes of the vibration amplitude (V_0), results in the generation of a sine wave potential signal ($V(t)$) with the same frequency (ω) than the vibration [214]:

$$V(t) = V_0 + d\sin(\omega t) \quad \text{Eq. 2.70}$$

where d is the average distance between the electrode and the sample. The potential can be related with the ionic currents $-I(t)$ - by use of Ohm's law [213]:

$$i(t) = \kappa V(t) \approx -\kappa \frac{\Delta V}{d} \quad \text{Eq. 2.71}$$

where κ is the conductivity of the solution. A map of current distribution can be obtained making a grid of points in a plane parallel or perpendicular to the surface of the sample and recording at each point $V(t)$.

The SVET measures the ionic currents in solution at a distance between 50 to 200 μm from the sample surface. These currents do not correspond to the currents measured at the very surface of the electrode; the correlation between these two currents can only be established in very specific situations, namely when the current source is a single point [109]:

$$I = 2\pi r^2 i_{SVET} \quad \text{Eq. 2.72}$$

where, I is the absolute current measured at the surface of the active spot and i_{SVET} is the current density measured by the probe at distance r from the sample. It is admitted the probe has sphere geometry.

In principle, the sum of the currents for all positive source and all negative sink points should cancel and the ratio between the total current and the area of the sample should provide the overall current density of the sample. This would be interesting as it would allow the corrosion rate obtained with the SVET to be compared with other techniques as EIS or potentiodynamic polarization. In practice, this is impossible because the probe only senses the current along a certain plane parallel to the surface and in the vertical direction. Further, current densities lower than $\sim 1 \mu\text{Acm}^{-2}$ cannot be detected by the technique. Similarly to other ultramicroelectrode techniques, the currents provided by the SVET are always underestimated making it a semi-quantitative technique. It is a good technique to visualize corrosion but kinetic studies are only qualitative and valid when comparing similar samples [109].

Instrumentation ^{109, 215}

A scheme of the experimental apparatus necessary to perform SVET experiments is shown in Figure 2.24. The SVET equipment used for the experiments described in this dissertation was manufactured by Applicable Electronics Inc. [215]. The main elements include

the electrochemical cell, the piezo-oscillators which produces the vibration of the probe in xx and yy planes, two lock-in amplifiers that measure and filter the signal produced in the probe in each plane and the 3D motors to control the movement and the positioning of the vibrating probe with micrometric precision. A high-resolution CCD camera is placed on top of the sample allowing both the positioning of the probe at an exact distance from the surface and recording of *in-situ* images. Quite often, the SVET shows activity well before any degradation signs become visible on the surface of the sample. The entire system is controlled by a computer equipped with ASET software from ScienceWares [216]. The data is plotted as current density maps with QuikGrid [217]. The electrochemical cell consists of the vibrating microelectrodes and the pseudo-reference electrode. The vibrating probe is a platinum wire having 250 μm diameter and 1.5 cm length, covered by an insulating polymer except for 3 μm of its sharpened extremity which is left exposed. A platinum black sphere is electrodeposited at this extremity using hexachloroplatinic acid. The potential is measured between the vibrating probe and the pseudo-reference electrode which is also a platinum wire with a platinum-black deposit. A second platinum wire is used to ground the electronics of the SVET pre-amplifiers.

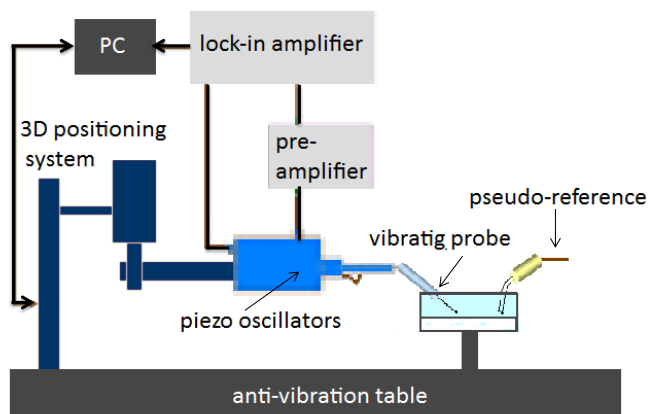


Figure 2.24. Schematics of instrumental apparatus of SVET. Adapted from [214].

Previously to conducting any experiments, the probe must be calibrated. The vibrating probe is placed at a distance r from a point source electrode with a known current I and detects the potential difference (ΔV) is measured. The current density generated by this potential difference is then compared with the one from Eq. 2.55 and a proportionality factor is determined. This factor depends on the conductivity of the solution, the amplification of the system and the amplitude and frequency of vibration of the probe.

Measurements made very close to the surface might seem interesting since are more likely to locally resolve phenomena. Despite the achieved great sensitivity, the used vibration can obviously interfere in the measurement by stirring the solution.

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3. EIS and SVET assessment of corrosion resistance of thin Zn-55% Al-rich primers: Effect of immersion and of controlled deformation

This chapter is focused towards the characterization of primers containing Zn-Al particles. It is a research paper with the same title published in *Electrochimica Acta* Vol. 148 (2014) 153-163. SVET experiments were performed by M. Taryba and SEM micrographs were taken by I. Nogueira. Experimental data, including SVET ones, were treated and interpreted by the author of this dissertation.

Abstract

The effect of biaxial strain on the electrochemical behaviour of a thin weldable primer containing zinc aluminium particles applied to galvanized steel was studied by assessing both the integral behaviour of the system and the micro-currents on the heterogeneous surface. The ionic currents near the surface were measured by the SVET and revealed to be sensitive to the shape and lifetime of micro-active areas of the coating. The EIS data on intact coatings revealed that immersion time caused a drop of the low frequency resistance while the capacitive slope remained constant; on elongated samples, a similar trend in low frequency was observed along with an increase of the capacitance. A model is proposed, based upon an electrical equivalent electric circuit that includes distinct elements mimicking the electrochemical behaviour of the exposed and embedded metal particles and for the polymer phase.

Keywords: corrosion; SVET; weldable primer; electrochemical impedance spectroscopy

3.1 Introduction

In the past twenty years automotive manufacturers, have definitely moved from plain steel to galvanized steel as the main material for car bodies. Zinc protects steel from corrosion by sacrificial anodic dissolution but also by the formation of a stable layer of zinc corrosion products that causes moderate inhibition of the cathodic reaction. Zinc-rich primers (ZRPs) are also based upon this principle. One more recent application of zinc additives to organic coatings concerns weldable primers. Weldable primers are organic coatings that are applied to metal substrates to protect them from early corrosion but which are due to allow subsequent spot-

welding and cathophoretic painting [1, 2]. Unlike the classical ZRPs, the main role of the zinc-aluminium particles is the conduction across the coating for weldability enhancement without compromising the life of the welding electrodes [2-7]. Conductive particles are added to the formulation with much lower content when compared to the ZRPs [8-15]. Industrially, the coated sheet composed of the steel substrate with the zinc layer and the weldable primer is cut, formed and finally spot-welded to the other body parts. During this process, forming operations are a major issue regarding the performance of the coating and ultimately the durability of the vehicle, due to the risk of formation of micro-cracks that later may act as preferential sites for corrosion initiation [16]. The correlation between deformation and corrosion performance is thus a matter of relevance for automotive manufacturers as the barrier properties can be significantly affected [17]. Electrochemical Impedance Spectroscopy (EIS) is probably the fastest method for assessing the corrosion resistance of painted metals, as it allows ranking of different coating systems in just a few days or even hours, while accelerated and field-exposure tests may require months or even years to be completed. Modelling of organic barrier coatings is usually made using the classical equivalent circuit proposed by Haruyama [18], which associates the coating properties with a high frequency capacitive loop, while delamination is revealed by the development of a second relaxation constant at lower frequencies [5]. Haruyama's model has been applied to painted systems with barrier coatings under increasing elongation [19–21] and it was concluded that the impedance decreased with the penetration of water and of ions from the outer medium and also with the loss of barrier properties. Water absorption models have been proposed by Brasher [22] and also by other authors [23, 24], including our own research group [25]. These models use either the variations of the coating capacitance associated with a growth of the dielectric constant, or the frequency distribution of the pseudo-capacitance, described as a constant-phase element [26]. In formed samples the corrosion process starts earlier and occurs at a higher rate, but also the capacitance of the coating tends to increase with strain [16, 27]. In a systematic study using different kinds of strain, an improved correlation with the low frequency impedance in a barrier coating has been obtained when the equivalent strain was used [19]. Further, the use of cells that allowed the measurement at small areas along the surface, has allowed computing of the overall impedance response based upon local results and partial equivalent electrical circuits [28]. EIS studies on coatings containing zinc and/or carbon particles have been reported by some authors. According to Abreu et al. [29], Touzain et al. [30] and Vilche et al. [11], the classical Randles-type circuit cannot adequately describe metal-rich primers, as it does not explain the formation of a third capacitive loop after long exposure times. Modelling using a transmission line has been applied, considering the contact impedance between several zinc particles embedded in a porous polymer matrix. In the case of two

capacitive loops, the contact impedance is measured at high frequencies while the low frequency response is attributed to a Warburg-type diffusion process related to growing of corrosion products inside-out the porous coating [9, 29, 31]. A third time constant is due to the corrosion process at the surface of the embedded particles. For a low porosity coating containing zinc particles, Meroufel [32] observed initially a single capacitive loop and proposed a model consisting of two mixed time constants corresponding to binder properties and the contact impedance, whereas a second loop, corresponding to the Faradic response of the embedded particles became visible only after several days of immersion [30]. Simple circuits, with two or three time constants, including or not Warburg diffusion, were used by Klüppel et al. [17] and Bastos et al. [2], who studied zinc-rich weldable primers comparable to our own system. In a recent work, Gergely [33] proposed also this kind of equivalent circuits for primers with zinc and carbon nanotubes, but only after long immersion times, suggesting that conduction across the particles becomes significant after absorption of electrolyte and consequent wetting of the particles. Akbarinezhad [34] studied a primer containing polyaniline-graphite nanocomposite and zinc. A circuit with two RC networks is proposed to fit data but an evident oxygen diffusion process at low frequencies is not clearly explained. Further to the effect of water and ions, are the mechanical stresses that affect coated systems at various levels [30–37]. They may cause cracking of the zinc layer, leading to galvanic coupling between zinc and the steel substrate, causing early failure of the system [38]; they may promote loss of adhesion either between the polymer and the substrate or at the interface between the polymer and the pigments, leading to weak sites where delamination starts from [39]. Modifications of weldable primers with the aim of improving the adherence between particles and polymer have been tried in recent years. Park et al. [40] claim that zinc particles modified with phosphoric and phosphonic acids increased the durability of polyester coatings. Other recent trends on zinc-rich paints technology include adding zinc or aluminium nano-particles [41–48] polypyrrole and polyaniline [48], ionic liquids [49] and carbon black [50] to the formulation. Compared to pure zinc, some zinc alloys are known to provide additional corrosion resistance and are therefore interesting alternatives to zinc-containing primers. In particular, the Zn-55%Al alloy benefits from the passive behaviour of aluminium and thus increases the stability of the material [47]. Most of the models proposed for conductive primers consider particles of small size, typically less than half of the coating thickness. In our system, however, the particles are quite large, in some cases exceeding the average thickness of the primer, and are partially exposed to the solution. Under these conditions, and given the content of metal in the coating, a residual electronic conduction across the metal particles can be expected, in parallel with the ionic conduction across the binder, which means that the models described in the literature do not adequately account for the

properties of the system. Further, the effects of mechanical deformation are not considered in most models, although there are a number of significant effects at several levels, namely the interfaces between metal particles/binder or binder/substrate. Our study deals with both the effect of water absorption and that of plastic deformation and is based mostly on EIS characterization and modelling.

3.2 Experimental

3.2.1 Materials

The substrate consisted of DC06 steel with 0.8 mm thickness, electrogalvanized with a nominal zinc thickness of 7.5 mm on each side. Cleaning was made using an alkaline bath, rinsing with deionised water and treating with Granodine 1456 (Henkel, Düsseldorf, Germany), which is a technical pre-treatment that imparts a thin conversion layer (< 20 nm) of Ti, Zr and Mn salts in a complexing pre-polymer. The metal-rich primer consisted of an epoxy matrix resulting from the reaction of 2-(2-butoxyethoxy) ethyl acetate and 1-methoxy 2-propanol, with 45 ± 1 wt% of dispersed Zn-55%Al microscopic particles with a diameter not larger than $10 \mu\text{m}$. This primer was applied using a lab-scale coil coater and the nominal film thickness (d) was $3.5 \mu\text{m}$, calculated by the weight difference before and after coating (Δm) and using the dry film density (ρ) and the section of the plate (A):

$$d = \frac{\Delta m}{\rho A} \quad \text{Eq. 3.1}$$

Complete curing was made in a continuous furnace at 360°C (well above peak metal temperature of 260°C). Following cure, the primed plates were formed by biaxial strain using the Marciniak flange test, resulting in specimens with elongations of 6%, 15% and 33%. In order to determine the effects of forming on the coating, a modified test was used, using cups with a flat surface, which generated a flat area of 100 mm diameter with constant forming conditions, as evaluated by FEM simulation and GOM1 grid evaluation (Gesellschaft für Optische Messtechnik, Germany). Samples were extracted from this flat area cutting them with a punch. More details on the forming system are provided in reference [21].

3.2.2 Scanning Vibrating Electrode Technique (SVET)

SVET measurements were performed using equipment from Applicable Electronics Inc. controlled by the ASET software (Science Wares, MA, USA). The microelectrode had a black platinum tip with a diameter of approximately 10 μm and vibrated with 20 μm of amplitude, at an average distance of 200 μm above the surface. Specimens were glued to epoxy sleeves, whereas an adhesive tape placed around the epoxy was used as solution reservoir. A mixture of beeswax and colophony bordered an exposed area of 3.3×3.3 mm^2 and each scan comprised 31×31 points corresponding to a step of 125 μm . The test solution was aqueous 0.05 M NaCl prepared with distilled water.

3.2.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical cells were made by gluing PMMA tubes to the coated plates with two-component epoxy adhesive, leaving an exposed area of 13.85 cm^2 . Samples were immersed in 0.05 M NaCl aqueous solution. Impedance measurements were made using a three-electrode arrangement, with a saturated calomel electrode (SCE) as reference and a platinum counter electrode. Experiments were performed at room temperature, inside a Faraday cage, with the solution quiescent and exposed to air, using a PC4 system (Gamry Instruments, PA, USA), under potentiostatic control and with the application of a sine wave of 10 mV rms amplitude around open circuit potential. A minimum of two samples were tested per condition. Fitting of the spectra was made using ZView 2.70 software (Scribner Associates, USA). For the fittings, depressed capacitive loops are treated as constant phase elements (CPEs), whose impedance is given by Q [51]:

$$Q = \frac{1}{Y_o(j\omega)^n} \quad \text{Eq. 3.2}$$

Here it is assumed that the micro-roughness and heterogeneity of the surface generate a non-uniform distribution of charge. The result is a dispersion of time constants $\tau = RC$ responding at different frequencies. With this interpretation, Y_o is the frequency-independent component and is proportional to the area of the active sites that contribute to the process. The exponent n indicates the deviation from an ideal dielectric behaviour [26].

3.2.4 Scanning Electron Microscopy (SEM)

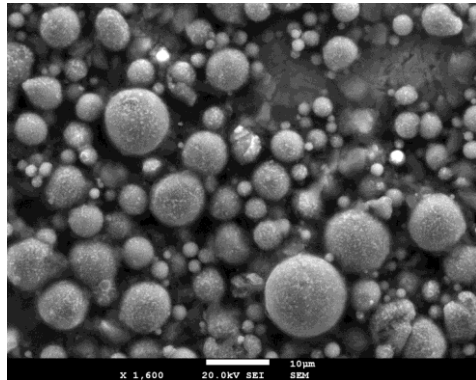
A Hitachi S2400 SEM equipped with Rontec standard EDS (Energy Dispersion Spectroscopy) detector was used to inspect the morphology and to obtain elemental mapping of the surface. Because the SEM could not easily distinguish the particles that are exposed from those that are fully buried in the polymer, identification of the exposed particles was made in some cases by immersion for 60 seconds in a CuSO_4 solution. Due to the differences in the electrochemical potentials, copper quickly becomes reduced on the zinc, forming corrosion products on the surface of the exposed particles.

3.3 Results and Discussion

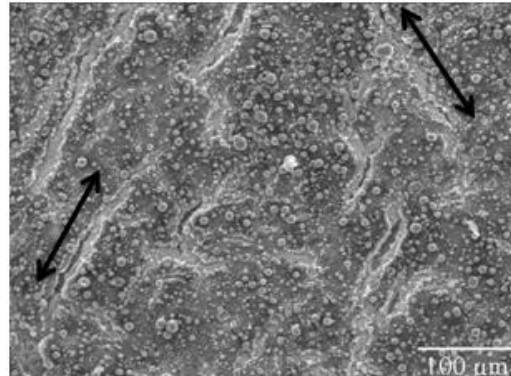
3.3.1 Morphology of the surface

The coating is a composite consisting of zinc-aluminium particles dispersed in an epoxy matrix—Figure 3.1 a. The size of the particles spreads over a wide range and reaches approximately $10\text{ }\mu\text{m}$ for the largest ones, which is above the thickness of the coating, therefore resulting in a rough surface, with many protruding particles. For the smallest elongation, the micrographs reveal the formation of microscopic gaps at the interface between the metal particles and the polymer matrix—Figure 3.1 b. With increasing elongation the loss of adhesion between polymer and metal particles becomes more extensive, as observed for the 15% elongation—Figure 3.1 c. Further, cracking of the polymer occurs, generating gaps with $30\text{ }\mu\text{m}$ or more. For the 33% elongation, the cracks become much larger, in some cases exceeding $100\text{ }\mu\text{m}$ length, and are spatially distributed in two directions, resulting from the biaxial strain—Figure 3.1 d. The fractured surface shows a highly rough surface and confirms the loss of adhesion between metal particles and polymer phase as well as the average thickness of approximately $3.5\text{ }\mu\text{m}$ —Figure 3.1 e. Tests made with cementation of copper at the exposed zinc-aluminium pigments reveal accumulation of copper products on most of the large particles, meaning that they are not totally coated by the polymer, whereas most of the small ones show no signs of copper precipitation and thus are fully embedded in the polymer—Figure 3.2 a. Further, at the sites where the plastic deformation was more intense, there were no signs of metal particles, Figure 3.2 b. Mapping of the surface by EDS reveals a precise distribution of aluminium at the metal particles, whereas for zinc the particles could not be distinguished from the layer underneath.

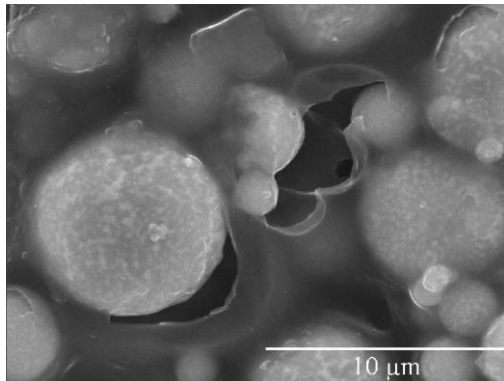
Finally, for the most severe elongation, some of the cracks went clearly all across the primer and the zinc coating, leaving the steel from the substrate exposed—Figure 3.3.



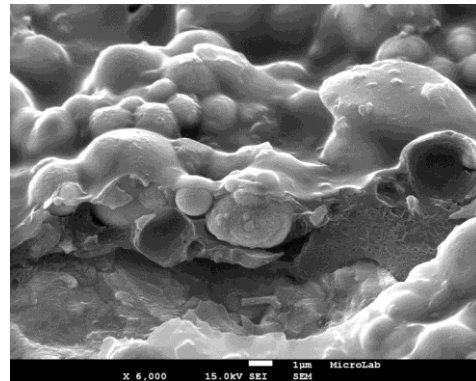
(a)



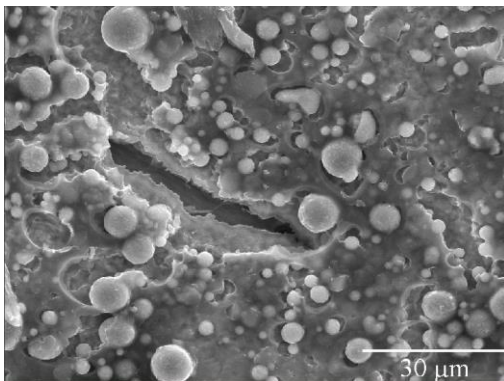
(d)



(b)



(e)



(c)

Figure 3.1. Micrograph of the primed samples, (a) as-received and after biaxial strain with elongation of (b) 6%, (c) 15% and (d) 33% (e) fracture after freezing of as-received sample.

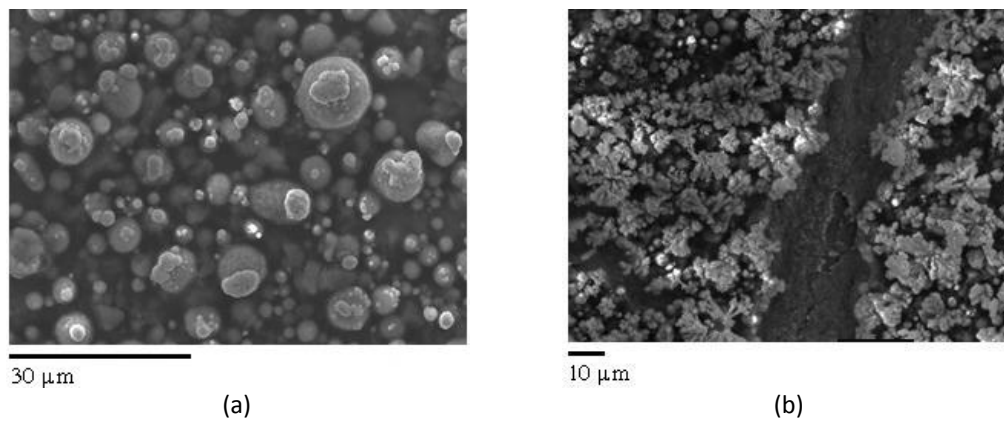


Figure 3.2. Micrographs of the primer after exposure to a copper sulphate solution, showing the sites where Zn-55Al particles emerge above the polymer layer, in (a) a reference sample and in (b) a formed sample.

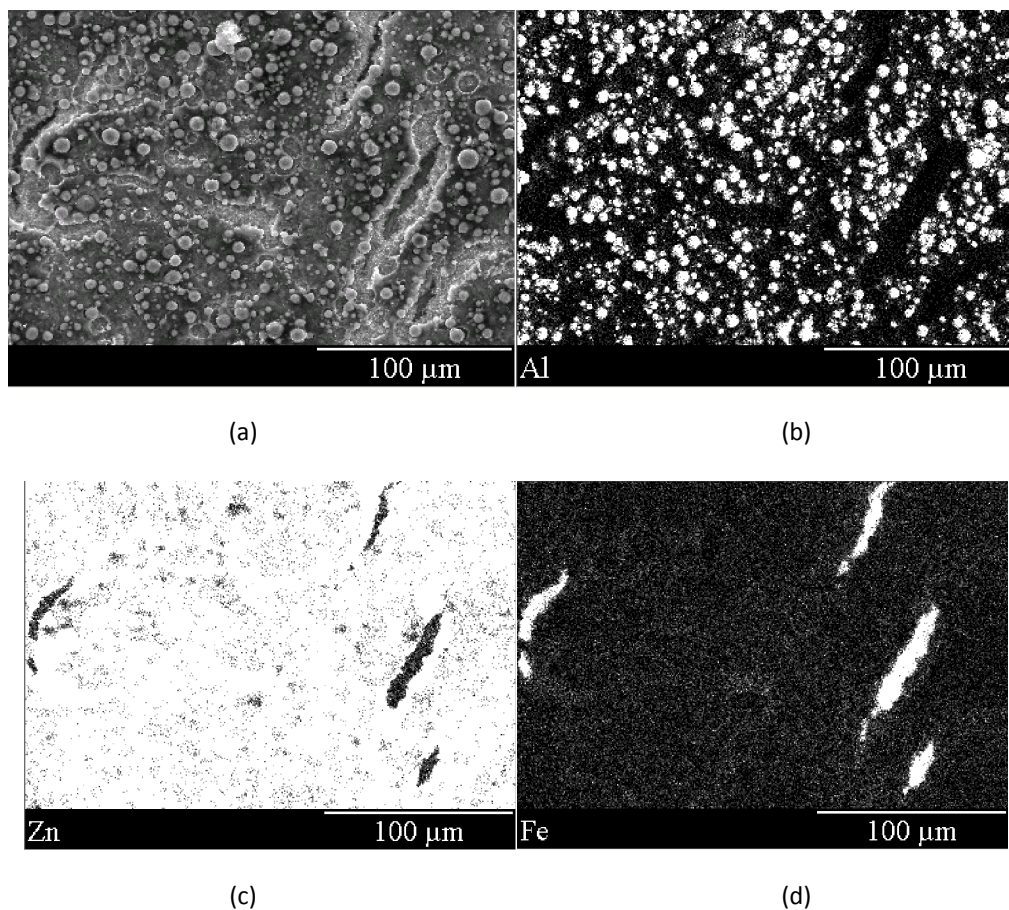


Figure 3.3. Metal-rich primed surface after 33% biaxial elongation, as (a) micrograph and as EDS maps of (b) aluminium, (c) zinc and (d) iron.

3.3.2 Distribution of Ionic Currents on the Surface

For the non-elongated samples, the readings were at the level of the noise ($2\text{--}4\ \mu\text{A cm}^2$) and thus it was not possible to unambiguously identify any activity on the surface. For the 6% elongation the signal was initially also very low, although plotting of the current profiles along a scanning line for different immersion times— Figure 3.4 –reveals two maxima that correspond to the anodes in the sample. The full maps show these anodes in the upper part of the image and also some disperse cathodic activity in the lower part, Figure 3.5 a–c. Finally, the highest elongation (33%) led earlier to well resolved anodic activity and also to larger anodic and cathodic areas - Figure 3.5 d–f. Since at this elongation the steel becomes exposed, the cathodes most likely correspond to the exposed substrate.

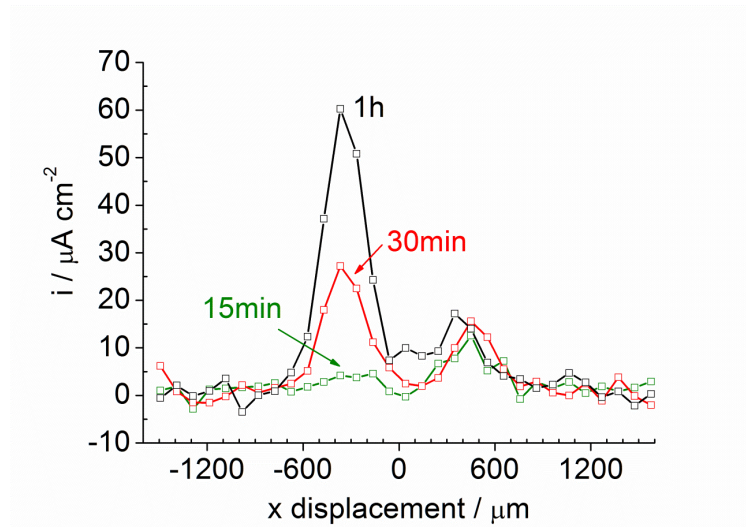


Figure 3.4. Ionic currents for the primed electrogalvanized steel, with biaxial elongation of 6%, corresponding to a linear scan along xx direction, extracted from SVET maps.

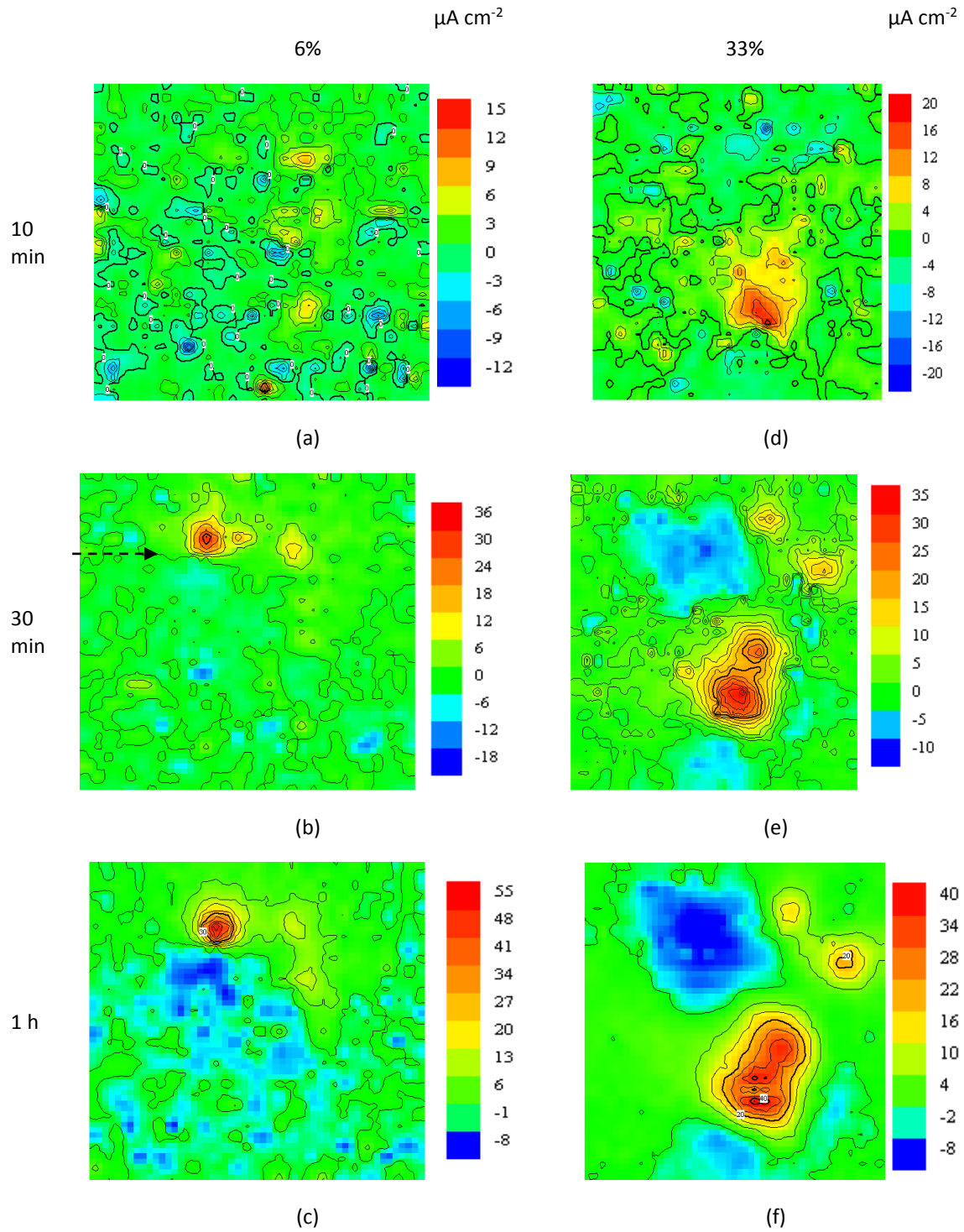


Figure 3.5. Maps of ionic currents for the primed electrogalvanized steel with biaxial elongation of (a)-(c) 6% and (d)-(f) 33%; scanned area: $3300 \mu\text{m} \times 3300 \mu\text{m}$; scale: $\mu\text{A cm}^{-2}$. The arrow in (b) shows the direction of the line scan in Figure 3.4.

3.3.3 Integral Electrochemistry

The primed system reveals an impedance spectrum with only one capacitive loop in a first stage. A small and not very well resolved loop can also be observed only in some spectra at the low frequencies. The major process has a resistive plateau at frequencies below ~ 1 Hz and a capacitive slope above ~ 100 Hz, Figure 3.6. Compared to the bare electrogalvanized substrate, the primer increases the resistance of the system by roughly four orders of magnitude, which means that it is able of providing a moderate but clear barrier effect to the substrate. The resistance can be assigned to a charge transfer process and was approximately $10^7 \Omega\text{cm}^2$ just after immersion, a value that is in the typical range for weldable primers [52,53] and a few orders of magnitude below that of barrier coatings, which can easily reach 10^{10} - $10^{11} \Omega\text{cm}^2$ [53].

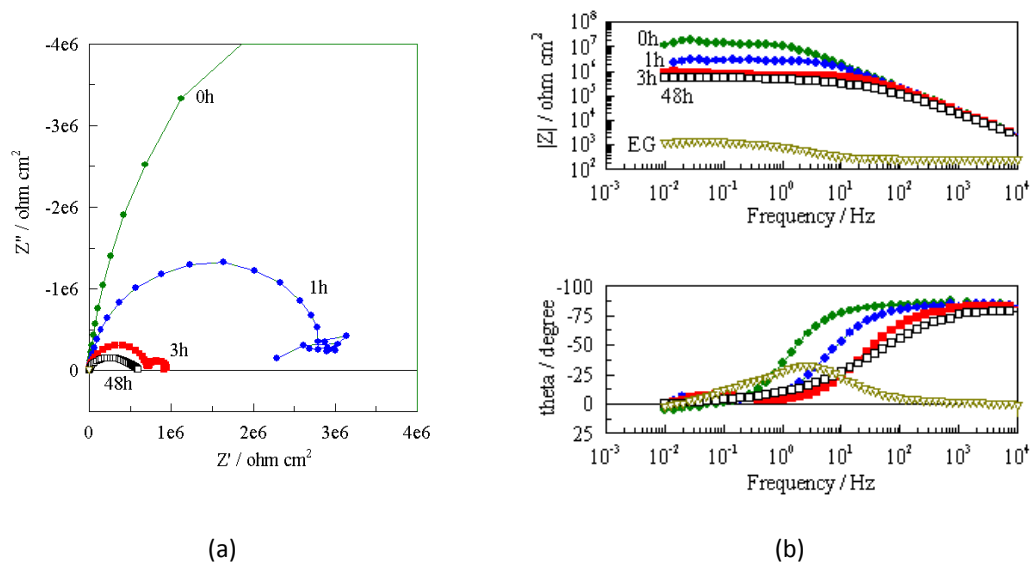


Figure 3.6. EIS spectra of the reference sample (non-formed, primed sample) for varying immersion times (0, 1, 3 and 48 hours), and also for the bare electrogalvanized steel (EG): (a) Nyquist and (b) Bode plots.

With time, the effect of the electrolyte caused a consistent decay of the resistance, especially in the first three hours of immersion. After that, the precipitation of stable zinc and aluminium hydroxides may be responsible by the slowing down of corrosion. The total drop after 48 hours was of more than one order of magnitude, but still the system was well above the performance of the bare substrate. Electrochemical activity should take place at the exposed surface of the larger particles, provided they establish electrical connection to the substrate.

Fitting of the spectra was made using an equivalent electrical circuit (EEC) with a single resistor and capacitor in parallel for the intact samples, Figure 3.7 a. For the elongated samples

a single depressed loop could be observed and two RC networks in cascade for the high (hf) and medium frequency (mf) ranges were found necessary to provide adequate fitting, Figure 3.7 b. An additional RC network was added to fit the low frequency (lf) loop below 0.1 Hz, Figure 3.7 c, which happened in the case of severely damaged coatings. The capacitive response on the intact coating has a CPE of $Y_o \approx 10^{-8} F cm^{-2} s^{n-1}$, with n between 0.90 and 0.94 and can be assigned to the capacitance of the polymer. Taking the classical assignment of high frequency capacitance to the dielectric properties of the primer, this corresponds to an apparent dielectric constant of approximately 40, which is well above the typical value for polymer films, of 3 – 6 and agrees with the conductive nature of the film, with a high metal content well above the percolation threshold of 0.16 found by Zallen [54].

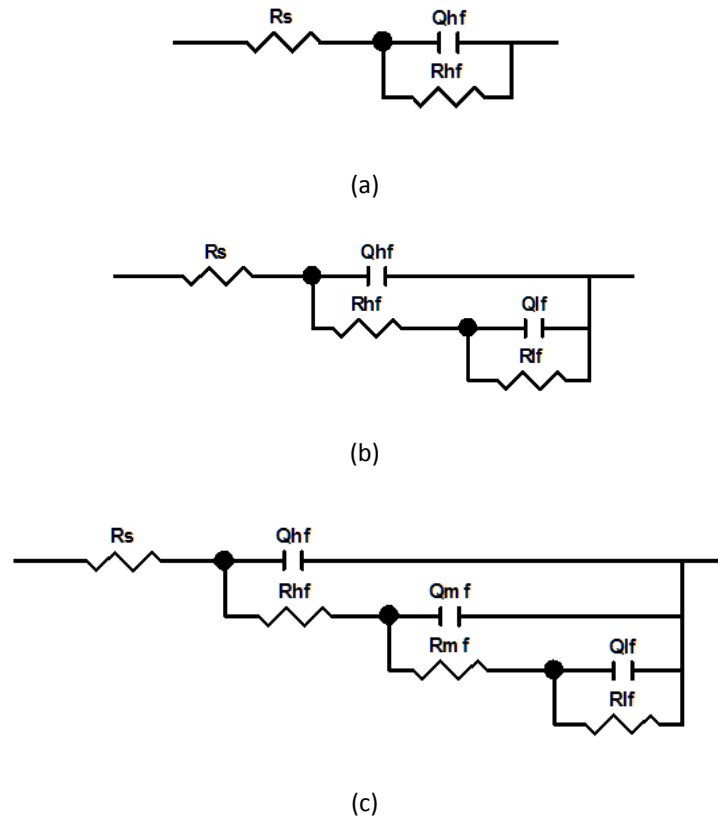


Figure 3.7. Equivalent electric circuits used to extract parameters from the EIS spectra: (a) for non-formed samples and short immersion times, (b) for long immersion times and/or medium elongation and (c) for severe elongation. Subscripts: hf: high frequency, mf: medium frequency, lf: low frequency.

The values corresponding to various immersion times – Table 3.1 - reveal a minor growth of Y_o , not observed by direct inspection of the plots. Immersion of the primer in an aggressive medium results essentially in a resistance drop, accompanied by a minor capacitance increase. Immersion of the coating is also reflected in a gradual deviation of the CPE from a pure capacitor, as the values of the exponent n_{hf} deviate from the ideal 1.0 [54]. This is a result of water

absorption by the polymeric matrix. For long exposure times a low-frequency relaxation constant appeared at frequencies below 0.1 Hz. It was usually ill-defined and can be due to a mass or charge transport component. A comparable behaviour has been reported for zinc [55] and assigned to the existence of adsorbed intermediates, either Zn_{ads}^I or Zn_{ads}^{II} [56, 57]. In formed samples the impedance is initially lower, the resistance decay during immersion is less significant and the spectrum is more complicated.

Table 3.1. Parameter values obtained from numerical fitting; time refers to immersion in 0.05M NaCl.

Samples	Time h	$Y_{0,hf}$ $F\ cm^{-2}\ s^{n-1}$	n_{hf}	R_{hf} $\Omega\ cm^2$	$Y_{0,mf}$ $F\ cm^{-2}\ s^{n-1}$	n_{mf}	R_{mf} $\Omega\ cm^2$	$Y_{0,lf}$ $F\ cm^{-2}\ s^{n-1}$	n_{lf}	R_{lf} $\Omega\ cm^2$
non-formed	0	9.52×10^{-9}	0.95	1.38×10^7	-	-	-	-	-	-
	1	1.11×10^{-8}	0.94	2.91×10^6	-	-	-	-	-	-
	3	6.87×10^{-7}	0.95	9.07×10^5				1.48×10^{-8}	0.92	2.53×10^6
	48	6.63×10^{-8}	0.87	4.97×10^5				4.50×10^{-8}	0.88	2.47×10^5
15% elongation	1	1.97×10^{-6}	0.83	9.29×10^2	1.71×10^{-6}	0.79	1.12×10^4	6.31×10^{-4}	0.96	6.15×10^3
	3	3.97×10^{-6}	0.75	7.30×10^2	3.44×10^{-6}	0.71	9.24×10^3	1.68×10^{-3}	1	3.64×10^3
	5	5.44×10^{-6}	0.71	7.73×10^2	4.74×10^{-6}	0.67	7.31×10^3	1.94×10^{-3}	1	3.87×10^3
	48	1.97×10^{-5}	0.60	4.59×10^3	6.88×10^{-6}	0.95	2.47×10^3	4.40×10^{-3}	1	5.25×10^3

The subscripts hf, mf and lf refer to high, medium and low frequencies, respectively.

The capacitive loop observed at high and medium frequencies is highly depressed and asymmetric – Figure 3.8, meaning that it requires two time constants for proper fitting. Further, a tail at low frequencies appears for the samples with 15% and 33% elongation. The results obtained from fitting of the 15% sample - Table 3.2 - show that the CPE of the two processes, merged in the high frequency capacitive loop, are two orders of magnitude above the CPE of the non-formed sample and are both in the order of magnitude of $10^{-6} F\ cm^{-2}\ s^{n-1}$. These values are typical of a double layer capacitance and are assigned to the activity at the exposed surface of the metal particles. The depressed loop suggests a Faradaic process occurring at the surface of the large metal particles and also at the surface of the embedded particles, where the adhesion to the polymer is weakened by the applied stress. The open circuit potential of pure zinc in NaCl solution is approximately -1.0 V, as measured for the bare substrate (EG) for $t = 0$, whereas for longer times cathodic polarization results from oxygen diffusion control – Figure 3.9.

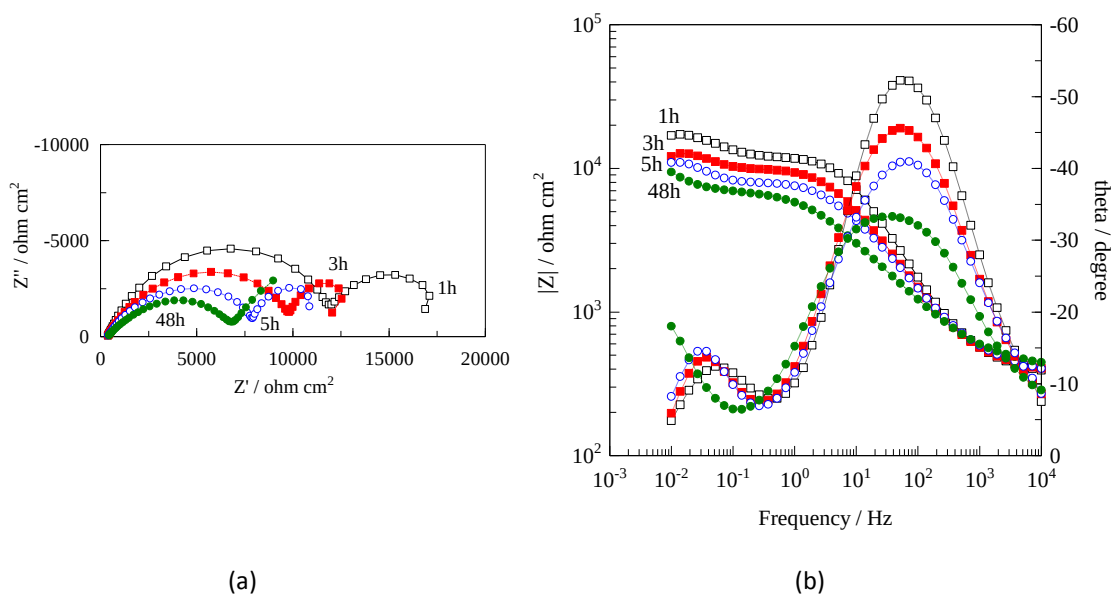


Figure 3.8. EIS spectra of the 15% elongated primed sample at 1 h, 3 h, 5 h and 48 hours immersion: (a) Nyquist and (b) Bode plots.

Table 3.2 Equivalent circuit parameter values after 1h exposure in 0.05M NaCl for non-formed and 6, 15 and 33% elongated samples.

% elongation	$Y_{0,hf}$ $Fcm^{-2}s^{n-1}$	n_{hf}	R_{hf} Ωcm^2	$Y_{0,mf}$ $Fcm^{-2}s^{n-1}$	n_{mf}	R_{mf} Ωcm^2	$Y_{0,lf}$ $Fcm^{-2}s^{n-1}$	n_{lf}	R_{lf} Ωcm^2
0	1.11×10^{-8}	0.94	2.92×10^6	-	-	-	-	-	-
6	1.34×10^{-7}	0.72	1.25×10^3	2.93×10^{-7}	0.69	1.56×10^5	-	-	-
15	1.97×10^{-6}	0.83	9.29×10^2	1.71×10^{-6}	0.79	1.12×10^4	6.31×10^{-4}	0.96	6.15×10^3
33	3.36×10^{-5}	0.82	2.60×10^3	-	-	-	-	-	-

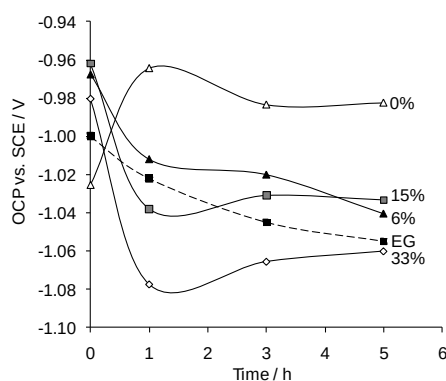


Figure 3.9. Potential evolution of primed samples elongated up to 33% equivalent strain, non-formed sample and of the electrogalvanized substrate.

The non-formed sample goes to more noble potentials after stabilization, whereas the elongated samples all become active within the first hour. The samples with 15% and 33%

elongation reach very low potentials that are too negative for zinc in this medium and thus can only be due to aluminium of the alloy. The effect of the elongation is summarized in Figure 3.10. The effect of the elongation degree followed a consistent evolution for both the resistance and the capacitance. The spectrum has apparently one or two loops and a tail below 0.1 Hz. There is a strong resistance decrease with growing strain, from $\sim 2 \text{ M}\Omega \text{ cm}^2$ down to nearly $3 \text{ k}\Omega \text{ cm}^2$, i.e., three orders of magnitude. According to the SEM study, this is associated with the increase of active area, as the metal particles become partially detached from the polymer phase and the substrate becomes exposed. For moderate elongations, i.e., for 15%, a third relaxation constant is visible at low frequencies ($\sim 0.1 \text{ Hz}$). For the 33% sample, the resistance became very close to that of the bare substrate, revealing severe degradation. The strain also results in a very significant change on slope of the capacitive part of the spectrum, with an increase of the capacitance and a shift towards lower frequencies, likely due to the development of a new time constant at intermediate frequencies that could not be fitted adequately.

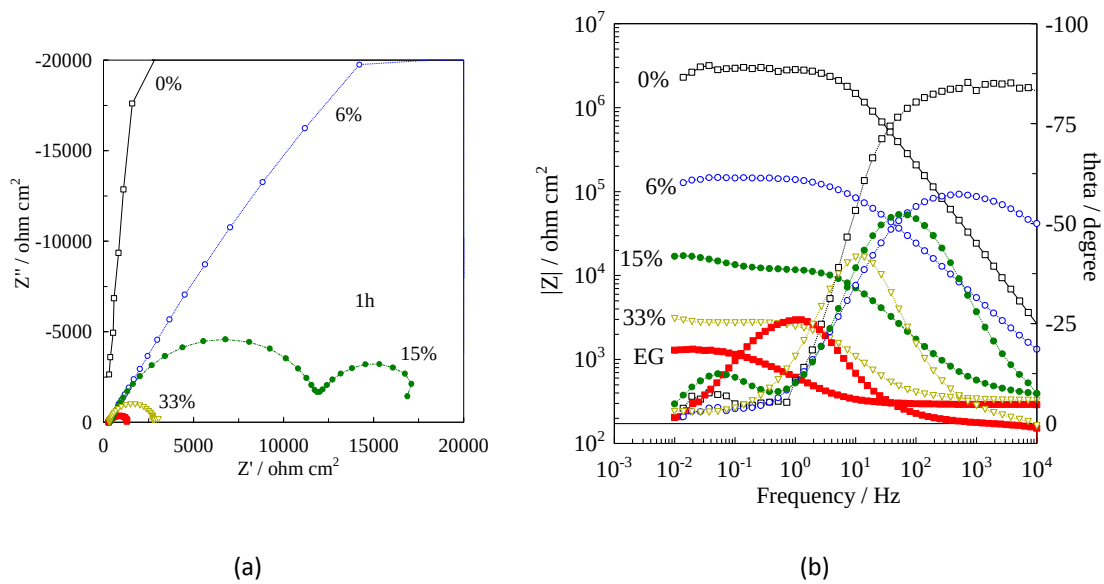


Figure 3.10. EIS spectra of the biaxially strained samples, with elongation up to 33% (after 1 hour immersion) and also of the electrogalvanized substrate: (a) Nyquist and (b) Bode plots are represented.

3.4 Physical Model

The weldable primer can be described by the scheme model of Figure 3.11, in which the coating is represented by a polymer matrix with dispersed conducting particles, some of them in contact with the substrate. R_s is the solution resistance, placed in series with R_{ct} , the charge transfer resistance, and C_{dl} , the double layer capacitance at the exposed particles. In parallel, R_p is the resistance along the pores of the coating, placed in series with the Faradic response of the embedded particles (given by C_{dl}^* , R_{ct}^*); also C_c , the coating capacitance.

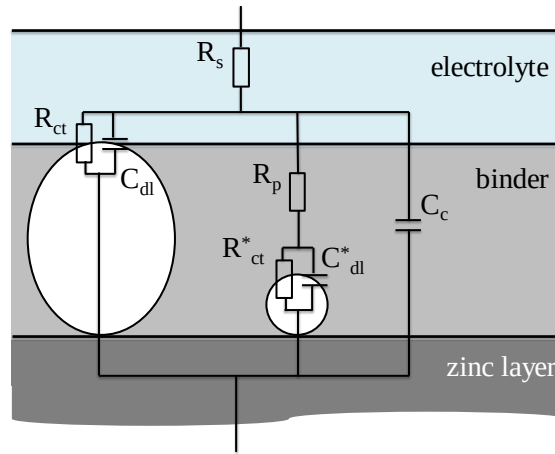


Figure 3.11. Proposed equivalent electric circuit for the description of a metal-rich primed system.

At small defects activity will occur, but an area effect can be expected. It is generally accepted that the double layer capacitance and the charge transfer resistance are dependent on the active area [54]. The apparent double layer capacitance is then given by:

$$C_{dl} = C_{dl}^0 \frac{A_{active}}{A_{sample}} = C_{dl}^0 F \quad \text{Eq. 3.3}$$

where F represents the fraction of the active surface (where the metal is exposed to the outer solution); the apparent charge transfer resistance, in its turn, shall be given by:

$$R_{ct} = R_{ct}^0 \frac{A_{sample}}{A_{active}} = R_{ct}^0 / F \quad \text{Eq. 3.4}$$

The pore resistance is affected by the area fraction and also by variation of the pore dimensions by water penetration. For simplicity, it is assumed that:

$$R_p \approx R_p^0/F \quad \text{Eq. 3.5}$$

As reference values, we used for the bare zinc electrode $C_{dl}^0 = 1 \times 10^{-5} F$ and $R_{ct}^0 = 1 \times 10^3 \Omega$, both referring to the large conducting particles [53]. The reference values for the double layer capacitance and the charge transfer resistance for the small particles in contact with just the electrolyte or just the zinc substrate, were taken as $C_{dl}^{*0} = 1 \times 10^{-4} F$ and $R_{ct}^{*0} = 1 \times 10^4 \Omega$; that would more accurately correspond to a mass transport component due to adsorbed zinc species, occurring at particles embedded in the polymer, and resulting from a large pore resistance that was taken as $R_p^0 = 1 \times 10^7 \Omega cm^2$. The binder capacitance does not present variation directly related to the active area fraction, as it depends rather on the water content. It may occur that the pore resistance decreases while the polymer capacitance remains fairly constant:

$$C_c = \frac{\varepsilon \varepsilon_0 A}{d} \quad \text{Eq. 3.6}$$

in this, ε is the dielectric constant, $\varepsilon_0 = 8.854 \times 10^{-12} Fm^{-1}$ is the vacuum permittivity, A the area covered by the coating and d the coating thickness. Simulations were performed taking $C_c = 1 \times 10^{-9} Fcm^{-2}$ at the beginning of immersion for non-formed samples, with $\varepsilon = 3.0$ for the pure epoxy binder [58].

3.4.1 Effect of immersion time

The fraction of area corresponding to the exposed particles should not increase significantly in an intact coating, but an effect resulting from water penetration is expected. As time evolves, the pores get filled with electrolyte and the corresponding pore resistance should decrease, affecting the low frequency impedance. The computed spectra in Figure 3.12 simulate this effect, i.e. a moderate decrease of the pore resistance in an initially intact coating, while maintaining the other properties constant. The model shows why the low frequency loop, associated with the corrosion at the embedded particles or at the substrate, only becomes visible when the barrier effect of the coating drops to very low values. When the coating is protective ($R_p > 10^5 \Omega$), the low frequency process is masked and thus cannot be seen in the spectrum, whereas for low coating resistance the low frequency loop becomes apparent.

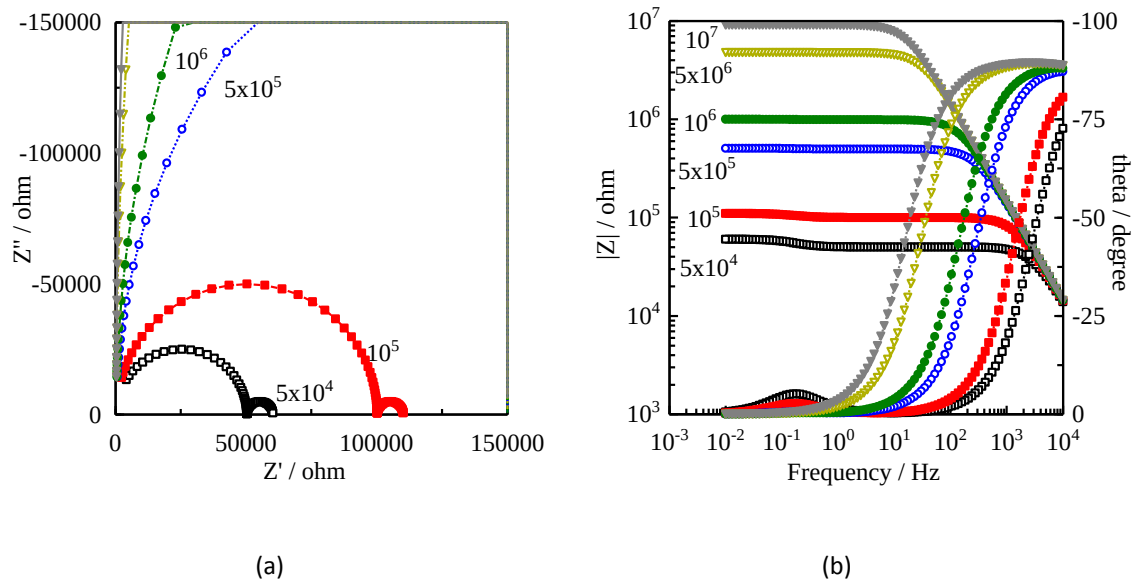


Figure 3.12. Computed spectra represented as (a) Nyquist and (b) Bode plots, using the proposed EEC. The numbers in the plot correspond to the value of R_p (in ohm). Constant values used for the other elements: $R_s = 300 \Omega$; $R_{ct} = 1 \times 10^8 \Omega$; $C_{dl} = 1 \times 10^{-10} F$; $R_{ct}^* = 1 \times 10^4 \Omega$; $C_{dl}^* = 1 \times 10^{-4} F$, $C_c = 1 \times 10^{-9} F$. A geometrical area of 1 cm^2 was assumed.

3.4.2 Effect of elongation

Forming of the samples results in loss of adhesion between the Zn-Al particles and the polymer matrix. This causes an increase of the active area and a regular variation of both the charge transfer resistance and the double layer capacitance. The values of the parameters are presented in Table 3.3. Starting from an active area fraction of $F = 10^{-4}$, the spectrum has a single capacitive loop, corresponding to parallel capacitors and to the pore resistance, Figure 3.13. As the fraction F increases, the conductive character of the particles become predominant and the capacitance measured is C_{dl} . Simultaneously, the low frequency resistance decreases as both R_{ct} and R_p decrease. The low frequency process ($\sim 0.1 \text{ Hz}$), corresponding to the time constant given by R_{ct}^* and C_{dl}^* , only becomes visible for 15% and 33% elongation. The model evidences that the low frequency process is resolved only when the fraction of exposed area exceeds 0.001. The theoretical spectra give good similarity with the experimental results, in which also the capacitance increased with the elongation, while the resistance decreased.

Table 3.3. Parameter values used for simulating impedance of elongated samples.

R_s Ω	F	R_{ct} Ω	C_{dl} F	R_p Ω	C_c F	R_{ct}^* Ω	C_{dl}^* F
300	1×10^{-4}	1×10^7	1×10^{-9}	1×10^6	1×10^{-9}	1×10^4	1×10^{-4}

"	1×10^{-3}	1×10^6	1×10^{-8}	1×10^5	"	"	"
"	1×10^{-2}	1×10^5	1×10^{-7}	1×10^4	"	"	"
"	1×10^{-1}	1×10^4	1×10^{-6}	1×10^4	"	"	"

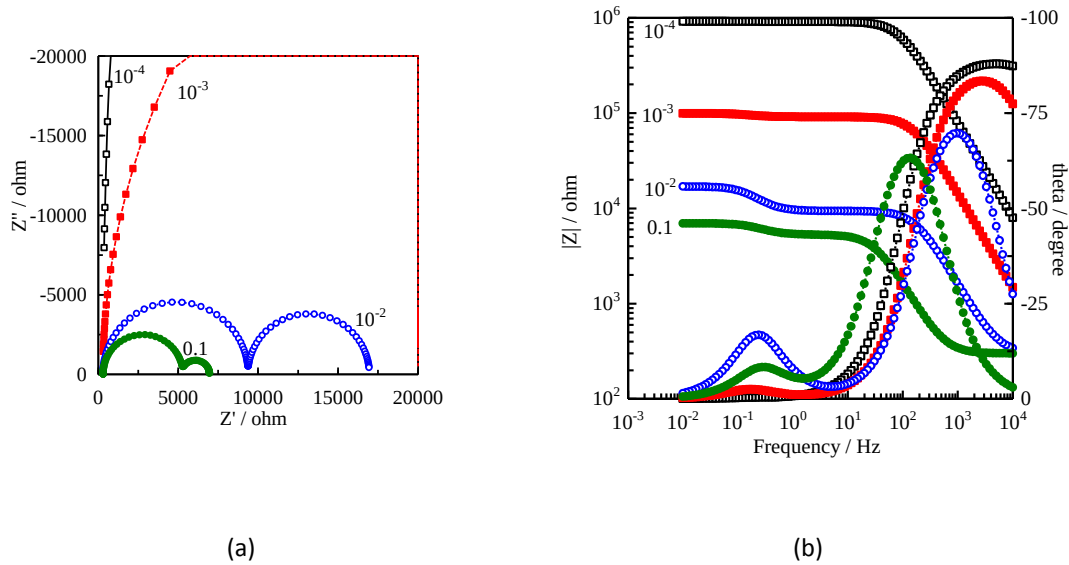


Figure 3.13. Effect of the fractions of active area on the computed spectra using the proposed EEC model, assuming 1 cm^2 area. The numbers indicate the fraction area F ; other values used for the calculations are in Table 3.3 (a) Nyquist plot and (b) Bode plot representation.

The model proposed differs from the previous ones as it describes the coating as a set of microelectrodes scattered along the surface of a polymer that has very low capacitance and high resistance. Corrosion at the embedded particles is measured only when the resistance of the polymer drops down to $\sim 100 \text{ k}\Omega$. Further, the size of those microelectrodes will increase as a consequence of plastic deformation. The corrosion process at the embedded particles can only be observed for fractions F of active metal above a certain critical value of approximately 0.001. The model provides a good approach to the experimental data, with the advantage of a straightforward interpretation to the number of loops in the spectrum. It provides an alternative to the models based on transmission lines, which enhance the contact impedances between embedded particles predominant over the electronic character of the larger ones. One limitation of the model is the use of pure capacitors in the equivalent electrical circuits instead of CPEs, which should provide a better approach considering the complex nature of the surface and the distribution of reactions and reaction rates along the surface.

3.5 Conclusions

An equivalent circuit was proposed for the impedance behaviour of the metal-containing weldable primer, in which the system is described by three relaxation processes corresponding to the active particles directly exposed to the solution, to the properties of the polymer and to the charge transfer occurring in the vicinity of the substrate. The simulations using our model mimic well the impedance response of these weldable primers and allow the distinction of three kinds of spectra. For the intact, non-elongated samples, only one relaxation process is observed, corresponding to the charge transfer at the conducting particles and the mixed double layer/polymer capacitance. As time of exposure to the aggressive medium increases, water penetrates the intact coating. As the pore resistance decreases, a second capacitive loop accounting for charge transfer becomes evident. With small elongation (6%) an increase in the active area, corresponding to more particles becoming exposed is responsible for the second capacitive loop. Finally, for large elongations (>15%) the substrate becomes exposed, giving rise to a third relaxation processes corresponding to a diffusion limited process, most probably due to the presence of zinc and aluminium corrosion products. Mapping of ionic currents in solution using the SVET technique provided information concerning formed samples in solution, with increasing degrees of elongation revealing larger anodic and cathodic areas. On intact coatings currents on the level of noise suggests that the Zn-Al particles protruding out of the polymer do not have a deleterious effect on corrosion performance of the painted system.

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4. SECM imaging of the cut edge corrosion of galvanized steel as a function of pH

This chapter is a research paper with the same title published in *Electrochimica Acta* Vol. 153 (2015) 238-245. All experiments were carried out by the author except SVET which were performed by Maryna Taryba, a PhD student from the group and FEG-SEM which was performed by Isabel Nogueira. Part of the work was developed during a research abroad on Universidad de La Laguna under the supervision of Prof. Ricardo Souto. The author acknowledges the important discussions with Prof. Souto and Dr. Javier Izquierdo concerning the interpretation of the results.

Abstract

Scanning electrochemical microscopy (SECM) and the scanning vibrating electrode technique (SVET) were employed to identify the local reactivity and the cathodes and anodes on a cut edge of galvanized steel. The SECM was used in the amperometric feedback mode, using a redox mediator, for sensing the conductivity of the surface and also in the redox competition mode for locating the depletion of the cathodic reactant. Good agreement was observed in acidic solution between the location of the conductive regions of the surface and the depletion of oxygen estimated from amperometric lines across the cut edge. In nearly neutral medium, non-uniform activity of the steel surface was observed and correlated well with the ionic current flows in solution and with the accumulation of zinc corrosion products on steel. In alkaline medium the entire steel surface operated as electron source for the regeneration cycle of the redox mediator. Irrespective of the pH of the solution, a maximum of the feedback observed over the cut edge is consentaneous with the thermodynamic stability of iron in the reduced form. SECM provided useful information regarding the steel conductivity, whereas the zinc anodes could only be resolved by the SVET.

Keywords: cut edge; corrosion; pH; SECM; SVET

4.1 Introduction

Galvanized steel is widely used in the automotive and construction industries due to the sacrificial protection provided by the zinc layer to the steel, which extends the lifetime of structures, especially when further coated with a paint layer, as in the case of automotive bodies. At the cut edges, however, the exposure of steel and zinc to air, humidity and aggressive ions create conditions for corrosion to propagate underneath the organic coating, causing delamination. Although zinc is anodic and thus provides cathodic protection to steel, this protection may be lost if zinc dissolution is fast or if the ionic flow between cathode and anode becomes blocked by precipitates. The small thickness of the zinc anode in comparison with the steel cathode, as well as the proximity between the electrodes and the high pH gradients, make this system a unique galvanic couple, with great scientific interest in addition to its technical relevance. Though many studies have dealt with the corrosion of galvanized steel, only few describe the phenomenon at a microscopic level. Conventional electrochemical techniques are widely used to study the metal/electrolyte interface phenomena in corrosion processes [1], but they lack spatial resolution, which can be a limitation when characterizing processes that are either triggered at micrometer scale or localized in nature. Investigations using the scanning reference electrode technique (SRET) [2–6], the scanning Kelvin probe (SKP) [7–11], and localized electrochemical impedance spectroscopy (LEIS) [12–17] have provided relevant information on the mechanisms of localized corrosion. These techniques are mostly based upon the use of microprobes to assess indirectly the electrochemical activity of the system, by measuring electric fields in solution, potential distributions on the surface of an active substrate, or the local impedance response to an AC perturbation. The scanning vibrating electrode technique (SVET) is probably the most popular of the surface-resolved electrochemical techniques, due to its ease of use and straightforward interpretation [18–20]. It can sense the intensity and direction of ionic currents in solution near a metal surface, thus identifying the microscopic anodes and cathodes in various systems, such as galvanic processes [21] or pitting corrosion [22]. The scanning electrochemical microscope (SECM) is another scanning probe technique, which has the advantage of probing indirectly a variety of electrochemical reactions and providing sensitivity to characterize either surface topography or conductivity of a metal surface [23–27]. Operation of the SECM in the amperometric feedback mode is done by applying a potential step to an ultramicroelectrode (UME) in the presence of a reversible redox couple, known as the electrochemical mediator. When the mediator is added to the electrolyte in its reduced state and the UME is biased to a potential within the range of diffusion controlled

oxidation of the mediator, then the oxidation rate will be given by the rate of the mass transport within the hemispherical diffusion layer of the tip. For a disk-shaped UME, that limiting current, i_L , is given by Eq. 4.1 [25].

$$i_L = 4nFDCa \quad \text{Eq. 4.1}$$

in this, D is the diffusion coefficient of the mediator, C is the bulk concentration, F is the Faraday constant, n is the number of electrons involved in the reaction and a is the conductive probe radius. Under these conditions, the current at the tip will be proportional to the bulk concentration of the mediator. When the tip is brought to the vicinity of a metal surface, and depending on the potential and conductivity of the surface, the current will decrease or increase thus generating a negative or positive feedback current, respectively. Further to this feedback current, concentration gradients of particular species can be assessed under some conditions. For example, if the reaction at the cathode is oxygen reduction, scanning the surface with the tip biased to a potential in the range at which oxygen reduction occurs under diffusion control, provides information on the detection of cathodic activity on the surface of a corroding substrate [23]. The SECM has also been employed to detect metal dissolution by sensing the released species [28–31], to image precursor sites for pitting corrosion [32–35], to monitor nucleation and propagation of corrosion pits [36–38], to visualize the permeability of protective coatings applied on metallic substrates to chemical species in the environment [39–42] and to follow the degradation reactions in defective coatings [43–48]. One of the factors that influence aqueous corrosion is the pH. There are several studies on the effect of pH on the corrosion of iron and of zinc, but hardly any studies deal with the effect of pH on cut edge corrosion. Thermodynamics predict oxidation of zinc at acidic pH with the formation of Zn^{2+} ions and alkaline oxidation via the formation of the bizincate ion (HZnO_2^-) [49]. At $\text{pH} < 3$, corrosion of zinc by itself proceeds under activation control of the cathodic reaction, predominantly hydrogen evolution reaction, HER [50, 51]. Despite the thermodynamic prediction of passivation for zinc at $\text{pH} 8\text{--}12$ [49], a pseudo-passive behaviour has been reported for pH above 4 [51], resulting from the precipitation of zinc oxides on the surface [51] which act as a barrier to the OH^- ions and thus protect the metal only up to a certain extent. Real passivation has been observed at pH around 13 [51], most likely associated with the formation of the zincate ion, ZnO_2^{2-} [52]. While zinc is the anode, the cathodic activity is concentrated on steel, with either the reduction of water in acidic solution or reduction of dissolved oxygen in neutral or slightly acidic solution. Precipitation of zinc compounds such as zinc oxide and hydroxides, but also simonkolleite $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ or hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ on the steel surface occurs due

to the alkalinisation of the solution near the cathode and take place relatively quickly [53], inhibiting to some extent the cathodic reaction and thus decreasing the rate of the corrosion process [54]. Despite the vast knowledge on the corrosion of zinc and of iron by themselves, the electrochemistry at a cut edge is a different phenomenon that results from the mutual influence of each of the electrodes. Not only the potential is influenced, but also the pH is affected locally and a specific electrochemistry is developed. Given these specificities, galvanic corrosion at cut edges opened a new field for the application of probe techniques.

The SVET and also pH sensors have been used to investigate cut edge systems [20, 55–65], but very little has been published using the SECM applied to galvanic corrosion [66, 67]. Our study is focused on the application of SECM and SVET to cut edge corrosion of polymer-coated galvanized steel, with the aim of analysing the sensitivity of these techniques to cut edge corrosion in various conditions. The main difference among the chosen electrolytes is the pH values, which were 2, 5 and 10, in non-buffered solutions, simulating three main regions of corrosion behaviour of the metals involved.

4.2 Experimental

4.2.1 Materials

The substrate consisted of electrogalvanized steel, with a nominal zinc thickness of $7.2\text{ }\mu\text{m}$ applied industrially on both sides of a steel sheet with a width of $800\text{ }\mu\text{m}$. A thin epoxy layer ($1.2\text{ }\mu\text{m}$) was applied to the zinc on one of the sides. The sheets were cut and mounted into an epoxy resin sleeve, leaving an exposed cut edge of approximately 5 mm long. The zinc layers were therefore located on both sides of the steel substrate, with a graphite-containing polymer on one of the sides of the metal. As a consequence of the resin contraction during curing, a narrow gap was formed between the epoxy layer and the zinc, which created a preferential side for anodic activity [67]. The scanning direction was always across the cut edge, starting from the side of the epoxy layer. The working surface of the mount was polished using silicon carbide paper under ethanol rinse, to 1000 grit finish, then washed thoroughly in an ultrasonic bath after each grinding step and finally rinsed in ethanol and allowed to dry in air. A small electrochemical cell was built by laterally surrounding the mount with Sell tape; the setup was completed with a platinum strip as counter electrode and the Ag/AgCl, 3M KCl reference electrode. All the potential values reported herein are referred to this reference electrode. Testing was made in quiescent 10mM NaCl aqueous solution, naturally-aerated and at ambient

temperature. Adjustment of the pH was made by adding HCl or NaOH to the electrolyte. Millipore deionised water and analytical grade chemicals were employed to prepare the solutions. The cut edge system was left non-polarized, i.e., under spontaneously-driven corrosion.

4.2.2 Potential-time curves

DC potential-time curves at open circuit measurements were made using an ACM Field Machine (ACM Instruments, U.K.) controlled by a personal computer equipped with ACM software, version 5. Testing was performed in cells similar to those described in the previous section.

4.2.3 SECM instrumentation and experimental procedure

Measurements were made using a Sensolytics Scanning Electrochemical Microscope (Bochum, Germany) and an Autolab PGSTAT 128N electrochemical interface (Ecochemie, Utrecht, The Netherlands). The system operated in a three-electrode configuration in which the SECM probe was a platinum disk UME of 12.5 μm diameter sheathed in a glass rod with a conical shape at the bottom. The diameter of the insulating sheath was about 20 times the size of the platinum disk. The electrochemical cell and the positioning device were placed inside a Faraday cage. Operation of the SECM was made sequentially in two modes, the feedback mode with a redox mediator and the redox competition mode for the cathodic reactant. The feedback mode was applied for studying the surface concerning distribution of electrochemical reactivity, using ferrocenemethanol (abbreviated as FcMeOH, Sigma–Aldrich) as mediator. This is a neutral species that undergoes a fully reversible oxidation at +0.216 V [24] to form a stable species, ferrocenium, according to Eq. 4.2:



The equilibrium potential for this reaction is very positive when compared to the open circuit potential of the cut edge samples, which means that ferrocenemethanol is the only form of the mediator in bulk solution. In the vicinity of a conductive surface and if the potential of the tip is sufficiently low to cause oxidation of the mediator, the oxidised species will quickly become reduced at the conductive surface, increasing the current at the tip compared to the bulk current. Voltammograms were recorded with the aim of verifying the stability of the mediator in the various electrolytes and help selecting the tip potential for the amperometric study. These

curves were obtained using the SECM instrumentation and the tip as the working electrode in a cell without the introduction of the cut edge sample and at 20mVs^{-1} scan rate. Measurements were performed after a stabilization period of 15min immersion in the electrolytes. Levelling of the sample was first made using a bubble level and then confirmed by performing z-approach curves at two distant points above the resin on each side of the cut edge, holding the tip at a constant potential of +0.50 V for diffusion limited oxidation of FcMeOH. The operating distance between the tip and the sample was set after recording z-approach curves above the resin and approaching the surface of the resin until the current dropped to 30% of i_L . Subsequently the tip was withdrawn by $10\text{ }\mu\text{m}$, to a distance to the surface estimated as $\sim 20\text{ }\mu\text{m}$; in this way the probe current is still affected by changes in the reactivity of the sample, while bumping against corrosion products accumulating on the surface during the experiment was prevented. We consider that polishing produced a sufficiently flat surface and that the chosen working distance was large enough in order to exclude topography effects from the interpretation of results. The competition mode was used for mapping the concentration of cathodic reactants in solution in the vicinity of the corroding surface [23]. The cathodic reactions occurring on steel are the reduction of oxygen – Eq. 4.3 – or water – Eq. 4.4 – when exposed to alkaline or neutral aqueous electrolytes and HER – Eq. 4.5, in acidic medium [51].



With the tip biased in the potential range at which oxygen reduction or hydrogen evolution proceeds under diffusion control, competition for these species is established between the tip and the substrate. A decrease in the reduction current measured potentiostatically at the tip is then associated with depletion of oxygen or of protons at the probe and thus with a cathodic site on the substrate [30, 40]. The concentration of ferrocenemethanol in the test electrolytes was 0.5 mM and the scans were made with the tip parallel to the surface, at constant height, at a scan rate of $5.6\text{ }\mu\text{ms}^{-1}$.

4.2.4 SVET instrumentation and experimental procedure

The SVET instrumentation (Applicable Electronics Inc, U.S.A) was controlled by ASET software (Science WaresTM, Falmouth, MA, USA). The microelectrode consisted of a platinum wire sheathed with an insulating polymer, except for the tip, which was electro-platinised to obtain a sphere with approximately 20 μm of diameter. Scans were performed with the tip positioned 100 μm above the surface and vibrating at 300 Hz in the vertical direction, with 20 μm amplitude, allowing the potential gradient in solution to be measured accurately. A calibration routine allowed converting potential gradients into current density and single lines across the cut edge were measured with step increments of 10 μm . The time required to record a single line scan was ca. 2 min. The plots presented depict the vertical component of the current density vector.

4.3 Results

The chemical stability and the potential range for the diffusion limited oxidation of FcMeOH at the UME were determined by recording the corresponding voltammograms in the electrolytes shortly after immersion, Figure 4.1 a. The shape and current values were practically independent of the pH. The experimental values of the half-wave potential for the oxidation of ferrocenemethanol were in the range +0.20 to +0.27 V, above which a limiting diffusion current for the oxidation process ($i_L \sim 0.4 \text{ nA}$) was registered. A constant potential in the range +0.45 to +0.50 V was applied to the tip for amperometric analysis of the regeneration of the mediator. This potential is located in the diffusion plateau for the oxidized form of the mediator species, making the current at the tip proportional to the local concentration of FcMeOH. This means that when the tip passes over a conductive region of the cut edge the current should increase, whereas at the insulating areas it should decrease relatively to i_L . A comparable principle was applied to monitor the cathodic reactions at the cut edge sample. Voltammograms recorded in the cathodic region show a plateau in all the solutions – Figure 4.1 b – corresponding to diffusion controlled reduction of oxygen. The tip potential was set in the region of the plateau for monitoring the concentration of oxygen in solution. The results presented were obtained at a constant tip potential of -0.50 V. The spontaneous potential of the cut edge electrodes was measured during immersion in naturally aerated NaCl solution. At neutral pH the potential was quite stable and in the range of the corrosion potential for zinc – Figure 4.2. In the alkaline solution the potential had some fluctuations but was also in the range of zinc corrosion potential, whereas at pH 2 the high rate of zinc dissolution resulted in loss of sacrificial protection of steel after approximately one hour; dissolution of the uppermost part of the zinc

layer possibly lead to blocking of the zinc by corrosion products, causing ohmic drop between the zinc at the bottom of the gap and the outer steel; under these conditions the potential shifted up to values at which steel is active.

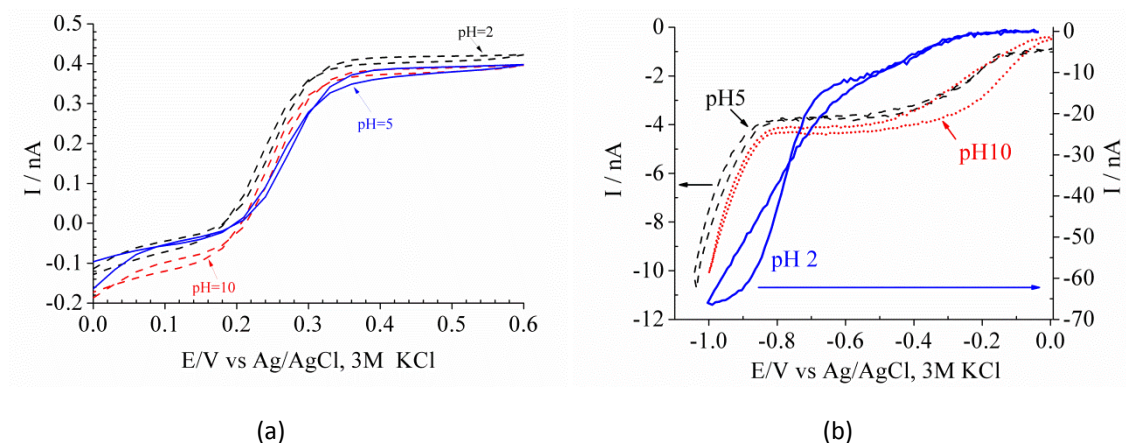


Figure 4.1. Cyclic voltammograms measured with the SECM tip in bulk 10mM NaCl electrolyte, at solutions of various pH for (a) the oxidation of FcMeOH under diffusion limiting conditions and (b) the cathodic potentials.

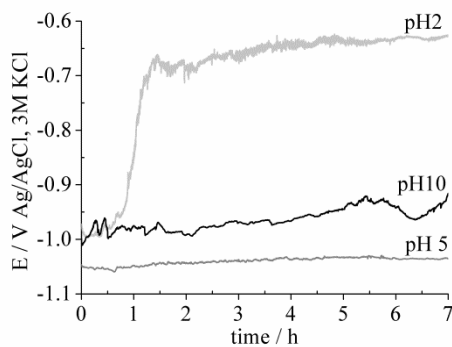


Figure 4.2. Evolution of the spontaneous potential for the cut edge samples in aqueous 10mM NaCl solution of various pH values; bulk pH is indicated next to each curve.

4.3.1 Localized measurements in acidic solution

The attack of the cut edge was revealed by intense hydrogen bubbling, which gradually became less intense and concentrated at the edges. The linear scans for the oxidation of the mediator revealed negative feedback above the resin and positive feedback over the cut edge, which means that the cut edge is conductive (i.e., the mediator is reduced at the cut edge surface at its spontaneous potential) while the resin is insulating. At short immersion times the cathodic current measured in the redox competition mode (tip potential = - 0.50 V) had a minimum over the entire cut edge which reveals depletion of the species reduced at the tip – Figure 4.3, while the curve at +0.50 V depicts a plateau extending across the cut edge. This plateau shows a current drift in the direction of the scan, which results not from tilting of the sample (the curves in the reverse direction reveal a continuous current drop), but most likely from a progressive change of the tip surface that decreases the rate of regeneration of the mediator, for example, due to adsorption of species from the solution [68, 69]. All subsequent scans showed the same trend and identical observations have been reported in previous studies [15].

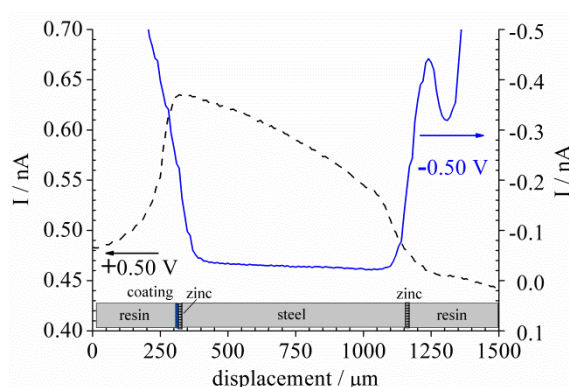


Figure 4.3. SECM amperometric line scans across the cut edge exposed to test solution of pH 2 for ~30 min exposure. Tip potential indicated in the graph.

As time elapsed, and after zinc had ceased protecting steel, a local peak in the feedback current was observed near the edge coated with an organic layer, matching a cathodic peak observed at the same location – Figure 4.4. These peaks were reproducible and their meaning is not totally straightforward. A maximum in the feedback current after some time of exposure might be explained by topography, i.e. by the development of a hill of conductive material on the surface. This hypothesis, however, seems unlikely, as the only species that might precipitate are corrosion products, which are normally not conductive and further, there were no signs of precipitates at this pH. Microscopic inspection of the cut edge at the end of the experiment has shown non-adherent corrosion products all over the steel surface, likely resulting from precipitation after removal of the electrolyte, during the drying stage. Therefore, the current profiles observed at long exposure times are probably due to corrosion activity of steel near the

gap. As expected, corrosion was quite asymmetric, with the edge at the bottom of the micrograph in Figure 4.5 corresponding to metal dissolution on the epoxy coated side.

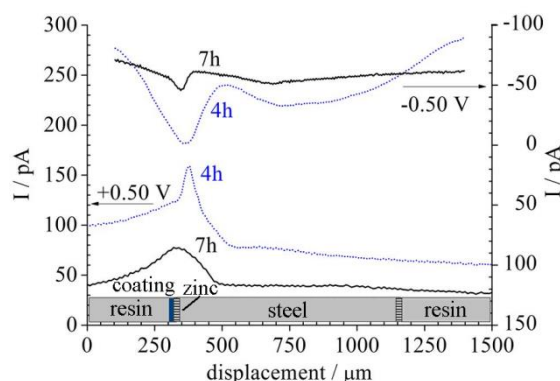


Figure 4.4. SECM amperometric line scans measured across the cut edge, in the pH 2 solution. Tip potential values and exposure times indicated in the graph.

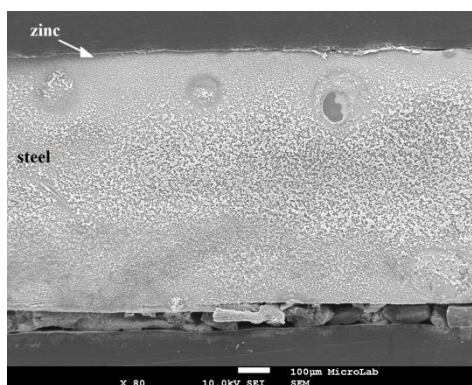


Figure 4.5. SEM micrographs of the cut edge retrieved from the test solution of pH 2 after 7 h exposure time. The side coated with the epoxy layer is located at the bottom of the micrograph.

4.3.2 Localized measurements in alkaline solution

At this potential, the thermodynamic stable forms of zinc are ZnO or Zn(OH)_2 , while iron is immune, according to their respective Pourbaix diagrams [49]. For these conditions, the cathodic currents at the microelectrode were very low and noisy and are not shown. Meanwhile, for a freshly ground cut edge immersed in solution of pH 10 and when the tip potential was set at +0.45V for the oxidation of ferrocenemethanol, the current at the tip exhibited a plateau approximately 880 mm wide, i.e., covering the entire width of the sample – Figure 4.6. The general shape of the plateau remained mostly unchanged within the first two hours, revealing no signs of heterogeneity in activity over the substrate.

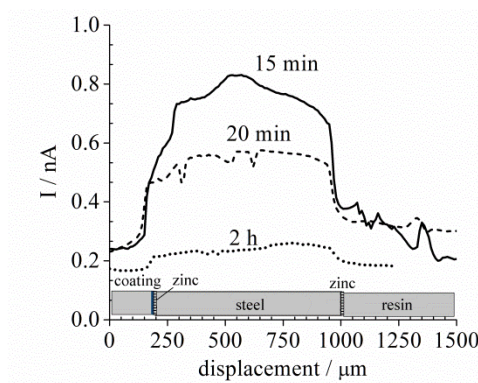


Figure 4.6. SECM amperometric line scans across the cut edge measured with the probe at an applied potential of +0.45 V. Test solution of pH 10, exposure times are indicated in the graph.

The decrease of the current in subsequent curves may result either from the precipitation of zinc oxides on the steel surface, making the surface less conductive and the tip-to-sample distance to decrease and therefore less effective in the regeneration of the mediator, or else from blocking of the tip by insoluble products, such as zinc salts or oxides. Further, the amperometric curves were obtained alternately under anodic and cathodic polarization of the UME. The cathodic polarization of the tip may cause a local pH rise within its diffusion layer, with consequent precipitation of zinc oxides at the tip. Ultimately, a local pH rise could also promote the precipitation of corrosion products at the substrate, along the line scanned by the UME.

4.3.3 Localized measurements in nearly neutral solution

The main electrochemical reactions at this pH are zinc oxidation, oxygen reduction – Eq. 4.3, and water reduction – Eq. 4.4 [65]. The amperometric line scans in Figure 4.7 reveal positive feedback for the oxidation current, in the shape of two broad peaks separated by approximately 400 μm . The width and intensity of these peaks varied with time, but still the distance between them was always below the total width of the cut edge sample (full width at half maximum = 700 μm). The spontaneous potential was nearly constant, approximately -1.05 V, even for long times; at this potential iron is immune, while zinc is active.

The zinc cations migrate towards the cathode and precipitate in rings [70, 71], ca. 200 μm from the steel-zinc interfaces, where the pH goes up by several units [65] due to the reduction of oxygen – Figure 4.8 This means that at these sites the pH is higher than on the remaining steel surface. Further, at pH above ~7, the most important forms of zinc are ZnO,

carbonates, hydroxychloride or possibly simonkolleite [49], i.e. zinc will be in a state of pseudo-passivity and therefore oxidation occurs in a relatively localized manner. The ionic current line scans obtained with the SVET are quite different from the SECM feedback currents. The SVET probe is placed at a distance from the surface that is roughly ten times larger than the probe-to-sample distance when operating the SECM, making the results more averaged.

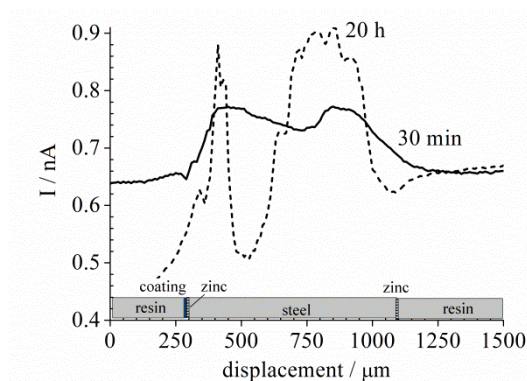


Figure 4.7. SECM amperometric line scans across the cut edge, measured with the probe at an applied potential of +0.45 V, exposed to test solution of pH 5. Exposure times are indicated next to the respective curve.

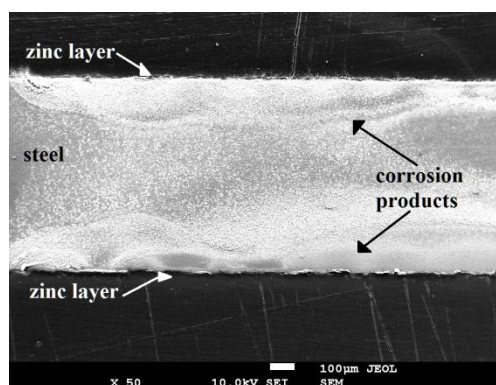


Figure 4.8. SEM micrograph of the cut edge exposed to test solution of pH 5 taken at the end of the experiment.

Arbitrary line scans measured with the SVET across the sample and depicted in Figure 4.9 distinguish clearly two narrow anodes and one central cathode. The cathodic plateau is approximately $\sim 500 \mu\text{m}$ wide and corresponds to the steel, while the narrow anodes correspond to zinc. After the first hour, the zinc anode on the right side becomes inactive and only the other zinc edge, corresponding to the side with the organic coating remained anodic.

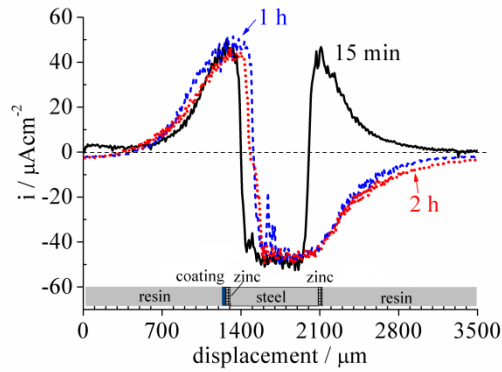


Figure 4.9. Ionic current density profiles measured with the SVET over the cut edge exposed to test solution of pH 5 for various exposure durations (indicated in the graph).

4.4 Discussion

One major issue of this study is the solutions bulk pH and its variations at microscopic level, at the surface of the cut edge. The solutions used were not buffered and so the pH will change within the diffusion layer of the cut edge as a consequence of local reactions at the substrate. The pH on the steel surface can increase by several units, from natural pH (~5) to 10, as shown by other authors [60, 62, 67]. Further, although steel is covered by a native oxide layer in atmospheric conditions, the cathodic polarization caused by zinc brings it down to a region of thermodynamic immunity. Reduction of the native oxide layer may then occur, providing a clean conductive surface effective in the regeneration of the mediator. In the alkaline solution the local pH is not expected to increase significantly when compared to the bulk value. The corrosion kinetics should be slow, with zinc dissolution taking place very much like in the neutral solution, i.e., in a localized manner, while steel is immune. The feedback current is very low and decreases rapidly, possibly due to blocking of the tip, and consequently measurements could only be performed for relatively short exposures.

In the acidic solution, the reduction of H^+ and of H_2O takes place on steel and contributes to alkanisation in the vicinity of the surface. At the free corroding potential of the sample, steel is expected to be immune for a wide range of pH, whereas zinc is active up to neutral pH. As the electrolyte becomes less acidic, reduction of O_2 becomes the main reaction on steel while HER is the main cathodic reaction in the vicinity of the zinc. The evolution of molecular hydrogen was visible at the sides of the sample during the whole duration of the experiment, meaning that the reduction of water proceeds on the zinc layer, or at least in its close proximity, where the pH is lower [62]. Although the equilibrium potential for water reduction is -0.49 V at pH 5 and -0.32 V at pH 2 [49] and thus the reduction of water at the tip biased to -0.50V cannot be excluded, the plateau observed in the voltammograms, indicates that the reduction current at the tip

corresponds mostly to reduction of dissolved oxygen. The shape of the amperometric scan lines revealed uniform distribution of the cathodic reaction over the steel surface in a first stage, whereas after the loss of protection, the cathodic process became localized near the active edge. At this stage, i.e., when the free corroding potential becomes shifted to the potential of corroding iron, the pH is likely to decrease again, as the production of OH^- ions occurs at a lower rate. The small maximum in the feedback current reveals a minor peak in the anodic scan lines, probably due to regeneration of the mediator, although some contribution from the oxidation of dissolved Fe^{2+} ions emitted from the active steel surface cannot be excluded [30,72].

In nearly neutral medium, the two maxima in feedback current were clearly located above the steel, at some distance from the edges. At this pH only the zinc is dissolving and corrosion products precipitate in specific regions, between the zinc, where the pH is acidic and the steel centre, where the pH becomes more alkaline. These maxima cannot reveal topographic effects, because the materials that accumulate on the surface are corrosion products, thus not conductive. The accumulation of zinc oxides on steel has been observed not at the steel/zinc interface, but rather a few micrometers away from that interface, thus leaving a narrow area of bare steel [57,72]. This correlates well with the pattern of ferrocenemethanol feedback current, with maxima located on each side of the sample. The maximum in the feedback current should then be located adjacent to the corrosion products. In order to compare the sensitivity of SVET and the SECM for the zinc, profiles obtained with both techniques after ~15min exposure in pH 5 are presented in Figure 4.10. The plot evidences good agreement and complementarity of the two techniques, as the distribution of ionic currents in solution measured with the SVET matches the locations for regeneration of the redox mediator employed in SECM. Ionic currents arising from the cathodic reaction were rather uniform above the steel centre, in the region limited by the corrosion products. The disappearing of one anode is explained by the localized character of zinc corrosion. The location for positive feedback currents in SECM was also above the steel, with the highest values located in the proximity of the interfaces between the corrosion products and the steel surface, where the density of current lines and the pH gradients are higher.

The step size employed in these measurements was $10\text{ }\mu\text{m}$ for both techniques and, despite the probe size being in the same order of magnitude as the zinc layer thickness, the location of the anodes was unambiguously established using the SVET while it could not be resolved by the SECM. In the SVET, the lateral anodes and the central cathode are clearly identified and the width of the cathode (estimated from the distance between the two zero current points) is $\sim 605\text{ }\mu\text{m}$, which corresponds to 75% of the actual steel thickness. The position of the microprobe, $100\text{ }\mu\text{m}$ above the surface, together with its large size ($20\text{ }\mu\text{m}$) results in

some attenuation of the signal. Therefore heterogeneities on the steel surface due to the accumulation of zinc corrosion products could not be resolved. Comparatively, the SECM uses a smaller probe and the distance to the substrate was only $\sim 20\text{ }\mu\text{m}$. Attenuation is therefore smaller and the fluctuations on surface reactivity more significant. The size of the UME is similar to that of the zinc electrodes and about ten times smaller than the steel, therefore the information on the zinc cannot be satisfactorily resolved as the feedback current measured at the sides of the cut edge will be masked by the higher currents measured close to its centre. Therefore the measured currents correspond to the steel (almost) exclusively. This is a difficulty when studying a cut edge configuration, compared to a galvanic couple with cathode/anode separation. Further research is necessary to clarify the microscopic processes occurring on zinc.

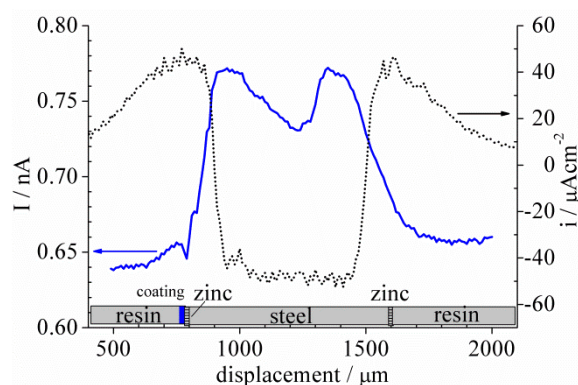


Figure 4.10. Profiles of ionic current density (SVET) and feedback current (SECM) for the cut edge exposed to test solution of pH 5. Plots are reproduced from Figures 4.7 and 4.9.

4.5 Conclusions

Imaging of cut edge corrosion using SECM and the SVET provided information on the conductivity and the evolution of the electrochemical reactions on the surface. The anodic activity on the thin zinc electrodes was identified only by the ionic currents provided by the SVET, whereas the feedback current for the oxidation of FcMeOH, used as mediator, provided information on the steel surface. The interpretation of the processes in each environment took into account the variations of the pH due to local electrochemical reactions. Measurements in alkaline medium showed homogeneous conductivity of the steel surface during the experiment duration. In acidic solution, the depletion of the cathodic reactant at the surface revealed uniform distribution of the cathodic reaction in a first stage, followed by a localized cathode once the galvanic protection was lost. This depletion of the cathodic reactant perfectly overlapped the region with capability for regeneration of the electrochemical mediator, i.e., the

conductive region. Non-uniform conductivity of the steel surface at nearly neutral medium correlates well with the heterogeneous accumulation of zinc corrosion products.

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5. Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in nearly neutral chloride solutions

This chapter is a research paper with the same title published in Corrosion Science. All experiments were performed and interpreted by the author of this dissertation except SVET/SIET which were performed by Maryna Taryba and HydraMedusa simulation which was performed by Dr. Svetlana Lamaka. The author acknowledges the collaboration and important discussions with these scientists concerning the interpretation of pH measurements.

Abstract

A model cut edge consisting of a zinc anode and a split iron cathode was used for studying corrosion mechanisms and assessing the suitability of scanning electrochemical techniques for corrosion studies at the microscale. Scanning electrochemical microscope (SECM), localized electrochemical impedance spectroscopy (LEIS) and scanning vibrating electrode technique coupled with the selective scanning ion-selective electrode technique (SVET/SIET) were applied. The corrosion products precipitated on the cathode once the critical pH and solubility limits were reached, which resulted from the diffusion of hydroxyl and zinc ions across the cathode. In nearly neutral chloride solutions there was no evidence of self-healing by the corrosion products.

Keywords: A. Iron; A. Zinc; B. EIS; C. Cathodic Protection

5.1 Introduction

Electrogalvanized steel sheet offers a cost effective and versatile solution for lightweight and weldable structures and has become the material of election for the production of automobile body parts [1, 2]. The key to its success lies on the good corrosion resistance of zinc in neutral atmospheric conditions, which results from the formation of insoluble basic salts that provide a reasonable protection, together with its sacrificial protection when steel becomes accidentally exposed [3,4]. The application of just a few micrometers of zinc results in significantly improved corrosion resistance, which becomes further reinforced by the

application of organic coatings [5-7]. Despite the remarkable improvement achieved by this composite system, the vulnerability of cut edges is a major problem [8], particularly in coil coated steel [5-7]. This results from the formation of a galvanic couple with a high electromotive force due to an unfavourable anode-to-cathode area ratio. The steel surface remains intact as long as there is enough zinc to ensure cathodic protection, although exposed zinc may dissolve at high rate from the cut edge, causing anodic undermining and delamination of the organic coating and consequently leading to aesthetic damage of the car part [9,10].

Although apparently simple, the corrosion in this galvanic system involves a number of reactions that can strongly vary along the surface. In aqueous environments of neutral pH, zinc dissolves into the solution (Eq. 5.1), whereas steel provides an interface for the cathodic reduction of both water (Eq. 5.2) and oxygen (Eq. 5.3), thus causing local alkalisation of the electrolyte in the vicinity of the cathode [11, 12].



At neutral pH (< 7 – 8), the dissolved Zn^{2+} may react with H_2O , producing zincyl ion (ZnOH^{+}), Eq. 5.4, whereas at pH 8 - 11 zinc cations become insoluble and precipitate above the steel as $\text{Zn}(\text{OH})_2$ (Eq. 5.5) and ZnO (Eq. 5.6) [11-14]:



Bonk et al. [15] identified both ZnO and $\text{Zn}(\text{OH})_2$ under neutral bulk pH and suggested that for increasing pH values, Cl^{-} present in solution diffuse into this layer and react with the cations to form zinc complexes, resulting in a porous layer with a $\text{Zn}(\text{OH})_2$ matrix. Complex species have been identified in the presence of contaminants, like carbon dioxide or chloride ions favouring the formation of hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), or of simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$), respectively [16,17].

The precipitation of the zinc-rich products on the steel surface is likely to interfere with the local chemistry and reactions. Local alkalisation near the steel surface on a cut edge configuration has been reported by Ogle et al. [18], who found values between 9-10 at the

centre of the steel plate and a nearly constant pH ~ 8 above the corrosion products precipitated on steel, whereas a nearly neutral pH was registered above zinc. Further, mapping of the ionic current density has led to the identification of hindered cathodic activity on the steel, on a thin region close to the zinc anode [19] and this was explained by the presence of a thin insulating film [20]. The transport of ionic species is thus essential in this process; according to Tada et al. [21-23], the transport of zinc cations is confined to a 1 mm thick layer of solution above zinc and part of the steel, corresponding to the lowest pH regions; away from the anode, at the highest pH regions, Zn^{2+} was nearly absent, whereas the boundary region, of intermediate pH values, was characterized by the precipitation of zinc cations as insoluble species.

Padilla et al. [24] and Krieg et al. [25], in line with previous work from Tanaka et al. [26], propose that, further to the barrier effect of zinc corrosion products, interaction of Zn^{2+} with iron oxides may cause inhibition of the cathodic reaction by suppressing the crystallization and growth of $\beta - \text{FeOOH}$. In recent publications, Ogle et al. [27-29] reported inhibition of the cathodic reaction on iron in the presence of synthetic simonkolleite, which was lost at strongly alkaline pH upon conversion of simonkolleite to either hydrozincite or zinc oxide, which revealed lower cathodic inhibition. Mouanga et al. [30, 31] found evidence that corrosion products in NaCl and NaOH solutions did not suppress cathodic reaction and instead supported the theory of a synergistic effect of iron and zinc cations as proposed by Tanaka et al. [26].

The research on cut edge corrosion has gained momentum with the development of electrochemical scanning techniques. These techniques provide enhanced lateral resolution and consequently the possibility of measuring small variations in the electric fields and local distribution of ionic currents, as revealed by the pioneer work from Isaacs et al. [32] and the later developments of Worsley et al. [33], Zou et al. [34] and Thébault et al. [19] to cut edge corrosion. Further to those studies, mapping of pH using a tungsten solid electrode over cut edges and model systems has provided useful information as it revealed strong pH gradients over the cathode [18, 21, 35]. The pH and zinc concentration gradients have been further studied by the use of scanning electrochemical microscopy (SECM) with antimony and mercury microelectrodes by Souto et al. [35-37] and with an ion-selective micro-electrode (ISME) by Terryn et al. [38]. In previous studies from our own group, the ionic current distribution was studied using the SVET [39] and the SECM [40] and cathodic inhibition was associated to the presence of zinc corrosion products; nevertheless, limitations of the SECM due to precipitation of zinc corrosion products on the microprobe surface was reported. More recently, mapping of the conductivity of a cut edge based upon the feedback current of regeneration of a redox mediator suggested a correlation with the distribution of zinc corrosion products [41]. Localized

electrochemical impedance spectroscopy (LEIS) has also been applied to the study of galvanic systems. Mouanga et al. [42] used a disk-type concentric steel-zinc electrode and concluded that the local ohmic impedance was highly affected by the radial position of the probe, while a local current maximum observed at the zinc/steel interface revealed localized corrosion.

Despite the enhanced spatial resolution of these techniques, the actual lateral resolution when it comes to cut edge corrosion is hard to establish, because of the small electrode size and of the direct contact between anode and cathode, which results in large gradients of current, potential and pH. Attempts to overcome this limitation have been made using numerical modelling to simulate current [19, 43] and pH distributions [13]. An alternative to overcome the resolution problem is the use of model systems with enlarged dimensions and physically separated anodes and cathodes. Ions spread over a larger area, making the concentration, current and pH gradients smoother and more easily detected by the microprobes. Bearing this in mind, we have designed a model for a single side coated cut edge, in which zinc is separated from iron by a thick resin layer; further, the iron is split in two halves, located on the same side of the anode. With this asymmetric geometry, we expect to prevent any influence of the signal from zinc on the measurements made over iron, allowing an improved resolution of cathodic and anodic regions. The discontinuity of the cathodes should allow for a better separation of the response from the regions covered and uncovered by zinc corrosion products.

5.2 Experimental

5.2.1 Electrodes and electrolytes

Samples cut from an iron plate with 1 mm thickness and a 50 μm thick zinc foil, both with purity 99.95% (Goodfellow, Cambridge, U.K) were employed as electrodes for building the model cut edge. The model consisted of two iron electrodes and one single zinc electrode, parallel to one another and all mounted on an epoxy resin sleeve - Figure 5.1. The working surface of the mount was polished with silicon carbide paper under ethanol until 1000 grit finish, then rinsed in ethanol and dried under blown cold air. The last polishing step was made along the direction of the iron-zinc interface to minimize spreading of zinc onto the iron surface. Electrical connection between the metals was established through an external circuit in the rear of the mount, consisting of copper wires joined to the electrodes with conductive silver paint (SPI® Supplies, USA). A small electrochemical cell was built by surrounding the epoxy sleeve with

adhesive tape and filling it with ca. 3.5 mL of electrolyte. All experiments were carried out in a quiescent 10 mM NaCl electrolyte with conductivity $k = 1088 \mu\text{S}$ at 22.5°C . The pH and conductivity of the solutions were measured using a PC 700 meter (Eutech Instruments, Singapore). Deionised water (MilliPore, $\rho > 18 \text{ M}\Omega \text{ cm}$) and analytical grade chemicals from Sigma-Aldrich were employed.

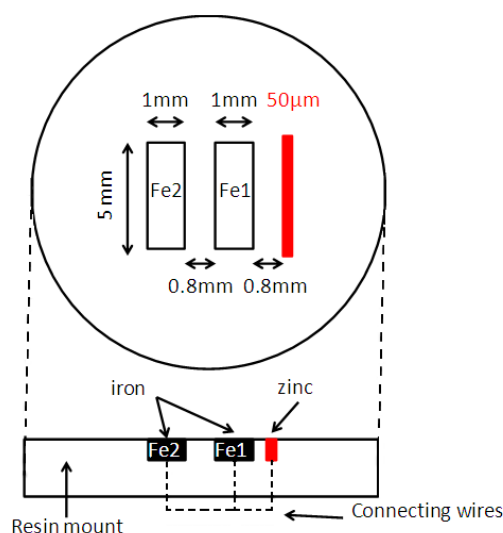


Figure 5.1. Schematic diagram of the model cut edge. The electrodes are identified as Fe2, for the iron electrode at the left and Fe1 as the iron electrode at the centre.

5.2.2 Corrosion monitoring

5.2.2.1 Potential-time DC curves

Open circuit potential was monitored using an ACM Field Machine (ACM Instruments, U.K.) and ACM software v5. A KCl-saturated calomel electrode (SCE) was used as reference. *In-situ* image recording of the cut edge model was performed using a DMS300 digital microscope system (Leica Microsystems, Switzerland).

5.2.2.2 Scanning electrochemical microscopy (SECM)

An electrochemical interface connected to a M370 workstation (Uniscan Instruments, U.K.) equipped with a piezoelectric motor positioning system was used for characterization of

surface topography/conductivity and oxygen depletion in the vicinity of the model. The system was operated in a three-electrode configuration, with the galvanic couple at its free potential in the test solution. The SECM probe (the working electrode) consisted of a platinum disk of 10 μm diameter sheathed in a conical glass rod and the cell was completed with a platinum mesh counter electrode and the SCE as reference. The experiments were performed at room temperature under natural aeration in a 0.5 mM ferrocenemethanol (abbreviated as FcMeOH, supplied by Sigma-Aldrich, 97%) and 10 mM NaCl (99%) solution. The operating height was set after recording z-approach curves with the tip approaching the resin surface until the current dropped to 30% of the limiting current value; subsequently, the tip was withdrawn to a level estimated as $\sim 20\ \mu\text{m}$ away from the surface. Although the ideal working distance should be in the range of the tip diameter or less, by proceeding in this way the sample was kept inside the diffusion layer of the probe, while preventing bumping against any corrosion products on the surface. Linear scans were made at constant height and at a scan rate of $0.5\ \mu\text{m s}^{-1}$. Measurements were performed by operating in sequence the feedback mode and the competition mode, with 60s conditioning of the tip at the adequate potential before starting the scan. The two operating modes are described below.

Feedback mode: this mode was used for the identification of the conductive regions and topographic features on the surface of the model system. It is based upon the variations of the diffusion limiting current at the probe due to reactions involving a redox mediator brought into the vicinity of an electroactive surface. The limiting current at the tip will increase if the (conductive) sample surface is able to regenerate the mediator or decrease if the (insulating) surface cannot regenerate the mediator [44]. The ferrocene / ferrocenium (FcMeOH/ FcMeOH⁺) couple was the mediator chosen for this work; its reversible potential is + 0.216 V, well above the free corroding potential of the cut edge [45]. The voltammetric curve of the ultra-microelectrode (UME) in the working solution - Figure 5.2 a - gave a typical sigmoid shape for the oxidation of FcMeOH to FcMeOH⁺. The tip potential $E = + 0.40\ \text{V}$ in the diffusion plateau, was chosen for the amperometric studies.

Competition mode: in this mode the tip and the sample compete for the reduction of oxygen within the diffusion layer of the cathode. Among the species available in solution (Na⁺, Cl⁻, O₂, H₂O, H⁺, Zn²⁺ and FcMeOH), only molecular oxygen and water can become reduced at moderate polarizations, but reduction of H₂O occurs at higher cathodic polarizations. Based

upon the voltammogram in Figure 5.2 b, a potential of -0.50 V was chosen for the detection of oxygen depletion.

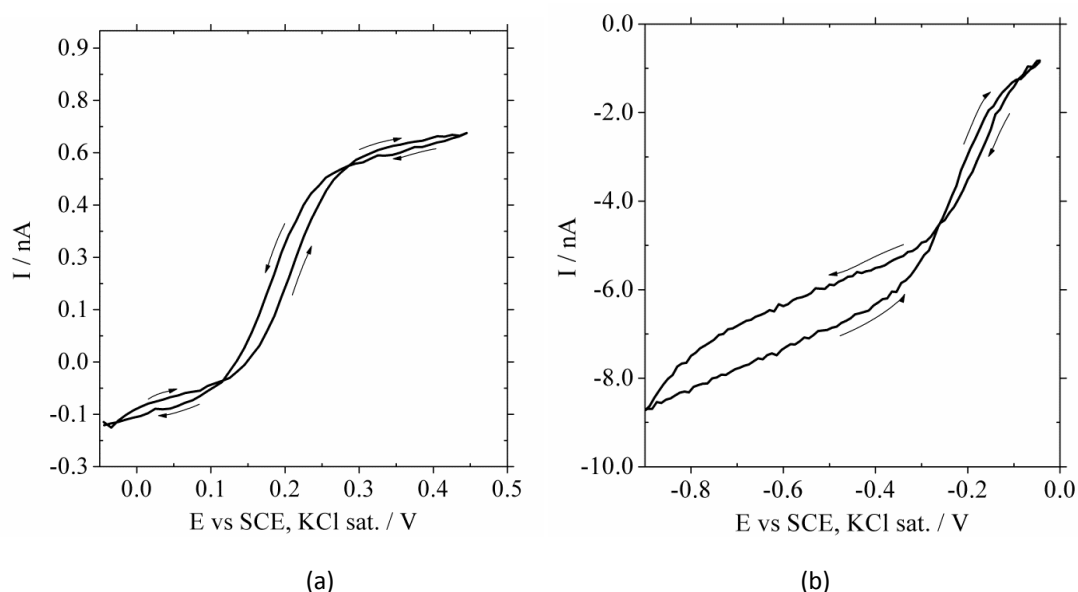


Figure 5.2. Voltammograms obtained with the UME in bulk solution for (a) the oxidation of FcMeOH and (b) oxygen reduction. Scan rate 20 mVs⁻¹.

5.2.3 Localized electrochemical impedance (LEIS) measurements

LEIS was performed with a M370 electrochemical workstation (Uniscan Instruments, UK) coupled to a 1286 potentiostat and a 1250 frequency response analyzer (both by Solartron Analytical, UK). For full spectrum analysis, the applied potential amplitude was 10 mV and frequencies ranged from 10 kHz to 1 Hz, at seven points per decade. The commercial bi-probe (Uniscan Instruments, U.K.) consisted of a 10 μm disk embedded at the bottom of a conical insulating holder and a platinum ring wire around it, placed at a distance of 1.5 mm. With this geometry, the probe measures the ionic currents along a direction which is displaced by $\sim 30^\circ$ from its axis. A platinum mesh counter electrode, a SCE reference and the galvanic model completed the cell. Local impedance [46] is determined as the ratio between the amplitude of the excitation potential applied to the sample (ΔV) and the local a.c. current (i_{loc}). The local current is computed from the a.c. voltage measured on the bi-probe ($\Delta \tilde{V}$), the electrolyte conductivity (k) and the separation between the two electrodes of the bi-probe (d), Eq. 5.7.

$$Z_{loc} = \frac{\Delta V}{i_{loc}} = \frac{d \Delta V}{k \Delta \tilde{V}} \quad \text{Eq. 5.7}$$

Local impedance spectra were measured with the tip positioned at the centre of each plate, whereas single-frequency scans (1 Hz) were performed by moving the bi-probe by steps of 127 μm across the model sample. The time taken for each line scan was c.a. 15 minutes. Results are presented using admittance modulus ($|Y|$), given by:

$$|Y| = \frac{1}{|Z_{\text{loc}}|} \quad \text{Eq. 5.8}$$

The capacitive component of impedance was treated using the constant-phase-element (CPE) approach [47], whose impedance is given by:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad \text{Eq. 5.9}$$

In Eq. 5.9, Y_0 is the frequency-independent term, ω is the angular frequency and the exponent n takes the value 1.0 for a pure capacitor and is null for a pure resistor.

5.2.2.4 Scanning Vibrating Electrode Technique (SVET) and Scanning Ion-selective Electrode Technique (SIET)

Commercial equipment manufactured by Applicable Electronics and controlled by ASET software was used to perform both the SVET and the SIET measurements. A dual head stage manipulator (Biomedizinische Geräte, Germany) was mounted on a 3D stepper motor system and used for precise positioning a vibrating probe (VP) and a pH sensing microelectrode (pH-SME). The vibrating probe was an insulated Pt-Ir microelectrode (MicroProbes, U.S.) with a $16 \pm 2 \mu\text{m}$ diameter Pt-black sphere deposited on the exposed metal tip. The probe was placed above the sample and vibrated in the vertical (z) and horizontal (x) directions, at 124 Hz (z) and 325 Hz (x) and with 34 μm amplitude.

The pH was measured using ion-selective microelectrodes (ISMEs) made of a silanized glass-capillary with a tip orifice diameter of $1.8 \pm 0.2 \mu\text{m}$, filled with a selective ionophore-based oil-like membrane and back-filled with an inner reference solution. Hydrogen Ionophore I-Cocktail B (Ref. 95297) of Selectophore grade (from Fluka) was used as a liquid pH-membrane. The column length of the membrane was $\sim 60 \mu\text{m}$. The pH-SMEs were calibrated using commercial pH buffers of pH 5.0, 7.0 and 9.0 with the adequate background concentration of NaCl (0.01 M). Microelectrodes showed a Nernstian slope of $-58.0 \pm 0.6 \text{ mV/pH}$.

The distributions of current density and pH were recorded quasi-simultaneously [46]. Each line scan had a length of 7545 μm and a step size of 49 μm and the time required for each scan was c.a. 12 minutes. The vibrating probe and pH-SME were positioned at a fixed height of 50 and 100 μm above the surface, respectively and the distance between probes was kept as $50 \pm 5 \mu\text{m}$ in the vertical plane and $30 \pm 5 \mu\text{m}$ in the horizontal plane [48]. The aqueous solutions were prepared with pro analysis grade salts and using de-ionized water (MilliPore, $\rho > 18 \text{ M}\Omega \text{ cm}$) and all measurements were performed in a 0.01 M NaCl pH neutral solution, using an Ag/AgCl reference mini-electrode with agar-stabilized 0.05 M NaCl salt bridge. The cell was kept in a Faraday cage at ambient temperature ($26 \pm 2 \text{ }^\circ\text{C}$).

5.3. Results

Corrosion of the galvanic couple occurred with precipitation of white corrosion products over iron. This precipitate was dense along a well-defined line and became diffuse, with a lower coverage and an apparently rougher morphology, away from the anode. The precipitate became visible in the inner cathode (Fe1) within the first 30 minutes of immersion, Figure 5.3 a-c, whereas the outer cathode (Fe2) remained clear of corrosion products for most of the duration of the experiment. The precipitate was rich in zinc and oxygen (Figure 5.3 d) and therefore it can be explained by the diffusion of zinc cations across the galvanic cell and by their subsequent precipitation over the cathode. The location of the precipitates was however surprising, as they were not visible at the edge, where the cathodic current should be maximum (due to a lower electrolyte resistance) but rather at the centre of the plate. This distribution is very similar to that observed on cut edges in our previous work [41] and also in the work from Thébault et al. [19], irrespective of the geometric differences, i.e., of the wide insulating surface separating the cathode and the anode. For zinc ions to remain soluble, the pH at the edge must therefore remain below the critical value given by the solubility product of $\text{Zn}(\text{OH})_2$, which is $K_{sp} = 2.66 \times 10^{-15}$ [49], i.e., precipitation cannot occur at pH lower than 9.21 [11] at trace concentration of zinc $\sim 10^{-5} \text{ M}$.

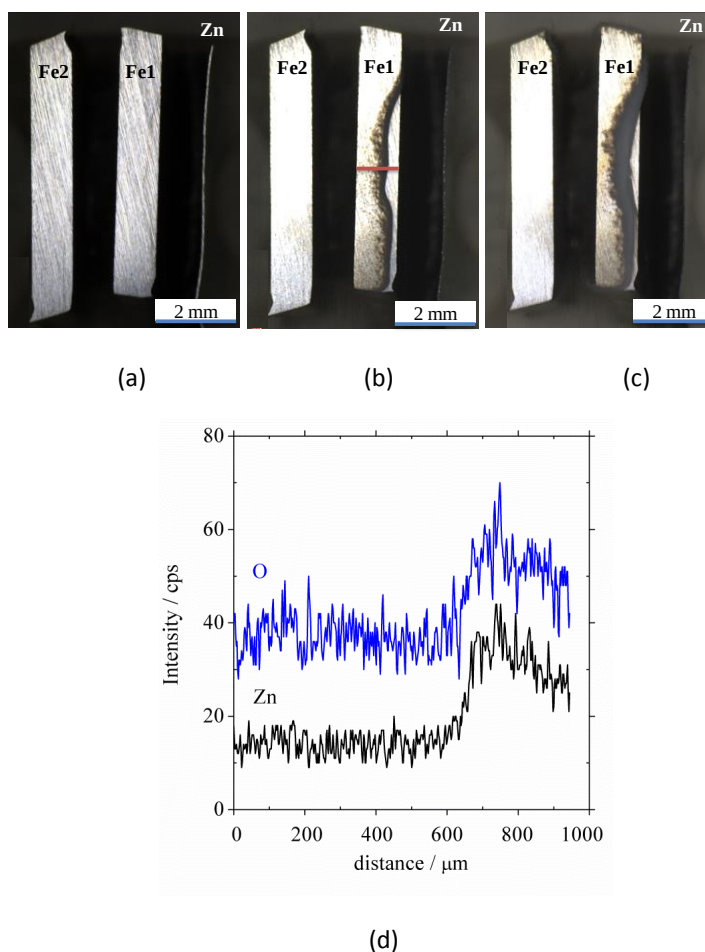


Figure 5.3. Optical micrographs of immersed sample at (a) 30 min, (b) 7h, (c) 24h and (d) *ex-situ* elemental EDS analysis measured across a line in Fe1 as marked in (b) after 7h.

The free corrosion potential of the galvanic couple, Figure 5.4, went through a minimum as the native oxides became dissolved and afterwards took a fairly steady value with some fluctuations resulting probably from the establishment of concentration gradients and formation of corrosion products. The total variation in the first seven hours was below 20 mV and after 24 hours the potential was relatively stable around -1.01 V, which is typical for zinc dissolution occurring under oxygen diffusion control [29, 50].

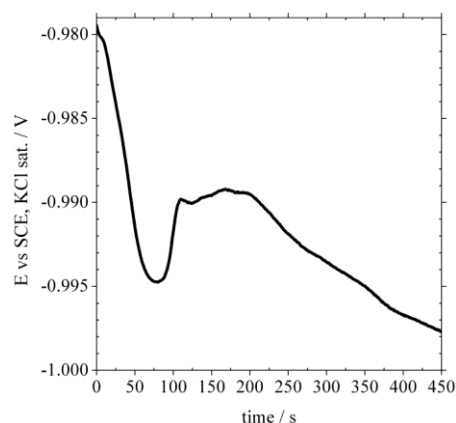


Figure 5.4. Free corrosion potential of the model cut edge in 10 mM NaCl.

5.3.1. Local Electrochemical Impedance Spectroscopy, LEIS

The local impedance spectra measured over each of the three electrodes show in some cases an inductive loop at the high frequencies, Figure 5.5. This loop was clearly observed on the zinc electrode and also on the remote cathode, but not in the inner iron electrode, possibly because of a smaller geometrical distortion of the ionic flow [42]. The high frequency portion of the spectra is resistive, whereas at frequencies below ~ 100 Hz a capacitive slope is observed, which corresponds to $Y_0 = 10^{-4} \text{ Fcm}^{-2}\text{s}^{n-1}$ (with $n = 0.85$) for both Fe1 and Fe2 and $Y_0 = 10^{-3} \text{ Fcm}^{-2}\text{s}^{n-1}$ (with $n = 0.89$) on zinc. Comparable values have been reported in the literature for the zinc dissolution process [16]. In this frequency range, a charge transfer resistance of $10^2 \Omega\text{cm}^2$ can be extracted from fitting of the spectrum over zinc, but not on the iron cathodes. A fixed frequency of 1 Hz was chosen to perform linear scans, as the low frequency range is associated with the corrosion processes. The admittance profiles reveal a well defined maximum on zinc and on the remote cathode, while on the inner cathode the admittance started at very low values and consistently increased with time - Figure 5.6. This trend was the opposite to what should be expected considering the progressive precipitation of corrosion products on the inner cathode; i.e., the progressive precipitation of zinc corrosion products is accompanied not by a decrease but rather by an increase of admittance.

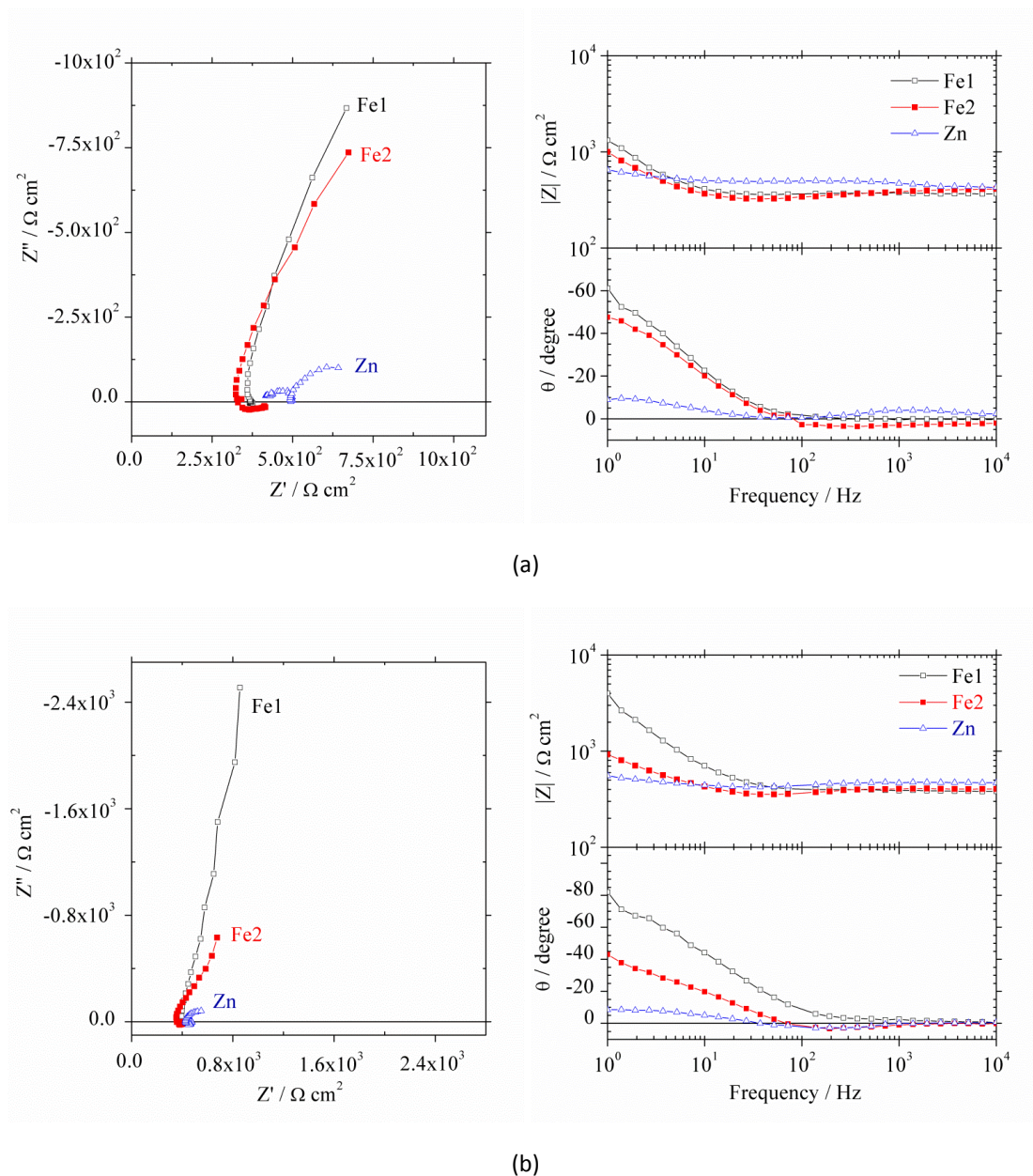


Figure 5.5. Local impedance spectra measured at the centre of each electrode (a) in the first hour of immersion and (b) after 24 hours.

5.3.3 Amperometric measurements with the SECM

The current at the tip showed a significant drift which was time related, such that the local currents near the surface easily became smaller than the limiting current (measured in bulk solution immediately before each scan), resulting in an apparent negative feedback across the entire sample. The z-approach curves (not shown) revealed a variation that effectively corresponds to negative feedback above the resin and positive feedback over the iron electrodes, which are observed as two sharp plateaux with width (FWMH $\approx 1050 \mu\text{m}$) and

position in good correspondence with the two cathodes. Representative line scans recorded with the tip biased at +0.40 V for the oxidation of the mediator along an arbitrary line across the sample are presented in Figure 5.7 a, using the raw current values. Apart from the variation in the base line, the shape of the feedback profiles is quite stable (the current increase after 24 hours resulted from electrochemical cleaning of the tip). The current profile measured over the remote cathode is uniform and shows a flat electrode with homogeneous conductivity/topography along the surface, while the inner cathode reveals local minima which are reproducible between scans. The signal for the zinc anode is residual, which is not surprising given the small size of the electrode and its recession due to dissolution.

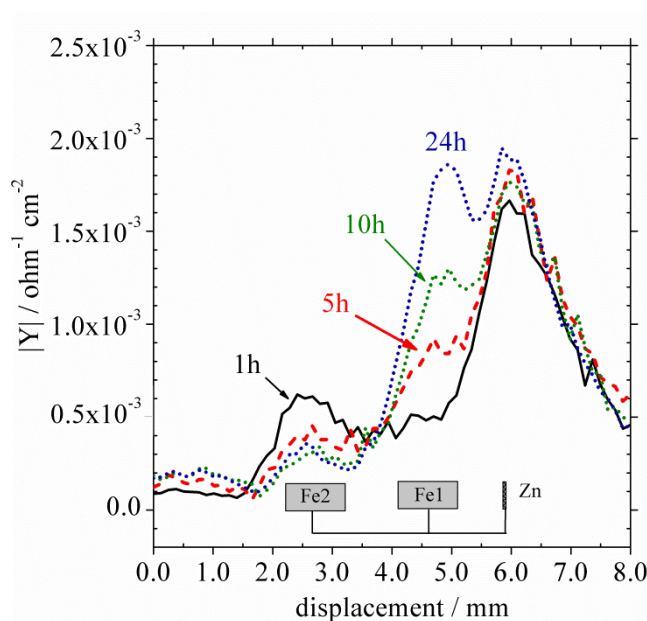


Figure 5.6. Admittance profiles measured at 1Hz across the model for various exposure times; scan direction from left to right.

Amperometric sensing of dissolved oxygen revealed a drop of the reduction current to nearly zero at the remote cathode, with the probe biased at -0.50 V, which is consistent with a significant and uniform depletion of oxygen. This depletion was also observed on the inner cathode, although in a less uniform way - Figure 5.7 b. On the zinc electrode there was no sign of depletion, mostly because the local alkalinisation at the tip determined by the cathodic reaction causes precipitation of zinc products on the platinum and consequent blocking of the tip. These zinc products became re-dissolved upon conditioning of the tip at an anodic potential.

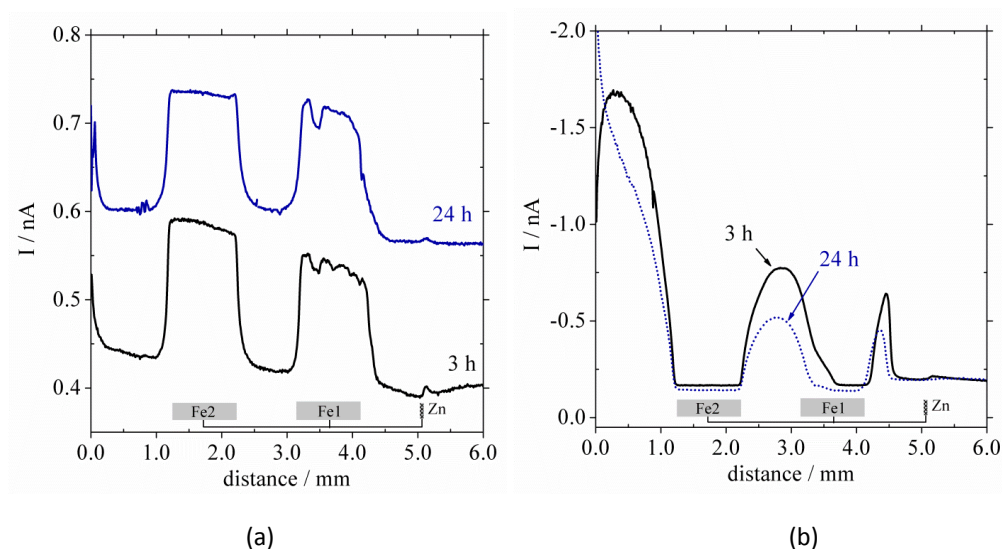


Figure 5.7. SECM line scans measured with tip biased at (a) +0.40V and (b) -0.50V. Scanning was performed from left to right. Immersion times are indicated next to the respective curve.

5.3.4 Ionic currents and pH distribution

The ionic current and the pH distribution measured by the SVET and the SIET are depicted in Figure 5.8. The ionic current profile reveals a single anode corresponding to zinc ions diffusing from the source of positive current flow, whereas the shape and size of the cathodes are in good agreement with the position of the iron plates and the current corresponds to an upward flow of OH^- anions, i.e. negative current.

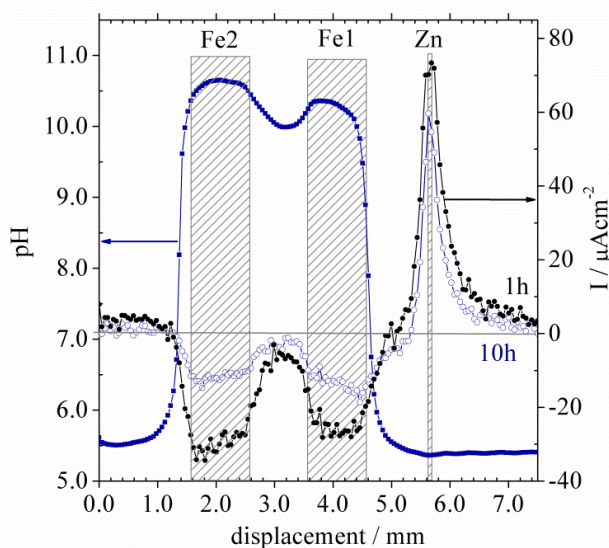


Figure 5.8. SVET/SIET line scans measured as the tip travelled over the model cut edge. The SVET curves are for 1h and 10h exposure and SIET for 10h; ionic currents estimated at $k = 1088 \mu\text{S}$.

Despite the noise associated with the measurements, the two cathodes are well resolved, i.e., they are separated by a region of nearly zero current, corresponding to the resin. The currents gradually decreased with time, although identification of the corrosion products or detection of local cathodic inhibition due to their presence was not possible.

The bulk pH measured with the ISME was ~5.5 and identical to the measurement performed with the pH meter before starting the experiment. On zinc there was no sign of acidification that could result from local hydrolysis, whereas a strong alkalisation on the cathodes was detected, with the pH reaching 10.5. A slightly lower pH was observed at the inner cathode, likely due to the consumption of OH^- in the precipitation process. Further, the insulating region between the two cathodes also reached a high pH as a result of the flow of hydroxyl ions from the remote cathode. Naturally, these values are measured at some distance from the surface and even higher values on the surface can be expected; in a point measurement made with the tip touching the iron, a pH value of 11 was recorded, which is roughly 0.5 pH units higher than the value measured at a distance of 50 μm from the surface.

5.4. Discussion

The cathodic reaction caused a very strong alkalisation from bulk pH 5.5 to pH 10.5 and reaching 11 at the very surface of the iron. Taking $\text{Fe}(\text{OH})_2$ as the passivating species, the reversible potential (for Eq. 5.10) at pH 11 is -0.941 V [11], which is above the measured mixed potential of the system.



This means that, although iron spontaneously becomes passive in alkaline and naturally aerated aqueous solutions, at the spontaneous corroding potential measured for the model cut edge, iron is cathodically polarized into its region of thermodynamic immunity, with a conductive surface exposed and available for the reduction of water and oxygen. While the primary cathodic reaction is the reduction of oxygen occurring under diffusion control, the potential for the reduction of water at pH 11 is -0.894 V (vs. SCE), i.e., above the spontaneous potential of the system. This means that the reduction of water will occur both on steel and on zinc. Thermodynamically, it is more favourable on zinc, where it will occur as a side reaction; on

iron, the alkaline pH makes it less favourable and thus the reduction of oxygen will be more important.

Meanwhile, the solubility of zinc ions at pH 5.5 is very high [51], as given by the equilibrium concentration for Zn^{2+} with $\text{Zn}(\text{OH})_2$:

$$\log[\text{Zn}^{2+}] = 12.26 - 2\text{pH} \quad \text{Eq. 5.11}$$

This means that zinc ions cannot precipitate on zinc, but instead diffuse along the surface and migrate towards the cathodes [22, 23, 13]. Hydroxyl ions resulting from the cathodic reaction counter-diffuse in the direction of the anode, as confirmed by the alkalisation of the electrolyte between the two cathodes. These ions react with the zinc cations, which act as a barrier to the diffusion, and form $\text{Zn}(\text{OH})^+$ or $\text{Zn}(\text{OH})_2$.

The precipitation sites were observed not at the edge of the cathode, but rather at a distance of $\sim 150 \mu\text{m}$. This location is remarkably similar to that of a cut edge [41] despite the different geometry of the sample under study. Naturally, the pH and zinc cation concentration dictate precipitation and interpretation of the stability diagram on Figure 5.9 allows some insight into the mechanism of this precipitation.

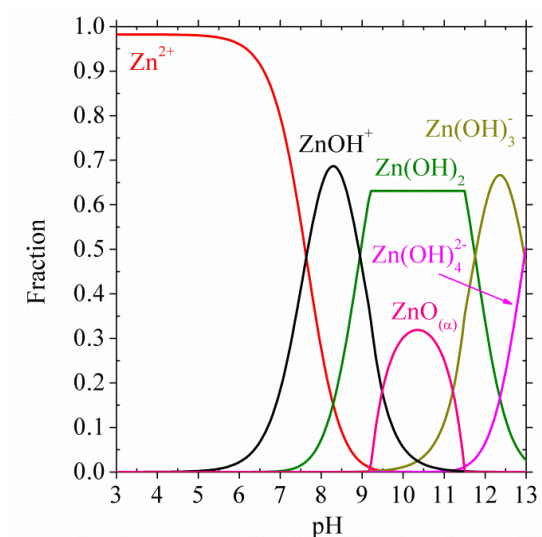


Figure 5.9. Stability diagrams of zinc species as a function of pH at 25°C calculated using the Hydra-Medusa® software and associated database version of 2009 [52] and considering $[\text{Zn}^{2+}] = 1 \times 10^{-5} \text{ M}$, $[\text{Cl}^-] = 1 \times 10^{-2} \text{ M}$ and $[\text{CO}_3^{2-}] = 5 \times 10^{-6} \text{ M}$.

The stability diagram of different zinc species in 10 mM chloride and 5 μM carbonate solution was calculated using Hydra-Medusa® software [52] and assuming a concentration of zinc in solution of 10^{-5} M [37]. The remaining constants used for calculation were provided by

the software database. For $\text{pH} < 9.0$ the conditions are not favourable for precipitation of zinc corrosion products, whereas for higher pH , $\text{Zn}(\text{OH})_2$ and ZnO become stable. This prediction is consistent with the visual aspect of the surface during the pH mapping with the SIET. Zinc hydrolysis has a buffering effect consistent with the maintenance of pH values below ~ 9.0 in the vicinity of the zinc and at edge of the inner iron cathode, favouring the stability of zinc soluble species (ZnOH^+), whereas closer to the centre of the iron plate, the pH is sufficiently high to allow the formation of $\text{Zn}(\text{OH})_2$ and ZnO [13].

A rough spatial correlation between the corrosion products and a decrease of ionic current measurements was observed in previous work in which cut edge electrodes were used, i.e., with no gap between anode and cathode [41, 53]. In the current work we don't see this correlation and this discrepancy may be explained by the cancellation of positive and negative currents when the electrodes are in very close proximity, i.e., by attenuation of the concentration gradients in a microscopic narrow region in the vicinity of the probe [54]. Therefore, we conclude that the local ionic currents did not detect any self-healing effect. Other authors, like, Krieg et al. [25], Mouanga [30,31] and Ogle et al. in recent works [27, 28, 29] suggested that corrosion products may cause cathodic inhibition not by themselves but rather by a synergistic effect between the zinc cations and the native iron oxides. However, we find no evidence of iron passivity and therefore exclude this synergistic effect. Most likely the corrosion products are not adherent and can be dragged by the convective currents of the probes, thus explaining the cathodic activity.

Globally, we observed that all the techniques provided valuable information about the model system. Naturally, the duration as well as the ease of setting up an experiment was quite different. Most importantly, the tip-to-sample distance and the scan rate have an influence on the ability of microprobe techniques to measure cathodic inhibition. The SECM is not a straightforward technique as the Pt-electrodes can easily become contaminated from species in solution and local alkalinisation while scanning at cathodic potentials may introduce some artefacts in the results. However, the small distance of the tip to the working electrode and the slow scan rate made it the most sensitive to the topography of the surface of the model. The zinc anode gave only a minor signal in the feedback mode possibly due to a small efficiency of the metal to the regeneration of the mediator but mostly because of recession of the dissolving surface during the experiment, bringing the surface away from the diffusion layer of the probe. The technique gave a distinct pattern on the "clean" cathode (Fe2) and on the cathode covered with corrosion products (Fe1), on which the regeneration current gave consistent local minima. These minima can be explained by the precipitation of corrosion products which create

topographic features that reduce the volume of electrolyte under the microprobe, causing a drop of the feedback current. A slight increase in the tip current operating in the redox competition mode while scanning the inner iron surface, suggests a minor barrier effect on the cathodic reaction due to the presence of those products.

The LEIS has a comparatively low resolution, due to the large separation of the bi-probe wires and a high probe-to-sample distance ($> 100 \mu\text{m}$). However, it was found to be quite sensitive to the zinc anode. A significant difference in the behaviour of each cathode surface was observed on the constant frequency scan. For shorter exposure times, the inner cathode did not produce a response to the excitation signal. Since the electrodes behave as a CPE at 1 Hz, a small perturbation in the sample potential should produce fluctuations in the double layer, i.e., on the charged particles at the sample/electrolyte interface which control the flow of ionic currents into bulk solution. The explanation for absence of a.c. current takes into account the reactions occurring above the inner cathode, in bulk solution, i.e. closer to the tip. These reactions, which correspond to the formation of salts occur at a high rate, are chemical in nature, and thus do not respond to the small a.c. stimulus applied to the system, thus decreasing the a.c. current below the noise level. At a later stage of the corrosion processes, once a pseudo-steady state is achieved, a higher concentration of free ions is reached over the inner cathode, with a consequent increase of conductivity of the electrolyte and thus an apparent increase of the admittance. Further, any variation in the capacitive response of the inner cathode due to the formation of a dielectric layer of zinc oxide would go easily undetected in impedance measurements as this dielectric layer is coupled in parallel with the double layer capacitance ($Y_0 = 10^{-4} \text{ F cm}^{-2} \text{ s}^{n-1}$, $n = 0.85$) of the bare iron interface.

In summary, as a result of the probe height and of the probe size, the SECM gives the best identification of the size and location of the cathodes, particularly in the feedback mode, but it is not adequate for the narrow zinc anode, which in turn was well identified and monitored by the SVET and the LEIS. The residual a.c. admittance in the inner cathode and in the initial stages of exposure provides an insight into the nature of the reactions occurring at different regions of the cathode. Except for the SVET, all localized techniques allowed observation of modifications on the electrochemical reactivity of the iron surface due to the presence of zinc corrosion products. For these conditions of pH and anode-to-cathode ratio, a self-healing effect caused by the precipitation of zinc corrosion products could not be observed, although a minor barrier effect of the poorly adherent oxides may be detected under conditions of little mechanical interaction of the probe with the substrate.

5.5 Conclusions

In the galvanic couple, zinc imposes a strong cathodic polarization, shifting steel into its thermodynamic immunity. Further, the solution around iron undergoes strong alkalisation, producing large gradients of pH. Precipitation of zinc oxide occurs at some distance from the cathode edge, at the region at which a critical pH is reached, whose location results from the counter-diffusion of Zn^{2+} and of OH^- ions. The diffusion processes occurring above the cathode, namely the diffusion of hydroxyl ion towards the anode is evidenced by the maintenance of high pH above the resin dividing the cathode plate. Reduction at the cathode leads to nearly uniform depletion of oxygen, as revealed by the SECM, with a minor barrier effect caused by the corrosion products. The local ionic currents measured using the SVET gave no evidence of local inhibition likely because the non-adherent corrosion products were stirred away by the tip vibration. The local impedance distribution provided good spatial information on the remote part of the cathode, whereas the precipitation of corrosion products leads to local variations of chemistry in the vicinity of the corrosion products, leading to masking of the cathodic activity, especially in the first stages of immersion.

The zinc anodic activity was sensed with a strong signal with both the SVET and the LEIS, which have little sensitivity to topographic effects and rather reveal the ionic effects in solution. The SECM is not adequate for the zinc because it is a small and recessing electrode. Further, during cathodic polarization of the tip, the zinc oxides precipitate on the platinum blocking the signal.

The use of an asymmetric three-electrode model cut edge system consisting of a thin zinc anode and two iron cathodes gave an improved insight of the galvanic corrosion of Fe-Zn cut edge systems at the microscopic scale, as it minimizes the direct interference of the distinct electrodes on the local electrochemical responses. All techniques provided adequate correlation between the parameters sensed and the geometry of the system, while the various scanning techniques provide complementary information which is beneficial in discarding artefacts related to stirring of the solution or interaction of the probes with the surface.

Acknowledgments

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6. Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in non-neutral chloride solutions

This chapter refers to unpublished work. All experiments were performed and interpreted by the author of this dissertation.

Abstract

Scanning electrochemical microscopy (SECM) and local electrochemical impedance spectroscopy (LEIS) were combined for the first time to obtain information concerning the corrosion mechanisms of a zinc-iron galvanic model under acidic and alkaline medium. The results were interpreted in terms of thermodynamic predictions. Despite the sensitivity of the SECM to the introduction of artefacts due to hydrogen bubbling at pH2 and tip contamination at pH10, it was still possible to detect the reduction of oxygen on both iron and zinc at pH2 and inhibition of the cathodic reaction due to the presence of zinc corrosion products at pH10. LEIS provided mechanistic information regarding the cathodic reactions at pH2: while there is zinc for sacrificial protection, it occurs under mixed activation-concentration control; at pH10, the technique revealed that the thin zinc oxide layer formed over the cathodes is very protective with very high resistivity.

Keywords: A. Iron; A. Zinc; B. EIS; C. Cathodic Protection

6.1 Introduction

Most of the literature dedicated to cut edge corrosion deals with neutral environments. However, in car bodies where cut edges of zinc galvanized steel can be found, significant pH changes occur due to confinement of solution and the presence of contaminants. The corrosion rate of pure zinc follows a U-shaped curve as function of pH, with significant corrosion rates in both strong acidic (< 3) and strong alkaline (>10) solutions [1-4]. Under galvanic coupling in neutral medium, the steel surface is cathodically polarized by the sacrificial zinc anode while the cathodic polarization lowers the corrosion rate of steel. Additionally, the release of zinc cations

combined with the alkalinisation caused by the cathodic reactions, lead to the precipitation of zinc based oxide compounds on the steel. A variety of zinc oxides and hydroxides may form, with a strong dependence on pH and the concentration of species such as chlorides, sulphates and carbonates. The nature of these products has a high impact on the oxygen reduction reaction and on the passivation of zinc and galvanized steel [5]. There is abundant literature dedicated to the study of zinc corrosion and zinc corrosion products in neutral [6-9] and alkaline medium [5, 10-12], including the study of the efficiency of corrosion inhibitors for cut edges in neutral medium, which have in some cases showed ability to reduce the efficiency of the sacrificial protection as they cause anodic polarization on the zinc [13, 14]. Acidic environments can be found in some situations like acid rains [1, 15], or condensation in industrial environments containing HCl, CO₂, SO₂, O₃ and H₂O₂ that lead to low pH electrolytes. Under acidic conditions, the stable zinc species is Zn²⁺, which is soluble, unlike what happens at neutral or alkaline pH. Zinc-aluminium electrocoatings may serve as an alternative to pure zinc coatings in acidic medium. However, Ogle et al [2] performed a study regarding the selective dissolution of Zn and Al from Zn-Al electrocoated steel at various pH using atomic emission spectroelectrochemistry (AESEC). Results have shown that zinc dissolves preferentially to aluminium in acidic medium (pH<4) while aluminium dissolves preferentially to zinc in alkaline medium.

Local electrochemical techniques have proven to be particularly interesting to study local corrosion phenomenon, including complex systems as magnesium alloys and conductive polymers [16]. However, literature dealing with the local measurement of iron-zinc cut edge corrosion is scarce, especially in alkaline and acidic medium. Ogle et al [17, 18] used the Scanning Vibrating Electrode Technique (SVET) and local pH measurements on a cut edge and found that the steel surface could be divided in two sections: close to the zinc there was absence of current, while far away from the zinc the cathodic reaction produced an increase of pH up to 10. Tada et al [19, 20] validated the suppression of ionic currents in the vicinity of the zinc using numerical simulation, whereas Souto et al [21] and Terryn et al [22] confirmed high alkalinisation over the cathodic region using potentiometric probes. In previous papers [23], we have demonstrated that the cathodic reaction on zinc electrogalvanized steel cut edge produces a local increase of pH up to 11. Predicting the evolution of galvanic coupling under alkaline conditions is thus relevant, as the cathodic reaction rapidly increases the pH of the medium. In previous works from our group [24-26], ionic current distribution (SVET) and Scanning electrochemical microscopy (SECM) were used to study iron-zinc corrosion in neutral and alkaline medium and the distribution of the cathodic currents was associated to the presence of zinc corrosion products; nevertheless, there were some uncertainties remaining concerning the resolution of

the tip to sense activity on the zinc coating as the dimensions of both tip and zinc electrode were in the same order of magnitude. Although some cathodic inhibition has been observed, caused by precipitation of zinc corrosion products on the steel electrode [27], it has also been reported that this inhibition seems to be lost in highly alkaline solutions because the corrosion products become unstable [11, 12, 28]. In these studies, an apparent discrepancy between local and conventional techniques is observed, with different conclusions being drawn by the same groups depending on the experimental approach used. This is probably associated either with the difficulties in the stabilization of the system (measurements are assumed to be made under steady state) or with the convection stirring of solution caused by the movement of the microprobes with consequent attenuation of the concentration gradients in a microscopic narrow region in the vicinity of the probe [29, 30].

Few studies report the use of localized electrochemical impedance spectroscopy (LEIS) to characterize galvanic corrosion [31-33] and there is still much to explore concerning the suitability of this technique to this type of system. Mouanga et al [33] used LEIS to study for the first time a disk-type concentric steel-zinc electrode and found a local current maximum at the interface between the dissimilar metals indicating that galvanic corrosion is highly localized. In our own work [23] we found a similar distortion which can be explained by the pH gradients and resulting composition and conductivity of the electrolyte in the intermediate region between the anode and the cathode.

The purpose of the current work is to characterize the local corrosion process of a model sample which mimics a cut edge of electrogalvanized steel under non-neutral conditions. This work is complementary to our previous work in which local corrosion process were studied under neutral conditions [23]. Scanning electrochemical microscopy (SECM) and Local electrochemical impedance spectroscopy (LEIS) were used and their suitability to perform localized corrosion studies under non-neutral conditions was assessed.

6.2 Experimental

6.2.1 Electrodes and electrolytes

Squared samples cut from an iron plate with 1 mm thickness and a 50 μm zinc foil, both with purity 99.95% (Goodfellow, U.K) were employed as electrodes for building the corrosion monitoring target, which consisted of one zinc electrode and a split iron electrode, mounted on

an epoxy resin sleeve - Figure 6.1. The working surface of the mount was grounded with silicon carbide paper under ethanol until 1000 grit finish, then rinsed in ethanol and dried under blown air. Polishing was made along the direction of the iron-zinc interface, to minimize spreading of zinc onto the iron surface. Electrical connection between the metals was assured through an external circuit in the rear of the mount consisting of copper wires joined to the foils with conductive silver paint (SPI® Supplies, USA). A small electrochemical cell was built by surrounding the epoxy sleeve with adhesive tape and filling it with ca. 3.5 mL of electrolyte. Experiments were carried out in quiescent 10 mM NaCl (PA grade from Sigma-Aldrich) solutions of pH 2 or 10 and non-buffered. The pH was adjusted by adding aliquots of 1M H₂SO₄ (95-98%, Sigma-Aldrich) or 1M KOH ($\geq 85\%$, Sigma-Aldrich). The conductivity of these solutions at 23.0 °C was $k = 6.20\text{ mS}$ and $k = 1.35\text{ mS}$, at pH2 and pH10 respectively, as measured by a PC 700 meter (Eutech Instruments, Singapore). For the SECM experiments, ferrocene methanol (abbreviated as FcMeOH; 97% purity from Sigma-Aldrich) was added to the solution to a concentration 0.5 mM.

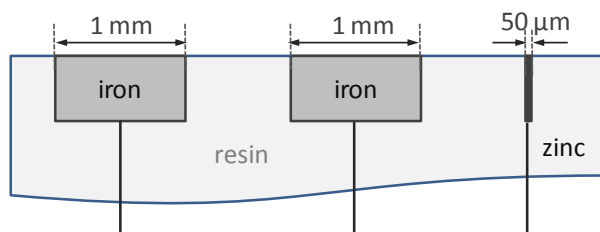


Figure 6.1. Schematic diagram of the model cut edge.

6.2.2 Measurement conditions

6.2.2.1 Open circuit potential

The open circuit was monitored using an ACM Field Machine (ACM Instruments, U.K.), with a potassium chloride saturated calomel electrode (SCE) as reference. *In-situ* image recording of the cut edge model was performed using a DMS300 digital microscope system and processed with LAS v4.3 software (Leica Microsystems, Switzerland).

6.2.2.2 Scanning electrochemical microscopy (SECM)

A Scanning electrochemical microscope M370 by Uniscan Instruments, U.K., including a piezoelectric motor positioning system, was used for characterization of surface conductivity/topography and oxygen depletion in the vicinity of the cut edge model. The system was operated in a three-electrode configuration with the galvanic couple at its free potential in the test solution. The SECM probe (the working electrode) consisted of a platinum disk ultramicroelectrode (UME) of 10 μm diameter sheathed in a conical glass rod and the cell was completed with a platinum mesh counter electrode and the SCE as reference. The experiments were performed at room temperature under natural aeration in a 0.5 mM ferrocenemethanol (abbreviated as FcMeOH, supplied by Sigma-Aldrich, 97%) and 10 mM NaCl (99%) solution of pH 2 and 10. The operating height was set after recording z-approach curves with the tip approaching the resin surface until the current dropped to 30% of the limiting current value; subsequently, the tip was withdrawn to a level estimated as $\sim 20 \mu\text{m}$ away from the surface. Although the ideal working distance should be in the range of the tip diameter or less, by proceeding in this way the sample was kept inside the diffusion layer of the probe, while preventing bumping against any corrosion products on the surface at pH 10. Linear scans were made at constant height and at a scan rate of $0.5 \mu\text{m s}^{-1}$. Measurements were performed by operating in sequence the feedback mode and the competition mode, with 60 s conditioning of the tip at the chosen potential before starting the scan. The voltammetric curves of the UME in the working solutions [26] gave a typical sigmoid shape for the oxidation of FcMeOH to FcMeOH⁺, Figure 6.2. The tip potential $E = +0.40 \text{ V}$ and $+0.30 \text{ V}$ corresponding to a diffusion limited current, was chosen for the amperometric studies in pH2 and pH10 respectively. The voltammetric curves of the UME in the cathodic direction [26] revealed the existence of a plateau corresponding to oxygen reduction under diffusion control in both acidic and alkaline medium. In acidic medium, water reduction is significant for potentials more negative than -0.6 V and therefore a potential of -0.50 V was chosen for the detection of oxygen depletion under diffusion control.

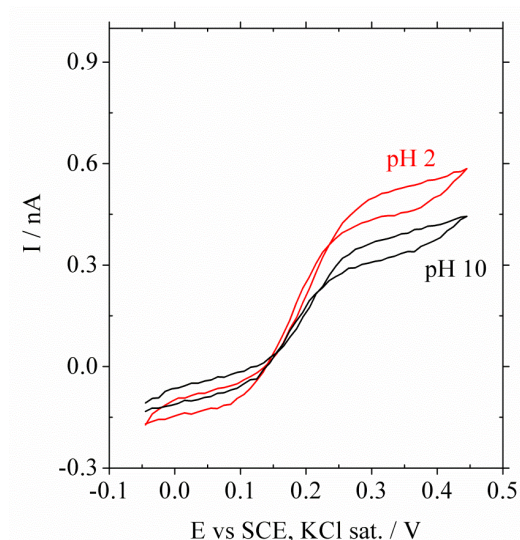


Figure 6.2. Voltammograms extracted with the UME in bulk solution for the oxidation of FcMeOH. Scan rate 20 mVs^{-1} .

6.2.2.3 Localized electrochemical impedance (LEIS) measurements

LEIS was performed with a M370 electrochemical workstation (Uniscan Instruments, UK) coupled to a 1286 potentiostat and a 1250 frequency response analyzer (both by Solartron Analytical, UK). For full spectrum analysis, the applied potential amplitude was 10 mV around the open circuit potential measured after a short stabilization period and frequencies ranged from 10 kHz to 1 Hz, at seven points per decade. The commercial bi-probe (Uniscan Instruments, U.K.) consisted of a $10 \mu\text{m}$ disk embedded at the bottom of a conical insulating holder and a platinum ring wire around it, placed at a distance of 1.5 mm. With this geometry, the probe measures the ionic currents along a direction which is displaced by $\sim 30^\circ$ from its axis. A platinum mesh counter electrode, a SCE reference and the galvanic model completed the cell. The sample was levelled with a bubble level placed on the polished surface and the bi-probe was placed at a distance of c.a. 1 mm from the surface. The experimental assembly does not allow rigorous measurement of the distance between the tip and the sample. Local impedance spectra were measured with the tip positioned approximately at the centre of each electrode, whereas single-frequency scans (at 1 Hz) were performed by moving the bi-probe by steps of $127 \mu\text{m}$ across the electrodes. The time taken for each line scan was ca. 15 minutes. Measurements were made after careful stabilization of the system at its spontaneous potential and therefore steady state is assumed. In order to ensure steady state, impedance spectra were repeated twice with a short time interval. Although a relatively scattering was observed within each spectrum, especially at

the low frequencies, the reproducibility of the general shape of the spectra and of the admittance scan lines was fairly good.

6.3 Results

In the acidic solution, the potential curve presents numerous spikes - Figure 6.3 - that reveal hydrogen evolution [34]. These spikes gradually became less intense as the pH becomes less acidic due to the onset of the cathodic reaction. The open circuit potential for alkaline pH is consistently more negative than that of the acidic solution and than the neutral solution from our previous work [23]. This variation reveals the Nernstian variation of reversible potential for the cathodic reaction but also the formation of a quasi-passive film of zinc corrosion products under alkaline conditions.

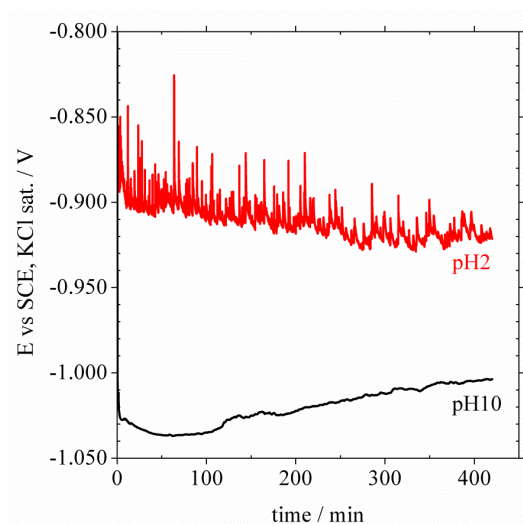


Figure 6.3. Free corrosion potential of the sample in 10 mM NaCl, the pH of the solution is indicated next to the respective curve.

Zinc corrosion products only precipitate on iron on regions where the pH exceeds the solubility limit of those zinc species. In neutral solution, the pH on the zinc vicinity is also neutral and the zinc corrosion products have high solubility, allowing zinc cations to diffuse freely into the solution ensuring sacrificial protection of the iron [23].

In the acidic solution, the oxidised forms of both metals are soluble ions and the reversible potential for the formation of soluble Zn^{2+} and Fe^{2+} is -1.15 V and -0.86 V, respectively [35]. This means that at pH2 zinc is active with an anodic overpotential of $\sim 0.25\text{V}$, while the iron plates are in their immunity region, thus with a clean surface available for the cathodic reactions to proceed. The evolution of hydrogen was confirmed visually - Figure 6.4 a. Further, there are

no visible white corrosion products, meaning that any local alkalinisation caused by the cathodic reactions does not reach the critical pH 7-8 level for the precipitation of ZnO.

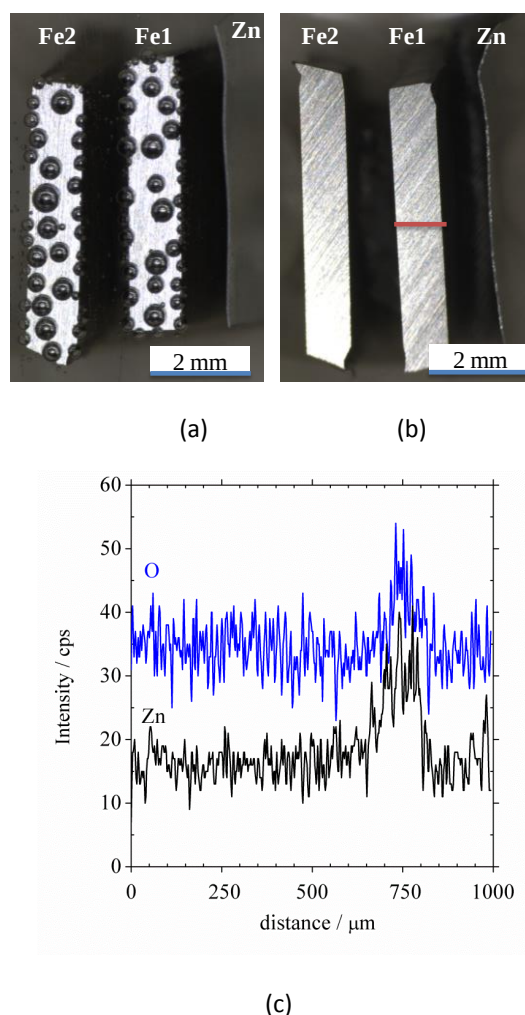
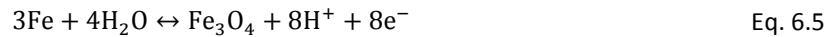


Figure 6.4. Optical micrographs of immersed sample (a) shortly after immersion in pH2 solution, (b) 2h after immersion in pH10 and (c) *ex-situ* elemental EDS analysis measured across a line in Fe1 as marked in (b).

At pH10, the oxidised forms of both metals are insoluble oxides which are passive in the absence or low concentrations of chloride ions. The reversible reduction potential for the reaction on Eq. 6.1, is -1.03 V, or -1.16 V if the formation of $\text{Zn}(\text{OH})_2$ is considered instead [35]. Therefore, at the spontaneous potential of the couple, zinc may either dissolve or else become covered with a layer of oxides, possibly in a state of quasi-passivation, or at least with a non-uniform oxidation. Local acidification due to zinc hydrolysis (Eq. 6.2) is not thermodynamically predictable [23,35], whereas slight local alkalinisation may occur due to the onset of the cathodic reactions, both the reduction of both water (Eq. 6.3) and oxygen (Eq. 6.4). The pH over the zinc is expected to be kept in the range of 10 to 12.



The reversible potential for the $\text{Fe}_3\text{O}_4/\text{Fe}$ equilibrium (Eq. 6.5) at pH10 is -0.920 V [35]. Since the spontaneous potential of the system remains below -1.0 V, this means that coupled iron is in its region of thermodynamic immunity. Any magnetite (Fe_3O_4) formed during exposure of the freshly polished surface to air should dissolve shortly after immersion.



With quasi-passive zinc, the corrosion process should be very limited. That is, cathodic protection is present but at very low currents. At pH10 a thin layer of zinc compounds precipitates in the cathode in the vicinity of the anode as confirmed by EDS analysis showing zinc and oxygen on this region Figure 6.4 b-c. This distribution is similar to that found in the pH5 solution, although the amount of precipitate was much lower [23].

6.3.1. Local Electrochemical Impedance Spectroscopy (LEIS)

The local impedance spectra measured for the iron in acidic medium for short immersion time are characterized by a straight line with a 45° slope at the low frequency end and a flattened semi-circle at frequencies above 10 Hz, Figure 6.5 a. The low frequency straight line reveals a diffusion process at the iron surface. This mass transport impedance is observed only on the iron, at pH2 and for short immersion times, i.e. when the charge transfer resistance is small. According to the literature [36], the Warburg impedance becomes measurable by impedance spectroscopy when the rate control is mixed, i.e., under both activation and mass transport control. In this case the major cathodic reaction on steel is hydrogen evolution, which is usually not associated with diffusion. Our results, however, suggest the development of a diffusion layer for hydrogen near the surface of iron, likely with a pH gradient that results in a mixed rate control.

For comparison, the local impedance spectra obtained after the loss of galvanic protection is presented in Figure 6.5 b. At this stage red rust was visible on both the iron plates, especially at the edges. Although zinc was still in contact with the electrolyte, its strong recession due to intensive dissolution and the accumulation of corrosion products caused the loss of

sacrificial protection. The low frequency time constant associated to mass transport is no longer measurable and the rate control of the reaction on iron is due to charge transfer.

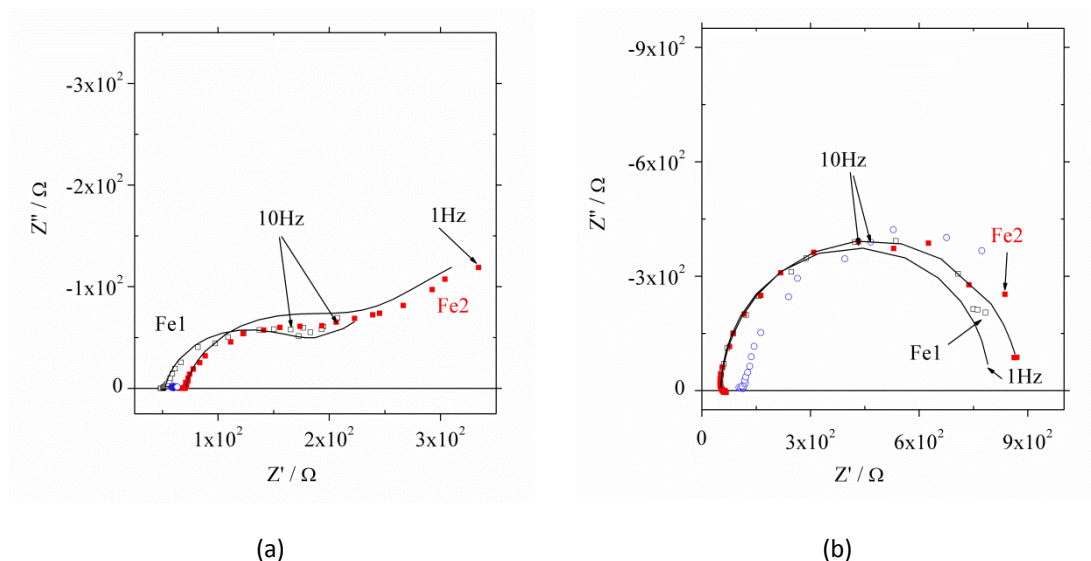


Figure 6.5. Local impedance spectra measured at the centre of each iron electrode in pH2 electrolyte after (a) 1h immersion and (b) 24h immersion.

At pH 10, the local electrochemical impedance spectra on iron show a single loop in the entire frequency range, Figure 6.6 a. The resistance associated to this process is very large, especially at the inner electrode and could not be measured within the frequency range of the experiment. This is consistent with the presence of a layer of zinc corrosion products on the surface of the iron, which is thicker closer to the zinc. After ca. 24h immersion, the resistance had increased, suggesting thickening of that zinc layer, or at least a more protective character. On the iron plate placed further away from the zinc, a second feature starts to appear at low frequencies and may be explained by diffusion limited oxygen reduction, Figure 6.6 b. The absence of mass transport process in the plate closer to the zinc may indicate inhibition of the cathodic reaction due to the presence of the zinc corrosion products.

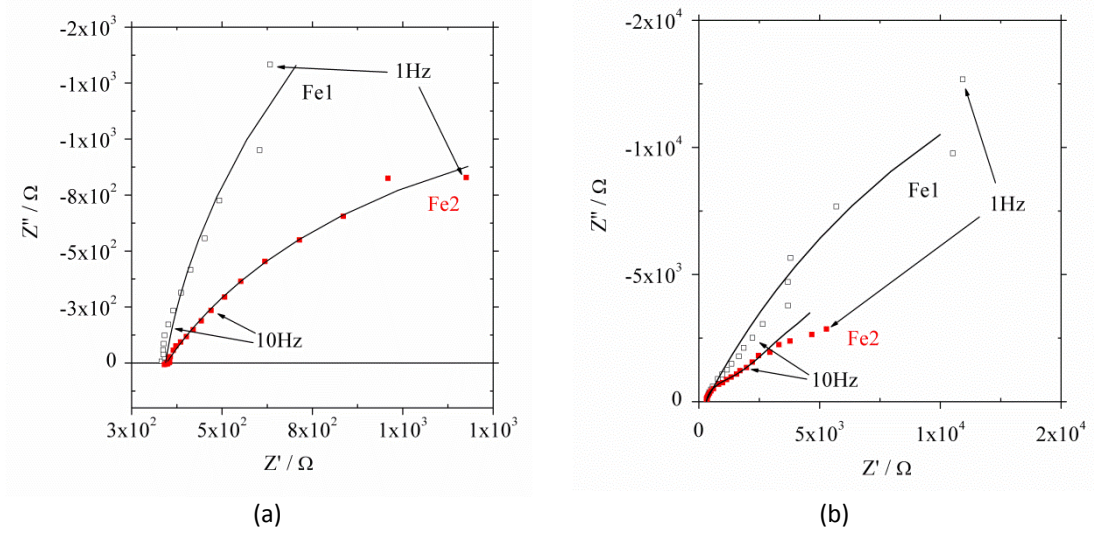


Figure 6.6. Local impedance spectra measured at the centre of each iron electrode in pH10 electrolyte after (a) 1h immersion and (b) 24h immersion.

Local electrochemical impedance spectra were fitted to the electrical equivalent circuits presented in Figure 6.7 using ZView software from Scribner Associates Inc. [37]. The semi-circles were adjusted to an in this RC circuit corresponding to a double layer-capacitance C_{dl} and a charge transfer resistance R_{ct} . The capacitive component of impedance was treated using the constant-phase-element (CPE) approach [38]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad \text{Eq. 6.6}$$

In Eq. 6.6, Y_0 is the frequency-independent term, ω is the angular frequency and the exponent n takes the value 1.0 for a pure capacitor and is null for a pure resistor. The features at low frequency showing a 45° slope were fitted with a Warburg impedance element, considering a diffusion layer of finite thickness [39]:

$$Z_W(\omega) = R_d \frac{\tanh\left(\sqrt{j\omega \frac{\delta_n^2}{D}}\right)}{\sqrt{j\omega \frac{\delta_n^2}{D}}} [\Omega] \quad \text{Eq. 6.73}$$

where R_d is the diffusion resistance, D the diffusion coefficient of the species under mass transport and δ_n the thickness of the diffusion layer. The parameters extracted for each condition are presented in Table 6.1 and the corresponding theoretical spectra are overlaid to the experimental data in Figures 6.5 and 6.6. The fitting error (χ^2) is fairly high; this was not surprising as the experimental data in LEIS are usually noisy. Further, the number of points is

relatively small because the range of frequencies is limited by the instrumentation. Nevertheless, the information provided by the fitting provides interesting mechanistic information.



Figure 6.7. Electrical equivalent circuits (EEC) used to fit LEIS data with ZView for processes controlled by (a) kinetics and (b) by mass transport.

In the acidic medium, the charge transfer resistance associated to the cathodic process is in the order of a few hundred Ohm, in the same order of magnitude as the resistance of the electrolyte, in agreement with an immune surface at the beginning of immersion [3]. This high discharge rate is responsible for the mass transport limitation of hydrogen. The capacitance in the order of 10^{-5} Fcm^{-2} is also in agreement with the formation of a double-layer on the bare metal. After 24h immersion, protection has been lost and the corresponding charge transfer resistance has a magnitude more typical for a corroding metal [3].

Table 6.1. Equivalent electrical circuit parameters extracted with ZView

		R_{ct} Ω	Y_0 Fcm^2s^n	n	R_d	$\frac{\delta^{0.5}}{D}$	χ^2
Bulk pH				0h			
2	Fe1	123	7.5×10^{-5}	0.88	410	4.1	0.00900
	Fe2	144	5.9×10^{-5}	0.88	482	1.5	0.00762
10	Fe1	>8191	1.3×10^{-4}	0.94	-	-	0.00614
	Fe2	>3075	1.6×10^{-4}	0.75	-	-	0.00116
				24h			
2	Fe1	742	2.0×10^{-5}	1	-	-	0.01050
	Fe2	830	2.4×10^{-5}	0.97	-	-	0.00737
10	Fe1	>50878	1.7×10^{-5}	0.68	-	-	0.02285
	Fe2	1000	1.8×10^{-6}	0.98	13575	1.1	0.00622

In alkaline medium, the charge transfer resistance increases by nearly two orders of magnitude while the capacitance increases by one order of magnitude to 10^{-4} Fcm^{-2} which is consistent with the properties of a thin passive layer of zinc [3].

The impedance measured over the zinc electrode in the various conditions is at least one order of magnitude smaller than that of the iron electrodes and for that reason they are plotted separately, Figure 6.8. The zinc plate is corroding intensively in the initial moments of

immersion in pH2 and thus the equivalent electrical element is a resistance represented in the impedance spectra by a point. The spectrum for pH10 shows two semi-circles that can be associated to the dissolution of zinc and to the properties of the zinc passive film. After 24h immersion, the plate becomes recessed due to dissolution of the metal, thus the corresponding current field is distorted and the spectrum has an unclear physical meaning.

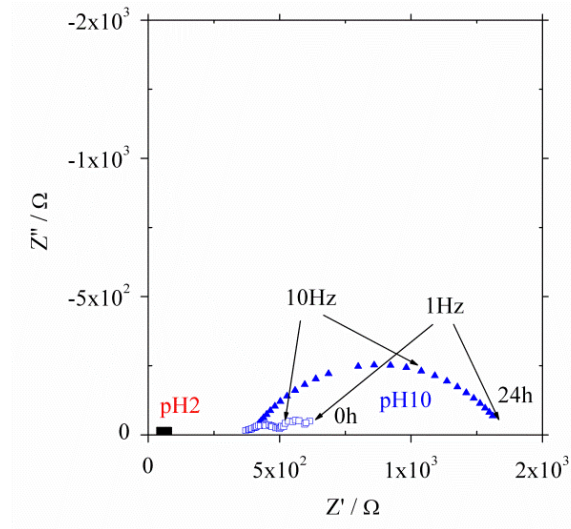


Figure 6.8. Local impedance spectra for zinc.

Our experiments have shown that the low frequency impedance provides more information on the evolution of cathodes and anodes than the high frequency impedance. At high frequencies the impedance reveals mostly the resistance of the electrolyte, thus being nearly constant with time and irrespective of the properties of the electrode, while at low frequencies it is the mass transfer processes or the charge transfer resistance that determined the spectrum, therefore 1 Hz was chosen to perform linear scans. Results are presented as admittance ($|Y|=1/|Z_{loc}|$) which is a preferred representation to impedance as it enhances the dielectric behaviour of the interfaces.

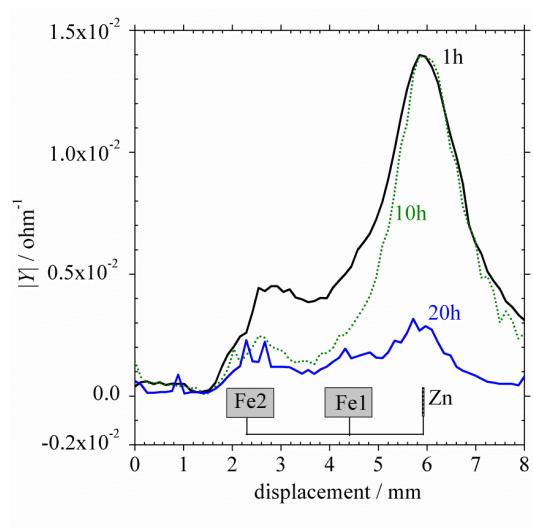
The admittance, Figure 6.9, was quite sensitive to the activity at the zinc anode but could hardly detect an a.c. signal over the cathodes. The same observation has been made in our previous work at pH5 [23]. This result agrees with local spectra in which the local impedance on zinc was orders of magnitude lower than on iron.

The decrease in the admittance measured above the zinc in acidic medium is consistent with the dissolution of the electrode in the initial stages of sacrificial protection, Figure 6.9 a. The dissolution of zinc corresponds to higher admittance, whereas lower admittance on iron can

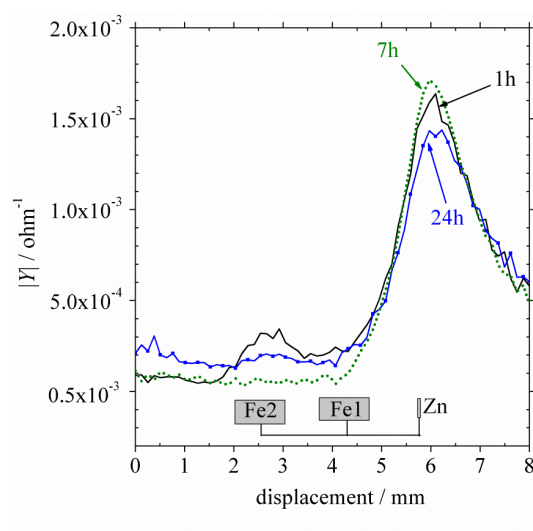
be explained by two factors: first, the larger cathodic area results in a smaller current density at the cathodes and concomitantly to a lower admittance; second, the application of a potential sine wave on the cathode has hardly any effect on the current corresponding to hydrogen evolution or oxygen reduction reaction, as they occur under mixed control. Further, the high intensity and width of the zinc admittance band at pH 2 totally masks any small peak at the inner cathode. The width of the zinc signal at half maximum is approximately 2 mm, which is 40 times the size of the anode. The remote cathode, being away from the zinc, gives a visible, although modest admittance. After sufficiently long exposure, when the zinc becomes dissolved and sacrificial protection is lost, the admittance decreases. Under these conditions iron corrodes with both anodic and cathodic reactions on its surface. The local admittance correlates with the local rate of electrochemical reactions and their evolution.

At pH10, the admittance is lower by approximately one order of magnitude, as expected since the solution is less aggressive for the cut edge system- Figure 6.9 b. Further, the pH 10 profiles reveal fluctuations of admittance during exposure. Since at this pH zinc oxides are thermodynamically stable, this means that zinc oxidation takes place in quasi steady-state fashion either through a quasi-passive layer [5] or else in a relatively localised manner, comparable to pitting dissolution.

The admittance profiles measured in the first hours of immersion reveal the same tendency regardless the pH of the bulk solution. The a.c. current measured above both cathodes rapidly decreases to noise levels. When the cathodic process is under mixed control, the explanation is apparently straightforward: an a.c. excitation around the mixed potential will not produce an a.c. potential as the cathodic reaction is under mixed control. At pH10 the resistance at low frequency is very high and the current passes through the path which offers the less resistance to electric flow which is the electrolyte (towards the counter electrode). At pH2, after 24h immersion the process is no longer under mixed control and in principle it should be possible to measure local potential field. In practice, the impedance of the interface is comparable to the ohmic impedance and thus the measurement is almost at noise level.



(a)



(b)

Figure 6.9. Admittance distribution measured along an arbitrary line across the electrode for various exposure times in (a) pH2 and (b) pH10.

At pH5 interpretation of the admittance variation over the cathodes was complicated by the formation of soluble and insoluble zinc species [23]. In the current work however it is more evident that the low admittance readings over the cathode are related to the kinetics of the cathodic reactions.

6.3.2 SECM amperometric results

The *feedback mode* was used for the identification of the conductive regions and topographic features on the surface of the model system whereas the *competition mode* was employed with the aim of identifying local oxygen depletion in the vicinity of the sample under diffusion limited current. Oxygen has a low solubility in water, of 2×10^{-4} M for air-saturated water [31] and therefore the current detected at the microprobe will be very small. Hydrogen evolution can occur as a parallel cathodic reaction, especially at pH2 where the reversible potential is shifted towards more anodic potentials and the reduction currents at the tip results from both oxygen and H^+ reduction. The consumption of protons under acidic corrosion will lead to a slight pH increase over the iron and therefore to a decrease of the rate of hydrogen evolution. In this situation, the relative contribution of the reduction of oxygen increases. Further, because water is an abundant reagent, its depletion in the space between the UME and the sample should not be sensed.

Feedback current profiles measured across the sample with the tip biased at +0.40 V for the oxidation of the mediator in pH2 are presented in Figure 6.10. A significant time drift in the feedback current is observed and is explained by tip contamination, probably hydrogen adsorbed on the platinum. The profile reveals two maxima roughly forming a plateau having good correspondence with the position of the iron electrodes, despite a poor definition of the electrode geometry, associated to convection caused by hydrogen bubbling, which also explains the local fluctuations registered at the initial stages of immersion within each plateau. The currents at the baseline correspond to the limiting current measured in the bulk solution, whereas the currents above the metal plates are four times larger indicating positive feedback, i.e. the metallic surfaces are conductive. The zinc surface did not give a feedback signal. These results are quite complementary to the admittance profiles: while the zinc is not detected, the iron surfaces give two distinct bands for the regeneration of the mediator. The profile taken with the probe biased to -0.50 V evidences depletion of oxygen above both cathodes and also on zinc. That is, although the net reaction on zinc is anodic, reduction also takes place as a side reaction.

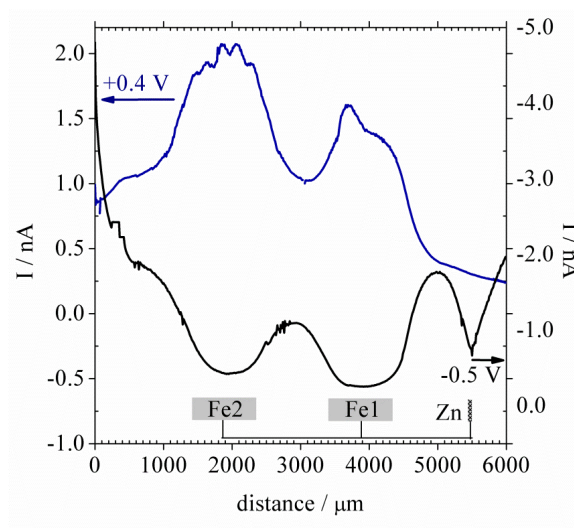


Figure 6.10. SECM line scans measured as the tip travelled over the samples exposed to test solution of pH2 with tip biased at +0.40V and -0.50V, for FcMeOH oxidation and oxygen depletion, respectively.

In the pH10 solution, the feedback current measured with the tip biased at +0.30 V is smaller than the limiting current measured in bulk solution (Figure 6.2). However, the approach curves revealed positive feedback at the centre of the iron plates. The amperometric profiles reveal two well-defined plateaus over the iron plates and a small peak over the zinc - Figure 6.11. Compared to the experiments in acidic solution, the definition of the geometry of the cathodes is now dramatically enhanced. Above the outer cathode, the feedback current reveals a well-defined step behaviour with a plateau of approximately 1 mm, whereas on the iron plate closer to the anode nearly half of the surface, in the region closer to the anode, reveals a lower feedback current. This is the region where corrosion products accumulate, as observed in EDS scan. The feedback current is affected by both the conductive nature of the substrate and topography and this local current decrease might reveal either of the two. However, in a conducting surface, a decrease of the tip-to-sample distance would result in an increase of the feedback current, and so this sub-step on the right hand side of the Fe1 can only be assigned to the precipitation of insulating zinc oxides. Further, the corresponding profile for the cathodic activity shows significant oxygen depletion at the iron plates except in the region where the corrosion products accumulate. These results reveal local inhibition of the cathodic reaction associated with the presence of zinc insoluble species [18, 40-42].

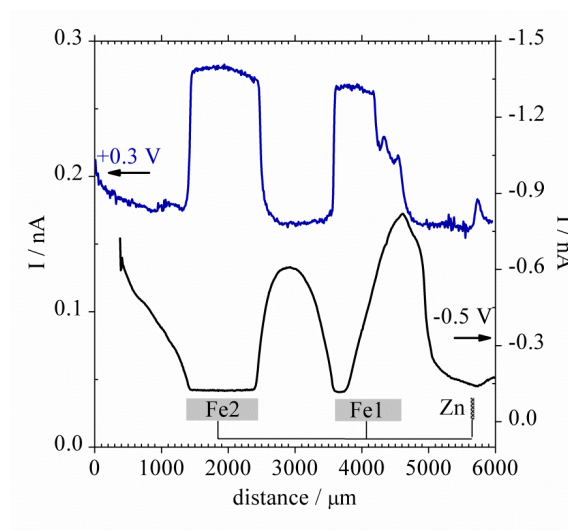


Figure 6.11. SECM line scans measured as the tip travelled over the samples exposed to test solution of pH10 with tip biased at +0.3 V and -0.5 V for 1h immersion.

6.4 Discussion

Cut edge is a system for which until recently only *ex-situ* techniques, like surface analysis, could give spatial resolution. Electrochemical macroscopic techniques, being based upon the averaged result of a surface, provide only limited information. Even electrochemical impedance spectroscopy, which has found interest to the point of becoming an almost mandatory technique when it comes to corrosion studies and corrosion monitoring, finds great limitations when it comes to cut edge corrosion. For *in-situ* studies, surface-resolved electrochemical techniques are likely the most powerful electrochemical tools for the study of cut edge corrosion. The SECM and the LEIS mapping were both capable of sensing the galvanic couple constituted by a narrow anode and two wide iron cathodes and with results that were significantly more clear than in the real cut edge, i.e., without the introduction of an insulating gap [26].

The amperometric profiles extracted with the UME were quite sensitive to the geometry of the cathodes, i.e., the iron plates, which were effective in the regeneration of the ferrocene methanol. A good correlation was also found between the conductivity/topography and the concentration of oxygen in solution, with the precipitation of zinc corrosion products resulting in a lower tip current for the oxidation of the mediator just at the region where the oxygen reduction was inhibited. The well-defined steps of the amperometric profiles in the alkaline solution correspond to a planar diffusion of species near the substrate, for both the oxygen and

the mediator [43]. in the acidic environment the wider bands measured over each metal plate result mostly from convection currents generated by hydrogen evolution.

The use of amperometric scans to map the sites for depletion of oxygen has to be made with care, since interferences from other species may occur. For the regeneration of the mediator, and excluding sodium and chloride ions, the species present in solution were zinc cations (which cannot be oxidised to any other form at this potential) and oxygen (which could be reduced but not oxidised) and therefore the oxidation current can only be assigned to the mediator. The oxidation of ferrous to ferric ion occurs after galvanic protection is lost and in this case the UME current corresponds to oxidation of both the mediator under diffusion control and the oxidation of ferrous ion.

The limiting current for the oxidation, as measured from the voltammograms in bulk solution, showed a minor difference between the two pH values, which is explained by statistical random errors in the experiments. Further, in the negative range of potentials, and particularly at -0.5V, apart from oxygen, hydrogen was excluded since bubbling at the tip was never observed.

Other limitations in the use of surface-resolved electrochemical techniques, is the pH of the solution and the evolution of hydrogen. Hydrogen bubbles produced by the cathodic reaction in acidic medium [34] may adsorb on platinum microprobes, modifying the reactive surface and producing distorted measurements of the potential fields in solution; further, dissolution of the metal produces changes in the sample topography, whereas in alkaline medium, oxides and hydroxides grown on the surface of the sample also change its topography, ultimately leading to crashing of the tip or these products may even precipitate on the tip itself [23,26].

The local impedance measurements are not normalized to an area. The potential stimulus is applied to the whole substrate and the current resulting from the processes at the interface is measured as an ionic current (or rather, as potential gradient) by the bi-probe at a selected frequency. This means that the area providing current in solution cannot be accurately defined although it is estimated as 1 mm². Further, local impedance spectra are critically affected by geometrical effects that are still under study [44]. Despite these limitations, it was possible to identify from local impedance spectra a process occurring under mixed control, associated with the cathodic reactions on cathodically polarized iron in acidic solution. The admittance profiles give a good idea of the time variation of the processes, although with various limitations. Because profiles are made at a single frequency, care has to be taken to ensure

stability of the system during the time of the experiments. The behaviour may shift from resistive to capacitive and therefore full spectrum should be made at regular intervals to guarantee the nature of the process sensed. Some studies have been made including monitoring and interpretation of the phase angle [33], but the high dispersion in the readings made that study quite hard.

The bulk pH resulted in a significant change in the behaviour of the galvanic model. At pH2 zinc dissolves and remains in solution. The iron plates work as a cathode, with hydrogen evolution occurring under mixed activation-mass transport rate control. After 24h the remaining zinc was insufficient to offer cathodic protection, triggering self-corrosion of iron. At pH10 zinc forms insoluble species that precipitate on the zinc itself and over the immune iron plates. This thin layer of zinc corrosion products formed under alkaline conditions is nevertheless more protective than the bulky products formed under neutral pH [23]. In fact, inhibition of the cathodic reaction at pH10 was clearly observed with the SECM operating in the amperometric mode and is also in agreement with the observations in our previous work [26]. The question of self-healing in cut edge corrosion due to the precipitation of corrosion products on the steel surface has been addressed by several authors, as described in the Introduction. The principle behind this model is that the cathodic reactions cause local alkalinisation at the cathode, so that the zinc ions formed in the anodic reaction and diffusing from the anode will reach the cathode and precipitate as ZnO or Zn(OH)_2 . These products create a barrier causing a drop in the rate of the cathodic reaction, thus slowing down the rate of the electrochemical processes, at both cathode and anode. This has been called “self-healing”. Although some authors [40-42] support the theory that self-healing might result from the stabilization of a FeOOH layer by action of the zinc cations, which would result in a more protective layer, our results indicate that iron is immune and therefore, the zinc corrosion products alone must be responsible for any self-healing. In neutral solution, the growth of the layer of zinc oxides has been explained by the diffusion of anions in solution towards the cathode, followed by their precipitation and their reaction with the cations to form zinc complexes, resulting in a porous layer with a Zn(OH)_2 matrix, with some moderate protection, that is, not blocking effectively the cathodic reaction [10]. Despite attempts made to characterize the nature and distribution of the corrosion products, identification was not achieved. The composition of the solid products seemed complex and the chemistry of the precipitating environments change constantly with time, possibly generating different products not just during the immersion process but also during the drying process.

Although the local pH has not been determined in this part of the work, the influence of the pH on the corrosion products layer was nevertheless evident. We have seen that in a NaCl solution with neutral bulk pH, the local pH can go up to approximately 11, while the anode remains in a neutral solution. In alkaline environment the pH in the vicinity of the cathodes should also rise but more moderately. Further, zinc hydrolysis is not expected to decrease greatly the pH and zinc becomes quasi-passive; while protecting iron, part of its oxides remain on the zinc surface and some part reach the cathode. In alkaline solution the zinc oxide layer is apparently thinner than the one formed under neutral conditions probably due to slower kinetics of zinc dissolution and precipitation, which results in a more compact and protective structure which is effective in blocking the cathodic reaction, in agreement with observations from other authors [3,4].

6.5 Conclusions

SECM and LEIS were used in combination to obtain information on the corrosion mechanisms of cut edge model under acidic and alkaline medium. Even though the application of these techniques, especially SECM, presented some complications due to intense hydrogen bubbling and changes in the topography of the samples, they proved valuable to study local corrosion phenomenon in extreme environments.

In acidic medium, amperometric measurements revealed cathodic reduction of dissolved oxygen mostly on iron but also over the zinc. According to the local impedance spectra, the cathodic reactions on the iron surface occur under mixed activation-mass transport rate control. Further, scanning of the surface by electrochemical impedance measurements revealed high admittance readings in the vicinity of the zinc anode with wide spreading of currents consistent with convection generated by hydrogen evolution.

Inhibition of the cathodic reaction by the precipitated zinc oxides was observed at pH 10 and in a region corresponding to approximately half the width of the cathode in the vicinity of the anode.

Good complementarity was found between the fixed frequency scanning and the full spectrum mode of local impedance spectroscopy. One limitation of the impedance scans is the lack of sensitivity to mixed activation-mass transport process associated to the cathodic regions.

The setup mimicking a cut edge, made of a small zinc anode and two iron cathodes at different distances from the anode allowed not just the identification of the narrow zinc anode but also of the two different regions of the cathode, being a useful substrate for the understanding of highly localised heterogeneous electrochemical reactions. Combination of thermodynamic predictions with the LEIS and SECM gave an improved insight of the mechanisms involved in cut edge corrosion.

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7. General Discussion

The research presented in this dissertation can be divided into two sub-topics. The first deals with the study and modelling of corrosion mechanisms of a thin weldable primer applied on electrogalvanized steel, while the second deals with the study of electrogalvanized steel cut edge corrosion in electrolytes of various pH.

These two sub-topics are part of the wider subject of the corrosion of coil-coated galvanized steel. Further, they deal with the two most relevant issues of industry concerning coil-coatings: the problems arising from forming of coil-coated steel and cut edges. The protection provided by organic primers has been studied and modelled by many authors, greatly based upon electrochemical impedance spectroscopy. Although the advantages of EIS compared to other techniques are well-known, it may be useful to recall them here. First, EIS allows the measurement of not just resistive elements but also of capacitive elements, thus opening the way for modelling using equivalent electric circuits – EEC's. Second, it allows the separation and identification of individual resistive elements, which is a major advantage for systems with a high resistance, like the case of organic coatings with pores. Third, when compared to d.c. techniques, like potentiodynamic polarization, it is a non-destructive technique, since the signal applied to the electrode is within the linearity region of the polarization plot, around the corrosion potential. Because of these advantages, and also because of its ease of use, EIS has become a popular tool for the characterization of organic coatings within the Materials Science research community [1].

Despite the popularity of the technique, the vast majority of the published studies deals with barrier primers and only a few papers deal with the characterization of weldable primers [2-7]. These are thin and thus prone to flaws and pores and further they include in their formulation conductive particles which reflect the dielectric properties and the EEC of the system. In this work, which was done within the scope of an EU-funded project and only partly presented in this dissertation, a new model is proposed. Complex models containing many electric elements often give better physical description of real systems but are hard to trust for numerical fitting routines since the uncertainty in the values of each parameter becomes high; further, the number of possible combinations of parameters increase significantly compared to a simple circuit, like the Randles circuit. This means that for complex circuits (with several RC networks not totally resolved in the spectrum), the use of theoretical spectra is often the safest way of interpreting the spectra, instead of the common fitting of Randles-type circuits. This was the

approach used in this study, not just on the characterization of the weldable primer but also to the study of the effect of elongation. Elongation and deformation of painted systems has been studied by several authors [8-12], but understanding their effect on thin primers with a high solid content was a challenge in this work; composite coatings containing particles with a size in the same range as the thickness of the polymer layer are complex systems for which the effect of strain had not been the object of deep studies in the literature. Mapping of the ionic current flow in solution has revealed activation/dissolution and de-activation of embedded metal particles that become exposed as a consequence of loss of polymer-pigment adhesion. It was also concluded that a direct correlation between the SVET measurements and the impedance data could not be established because the non-percolating metal particles exposed at the surface contribute to the ionic currents in solution but not to the charge transfer across the polymer, while the large particles that go across the coating (percolating) establish a short-circuit between the zinc substrate and the outer surface of the binder, thus lowering the impedance of the primer very much like a defect. These conclusions were published in 2014 (*EIS and SVET assessment of corrosion resistance of thin Zn-55% Al-rich primers: effect of immersion and of controlled deformation, Electrochimica Acta 148 (2014) 153-163*).

The second sub-topic is concerned with cut edge corrosion and with the application of surface-resolved electrochemical techniques. This part of the work is presented in three papers, one of them published in 2015 (A. G. Marques, J. Izquierdo, R. M. Souto, A. M. Simões, *SECM imaging of the cut edge corrosion of galvanized steel as a function of pH, Electrochimica Acta, 153 (2015) 238-245*), a second one published in 2016 (A.G. Marques, M. Taryba, A. S. Panão, S. Lamaka, A.M. Simões, *Application of scanning electrode techniques for the evaluation of iron-zinc corrosion in nearly neutral chloride solutions, Corros. Sci. 104 (2016) 123-131*) and a third one that is expected to be submitted shortly. While uniform corrosion can be easily characterized by techniques that measure the overall behaviour of interfaces, surface-resolved techniques come up as useful techniques for the study and characterization of galvanic corrosion, particularly when small electrodes are involved. Although galvanic corrosion may seem a simple subject, several reports in the literature [13-15] have pictured it as a complex process, namely as a result of the pH gradients and the ion flow in solution. Localized techniques such as the Scanning Vibrating Electrode Technique (SVET) and the mapping of ionic species concentration using specific ion-sensitive electrodes (Selective-ion scanning electrode technique SIET) had been used before, but techniques such as amperometric mapping using scanning microelectrodes or Localized Electrochemical Impedance Spectroscopy (LEIS) had not been used with this specific purpose until very recently [16].

At the start of this work, and even at this final stage, the works of reference on the use of LEIS are lead mostly by V. Vivier, from the research group at the Université Pierre et Marie Curie, in Paris. This research group has studied in detail some of the features of the spectra, particularly the effect of cell geometry on the development of an inductive loop at the high frequencies [17, 18]. In fact, the inductive loop that typically appears at high frequencies has been observed to vanish near recessed electrodes and therefore it has been correlated with the existence of lateral ionic currents near the microprobe. Further, galvanic corrosion on copper-aluminium [19] and iron-zinc [16] systems has been studied using a concentric system consisting of a disk and a concentric ring electrode and the geometric distribution of admittance was determined. It was shown that the current distribution was higher at the interface between both materials and further, it was shown that local impedance responses were drastically different when the bi-electrode was positioned above zinc alone in self-corrosion or zinc in galvanic coupling with steel even though zinc was polarized at the same potential in both cases. In the research presented in the current dissertation, experiments were performed using plate-like electrodes and despite the limitations introduced by the geometry, it was possible to monitor the kinetics of zinc corrosion in various pH conditions and to detect a mixed activation-concentration cathodic process occurring on iron coupled to zinc in acidic environment.

The two sub-topics are discussed in more detail below.

7.1 Modelling of corrosion on a thin weldable primer

This study has dealt with the characterization, monitoring and modelling of the corrosion behaviour of a Zn-55% Al-rich primer. The system is complex, as it encompasses the binder phase, the Zn-Al embedded particles, the zinc layer and eventually the steel substrate. Zinc protects the underlying steel by isolating it from aggressive species (namely oxygen and chloride ions) that permeate through the primer, but also by sacrificial protection at defective areas. The models proposed for conductive primers consider particles of small size, typically less than half of the coating thickness [2, 3-7]. The system differs from those reported in the literature since there is a distribution of particle size in which some particles are quite smaller than the primer thickness and are fully embedded within the binder while others exceed the average thickness of the primer. Under these conditions a residual electronic conduction across the metal particles in parallel with the ionic conduction across the binder was expected, meaning that the models

described in the literature for barrier coatings did not adequately account for the properties of the primer.

The circuit in Figure 7.1 a, is usually used to fit the experimental data corresponding to the behaviour of the EG substrate, in which R_s is the solution resistance, C_{dl} and R_{ct} are the double-layer capacitance and the charge transfer resistance and Z_{dif} is the impedance of a mass transport process. Fitting of EIS response of Zn-Al weldable primers was performed in the past by Bastos et al [2] and Touzain et al [6] using the circuits in Figure 7.1 b-e. The various circuits were used to fit the EIS spectra according to the evolution of the coating degradation caused by water penetration. The circuit in Figure 7.1 b, was used to fit the spectra of intact coatings shortly after immersion while the circuit in Figure 7.1 c, was used for intact primers containing Zn-Al particles after a few hours of immersion. Touzain et al [6] have also used in their work this last circuit, to describe the behaviour of the intact metal rich primers, while the circuits in Figure 7.2 d-e were used to fit the behaviour of the systems after 1 day and 7 or more days of immersion, respectively. The new time constant (R_{ox} and C_{ox}) was attributed to the contribution of corrosion products deposited on the top of active metal area.

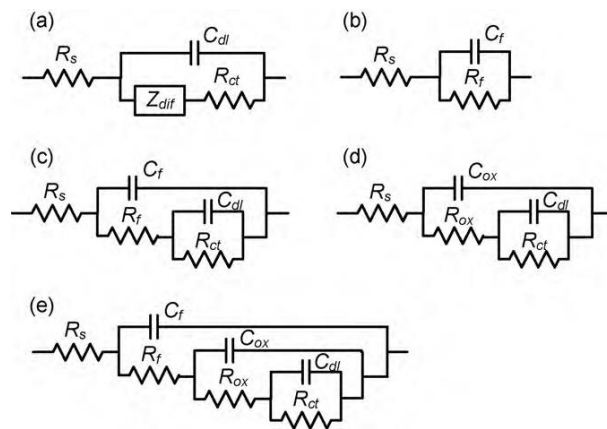


Figure 7.1 Equivalent electric circuits used by Bastos et al [2] and Touzain et al [6] to fit the impedance response of weldable primers.

In the current research, similar circuits were used in the fitting routine but the timing of their application to describe the degradation stages of the primer is different. The intact primer was described with a single RC (Figure 7.1 b), while a circuit with two RC s (Figure 7.1 c), one for paint response and another for metal corrosion, was used to fit the behaviour of the primer after some hours of immersion. For the intact Zn-55Al primer, Figure 7.2, fitting to an EEC (Figure 7.1 b) revealed a coating with $Y_0 \sim 10^{-8} \text{ Fcm}^{-2} \text{ s}^{n-1}$ and $n = 0.94$, with Y_0 assigned to the pseudo-capacitance of the primer and a resistance of $\sim 10^6 \Omega \text{ cm}^2$ was assigned to the resistivity of the

conducting primer. Taking the classical assignment of high frequency capacitance to the dielectric properties of the primer, this corresponds to an apparent dielectric constant of approximately 40, which is above the typical value for polymer films, of 3 – 6, and agrees with the conductive nature of the film. The current research was performed for short immersion times (a few hours) and there was no need to use the EEC with three RC (Figure 7.1 e). Fitting the data with three RC networks was only necessary to describe the behaviour of highly deformed samples; a low frequency loop, usually ill-defined (Figure 7.2), was assigned to a mass transport process. A comparable behaviour has been reported for zinc [20] and assigned to the existence of adsorbed intermediates, either Zn_{ads}^I or Zn_{ads}^{II} [21, 22]. Touzain [6] and Gergely [23] used a Warburg element to fit the mass transport process at the low frequencies.

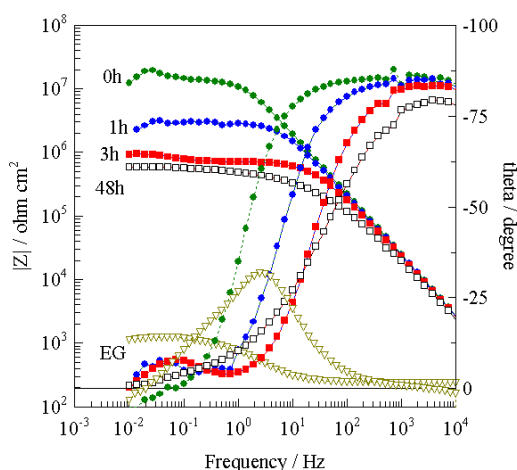


Figure 7.2. EIS spectra of the Zn-Al primer, non-formed, for varying immersion times and also for the bare electrogalvanized steel (EG).

The most popular model used to describe the behaviour of a metal-rich primer, was developed by Touzain, Figure 7.3, in which all of the following elements are considered: C_f , the capacitance related to the epoxy binder without conducting pigments; R_f , the resistance of percolating particles between the two coating interfaces; C_{gs}, R_{gs} , the capacitance and resistance between isolated particles and interfaces; C_{ig}, R_g and R_{ig} are the capacitance, the resistance and the ionic resistance, respectively between isolated or semi-isolated particles contributing to the transmission line.

The Faradic response of the (non-percolating) embedded particles, correspond to a fraction $(1-\alpha)$ of coating particles, is measurable only after several days of immersion is and is described by the following elements: C_{dl} , the double layer capacitance, R_{ct} , the charge transfer resistance,

W_s is the diffusion impedance and R'_{gs} , the resistance between semi-isolated particles and the metallic interface, without interaction with other particles.

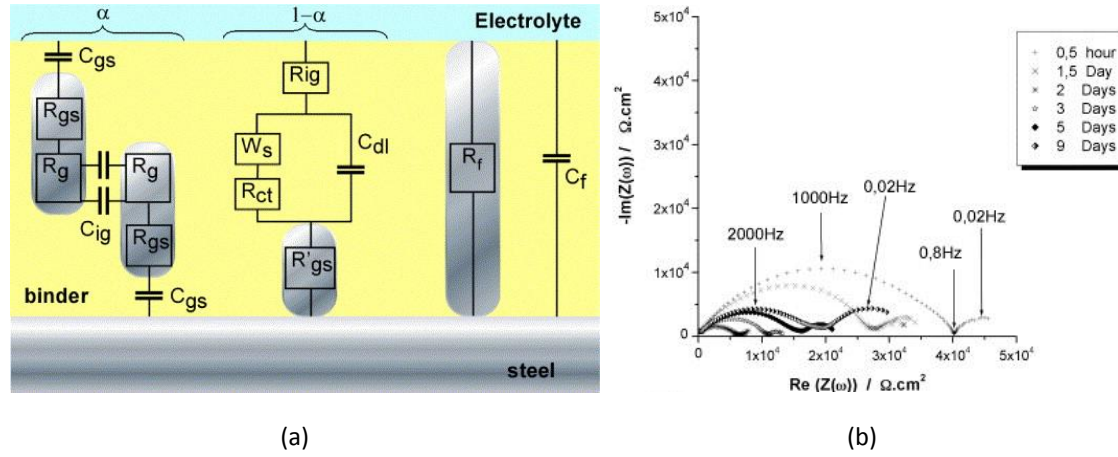


Figure 7.3. (a) Equivalent circuit used to model powder zinc-rich coating behaviour and (b) experimental spectra [6].

In this model, the coating consists of semi-isolated zinc particles in electrical contact with only one side of the coating ($1 - \alpha$), isolated zinc particles in capacitive interaction between themselves and with the nearest interface electrode (α) and percolating particles that might exist between the two interfaces. However, this model presents some limitations for application in the primer studied in the context of this dissertation; first, for short immersion times it is admitted that the impedance of the fraction ($1-\alpha$) of non-percolating particles is too high and therefore is not included in the EEC for the theoretical spectra; second, the effect of deformation was not studied.

The model proposed in this dissertation differs from the existing ones based on the model of Touzain [3,4,5,7,23] as it provides a good approach to the experimental data, with the advantage of a straightforward interpretation to the number of loops in the spectrum. Further, it includes the response of the embedded particles since the first moment of immersion. In the proposed model, Figure 7.4 the coating is represented by a polymer matrix with dispersed conducting particles, some of them in contact with the substrate. Three RC networks are used, in which R_s is the solution resistance placed in series with R_{ct} , the charge transfer resistance and C_{dl} , the double layer capacitance at the exposed particles; in parallel, is R_p , the resistance along the pores of the coating, placed in series with the Faradic response of the embedded particles (given by C_{dl}^* , R_{ct}^*); also C_c , the coating capacitance. The model evidences that

immediately after immersion only one relaxation process can be observed, corresponding to the charge transfer at the conducting particles and the mixed double layer/polymer capacitance. The corrosion at the bottom of the micropores is therefore masked when the primer is intact ($R_p > 10^5 \Omega$). As water penetrates in the primer, a second capacitive loop accounting for charge transfer at the bottom of the pores, either on the substrate or the non-percolating particles, becomes apparent.

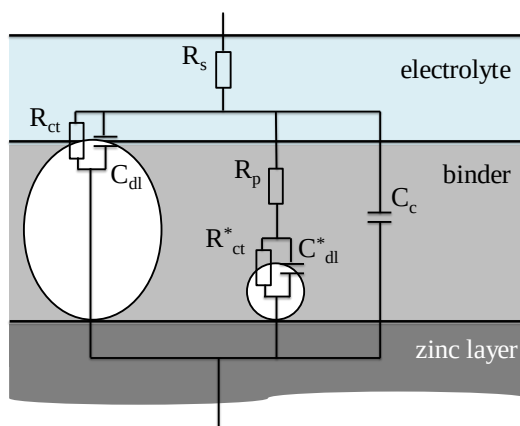


Figure 7.4 Proposed EEC model for the description of the Zn-55Al rich primer.

As time evolves, the pores get filled with electrolyte and the corresponding pore resistance decreases affecting the low frequency impedance. The theoretical spectra in Figure 7.5 a, simulates this effect, i.e. a moderate decrease of the pore resistance in an initially intact coating, while maintaining the other properties constant. The model shows why the low frequency loop, associated with the corrosion at the embedded particles or at the substrate, only becomes visible when the barrier effect of the coating drops to very low values. When the coating is protective ($R_p > 10^5 \Omega$), the low frequency process is masked and thus cannot be seen in the spectrum, whereas for low coating resistance the low frequency loop becomes apparent.

The effects of mechanical deformation were not considered in most models, although there are a number of significant effects at several levels, namely the interfaces between metal particles/binder or binder/substrate. The effect of elongation on the painted system is felt on the primer but also on the zinc layer. It is known that electrodeposited zinc crystals have the capability of sliding over one another in the direction of the elongation, which explains why at small elongation the zinc layer was able to maintain its integrity. Meanwhile, large elongations (33%) generated cracks on the zinc coating, exposing the steel substrate and determining the onset of sacrificial protection. Starting from an active area fraction of $F = 10^{-4}$, the spectrum has

a single capacitive loop, corresponding to parallel capacitors and to the pore resistance, Figure 7.5 b. As the fraction F increases, the conductive character of the particles become predominant and the capacitance measured is C_{dl} . Simultaneously, the low frequency resistance decreases as both R_{ct} and R_p decrease. The low frequency process, (0.1 Hz), corresponding to the time constant given by R_{ct}^* and C_{dl}^* , only becomes visible for 15% and 33% elongation. The model thus evidences that the low frequency process is resolved only when the fraction of exposed area exceeds 0.001. The theoretical spectra give good similarity with the experimental results, in which also the capacitance increased with the elongation, while the resistance decreased.

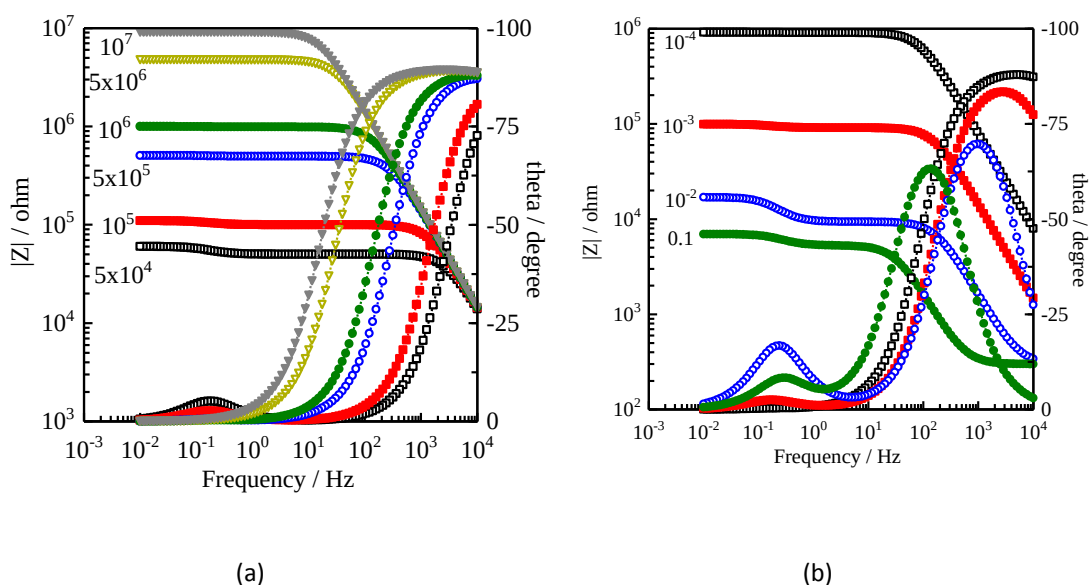


Figure 7.5. Computed spectra using the proposed model to simulate the effect of (a) water absorption on the resistance of the primer R_p (in ohm) and (b) the fractions F of active area.

One limitation of the model described here is the use of pure capacitors in the equivalent electrical circuits instead of CPEs, which should provide a better approach considering the complex nature of the surface and the distribution of reactions and reaction rates along the surface. Although the use of CPEs could result in better agreement with the experimental plots, in practical terms this type of element has two parameters which complicates further the complexity of building a physical model. Therefore, it is usually admitted that the use of a pure capacitor provides a sufficiently good approach.

7.2 Assessment of physico-chemical processes of corrosion on zinc-coated steel with scanning electrochemical techniques

Even when studying apparently simple systems as galvanic couples, the use of scanning electrochemical techniques, namely the SVET and the SECM, presents some challenges. Especially when it comes to performing studies in environments of. In acidic medium, hydrogen bubbles produced by the cathodic reaction in acidic medium [24] may adsorb on platinum microprobes modifying the reactive surface and producing distorted measurements of the potential fields in solution; further, dissolution of the metals (Zn or Fe) produces changes in the sample topography. In alkaline medium, oxides and hydroxides grown on the surface of the sample also change its topography, ultimately leading to crashing of the tip or precipitation of these products on the tip itself. Even under near-neutral solutions, there is much to be fully understood concerning the role of zinc corrosion products precipitated on steel [25]. Probably these complications explain why there are so few studies with microprobe scanning techniques on extreme pH solutions. When it comes to the use of LEIS to study galvanic corrosion, the number of studies is even shorter [16, 26, 27]. There is still much to explore concerning the challenges of the use of this technique to study galvanic corrosion, especially in solutions of varying pH. As far as the author of this dissertation knows, there is only one work [16] from the group of V. Vivier, using LEIS to study steel-zinc corrosion.

Thermodynamic diagrams were used as an important tool in this dissertation as they serve as a basic guide to understand the corrosion and passivation of cut edge corrosion in a given pH range. They predict that a well defined region of passivity of zinc exists only under alkaline conditions. However, the thermodynamic diagrams do not consider the influence of kinetics within the system. Further, while the formation of the oxides is a function of the sample potential, the morphology (porous or compact) and susceptibility to break down depends on the local solution chemistry, namely the pH. Precipitation kinetics and product morphology thus have a strong influence on the electrochemical behaviours of zinc corrosion products.

In Chapter 4, Scanning Electrochemical Microscopy (SECM) and the Scanning Vibrating Electrode Technique (SVET) were employed to identify the local conductivity/topography and the cathodes and anodes on a cut edge of galvanized steel. The SVET and also pH sensors have been used by other authors to investigate cut edge systems [8, 28, 29-38], but very little has been published using the SECM applied to galvanic corrosion [39, 40]. The research focused on the application of SECM and SVET to study cut edge corrosion of polymer-coated galvanized

steel, with the aims of analysing the sensitivity of these techniques to cut edge corrosion in various conditions and of getting a better insight on the mechanisms of cut edge corrosion. Experiments were performed in non-buffered solutions of pH 2, 5 and 10, simulating three main regions of corrosion behaviour of the metals involved [41]. One major issue of this study was the local pH variations at microscopic level, in the vicinity of the cut edge. The solutions used were not buffered and so the pH changed within the diffusion layer of the cut edge as a consequence of local reactions at the substrate.

The application of the SECM to the study of iron-zinc corrosion is not straightforward, as already mentioned the UME may easily become contaminated especially when it is polarized to cathodic potentials. While detection of dissolved ferrous ions can be done by oxidation at a constant anodic tip potential, it is not very useful because the iron is polarized by zinc into its thermodynamic region of immunity. Detection of zinc ions by amperometry, either through oxidation or reduction, is not feasible, as soluble zinc ions have only one oxidation state (2+) and the reduction of Zn^{2+} to its metal state cannot be done inside the potential window of stability of water. Therefore, the approach to the study of cut edge was based upon the regeneration of a redox mediator, ferrocenemethanol, on the metal surface and amperometric mapping of the depletion of oxygen. In both measurements the tip was polarized at a potential within the range of the limiting current for the reaction searched, either the oxidation of the mediator or the reduction of oxygen. Unlike the SVET, the measurements are indirect and susceptible to interferences from other species. One of the issues might be the influence of the local pH since the reversible potential for the reduction of oxygen changes with the pH according to Nernst law; the potential region for diffusion-limited rate becomes wider as the solution becomes more alkaline and narrower and shifted towards more negative potentials as the solution becomes more acidic. The establishment of the right potential is thus essential and has been ensured by cyclic voltammetry measurements made in the various solutions. The stability of the FcMeOH mediator was checked in the solutions of various pH. In the absence of the cut edge, the shape and current of the voltammogram were independent of the pH and the limiting current was stable up to at least to 24h immersion. In the presence of the cut edge, the limiting currents dropped quickly in the first hour of immersion, especially in the alkaline solution. At pH=5 measurements could be performed until 24h, at pH=2 until 7h and at pH=10 the current would drop reaching values close to zero in less than 3h. It follows that the ferrocenium ion is fairly stable in the solutions tested. However, in the presence of the cut edge, the results suggest an irreversible reaction of the mediator being more relevant at pH=10. Since the probe was placed

at a large distance from the surface, the blocking of the probe doesn't have its origin on the accumulation of corrosion products on the Pt surface.

In the acidic solution, the amperometric scan lines revealed uniform distribution of the cathodic reaction over the steel surface in a first stage, (Figure 7.6 a) whereas after the loss of protection, the cathodic process became localized near the active edge (Figure 7.6 b). Both the reduction of H^+ and of H_2O takes place on steel and should contribute to alkalisation in the vicinity of the surface. The feedback current also becomes localized revealing a minor peak in the anodic scan lines, probably due to regeneration of the mediator, although some contribution from the oxidation of dissolved Fe^{2+} ions emitted from the active steel surface cannot be excluded, Figure 7.6 c.

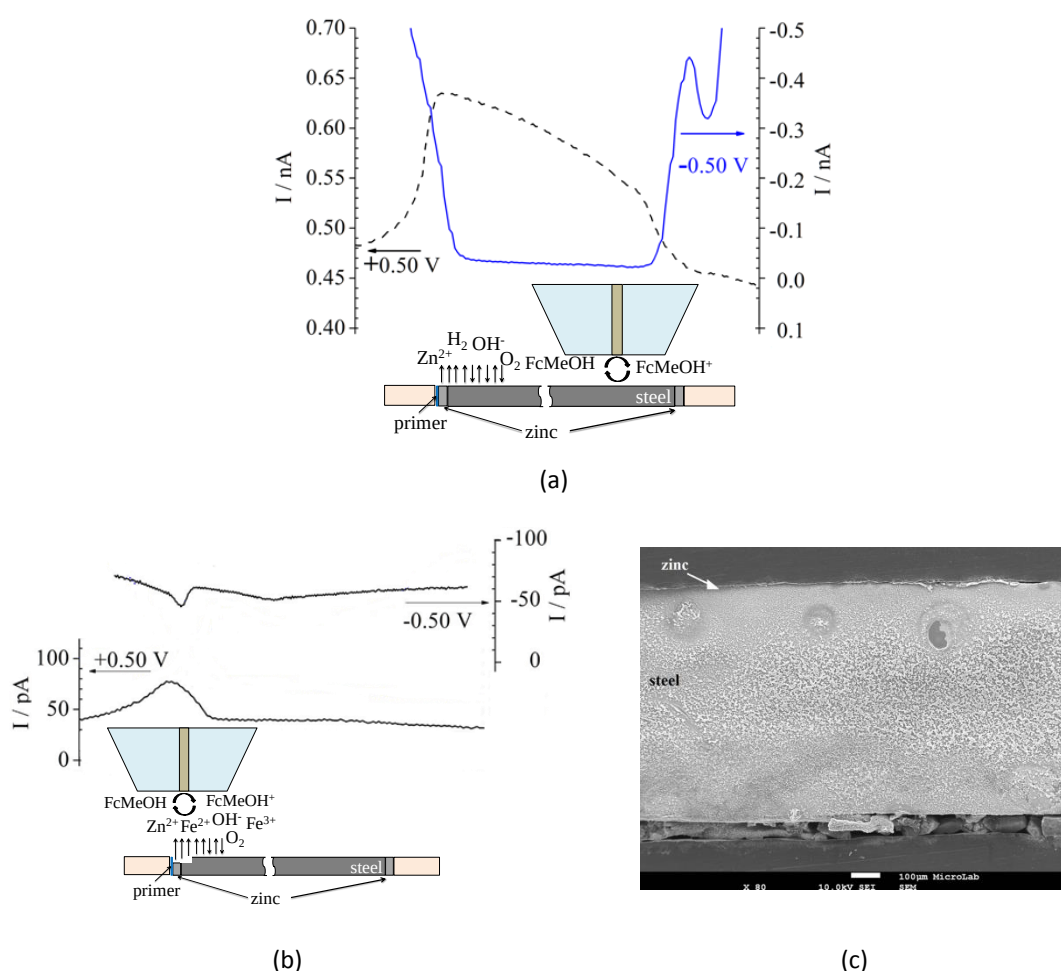


Figure 7.6. Schematic representation of the electrochemical reactions occurring at the interface of the cut edge immersed in pH2 solution at (a) the beginning of immersion (b) after 7h immersion (no cathodic protection) and (c) SEM micrograph at the cut edge at the end of the test.

At the free corroding potential of the sample, steel is expected to be immune for a wide range of pH, whereas zinc is active up to neutral pH. As the electrolyte becomes less acidic,

reduction of O_2 becomes the main reaction on steel while HER is the main cathodic reaction in the vicinity of the zinc. Although the equilibrium potential for water reduction is -0.49 V at pH 5 and -0.32 V at pH 2 [42] and thus the reduction of water at the tip biased to -0.50 V cannot be excluded, the reduction current at the tip corresponds mostly to reduction of dissolved oxygen especially after the protection is lost.

In nearly neutral medium, two maxima in feedback current were clearly located above the steel, at some distance from the edges, Figure 7.7 a. The accumulation of zinc oxides on steel has been observed not at the steel/zinc interface, but rather a few micrometers away from that interface, thus leaving a narrow area of bare steel, Figure 7.7 b. This correlated well with the pattern of ferrocenemethanol feedback current, with maxima located on each side of the sample. The maximum in the feedback current should then be located adjacent to the corrosion products.

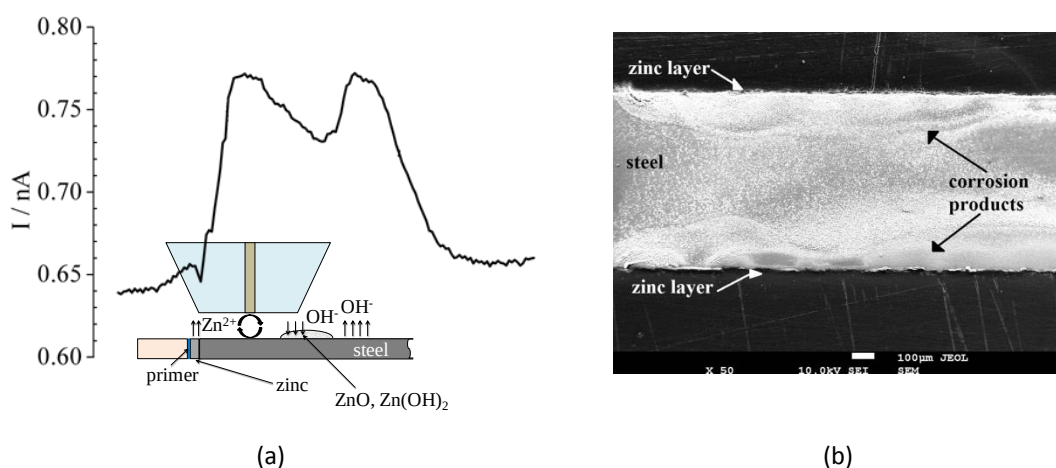


Figure 7.7. SECM amperometric profiles for the cut edge immersed in neutral solution (a) schematics of electrochemical reactions responsible for generating a feedback current and (b) SEM micrographs of the cut edge at the end of the experiment.

At pH 10, the amperometric profiles exhibited a plateau covering the entire width of the sample and the tip current decreased rapidly as a result from blocking of the tip by insoluble products (ZnO and $Zn(OH)_2$), Figure 7.8. Because the amperometric curves were obtained alternately under anodic and cathodic polarization of the UME, the cathodic polarization of the tip caused a local pH rise with consequent precipitation of zinc oxides at the tip. Ultimately, a local pH rise also promoted the precipitation of corrosion products at the substrate, along the line scanned by the UME; still, these products probably re-dissolved due to a decrease in the pH as the probe moved away from the surface.

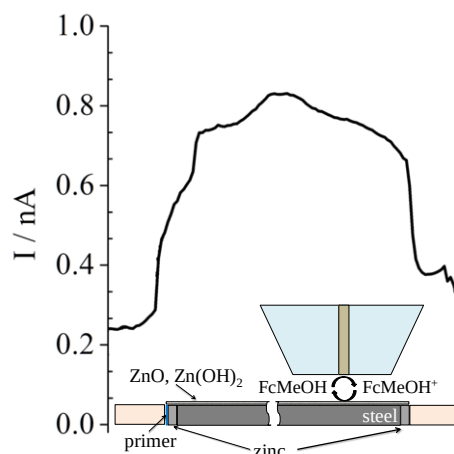


Figure 7.8. Schematics of electrochemical reactions responsible for generating a feedback current in pH10 solution.

In order to compare the sensitivity of SVET and of the SECM for the zinc, profiles obtained with both techniques were performed in the neutral solution, Figure 7.9. There was good agreement between the two techniques, as the distribution of ionic currents in solution measured with the SVET matched the locations for regeneration of the redox mediator employed in SECM. Ionic currents arising from the cathodic reaction were rather uniform above the steel centre, in the region limited by the corrosion products.

The diameters of the probes employed, 10 μm in the SECM and 20 μm in the SVET, are above the thickness of the zinc layer ($\sim 7.5 \mu\text{m}$). This definitely limits the resolution and for that reason it was not possible to resolve the shape of the anodes developed on the substrate. However, it was shown before [43] that identification of small anodes can be achieved, provided the electrochemical activity is sufficiently high.

The step size employed in these measurements was 10 μm for both techniques and despite the probe size being in the same order of magnitude as the zinc layer thickness, the location of the anodes was unambiguously established using the SVET while it could not be resolved by the SECM. The lateral anodes and the central cathode were clearly identified and the width of the cathode (estimated from the distance between the two zero current points) is ca. 605 μm , which corresponds to 75% of the actual steel thickness.

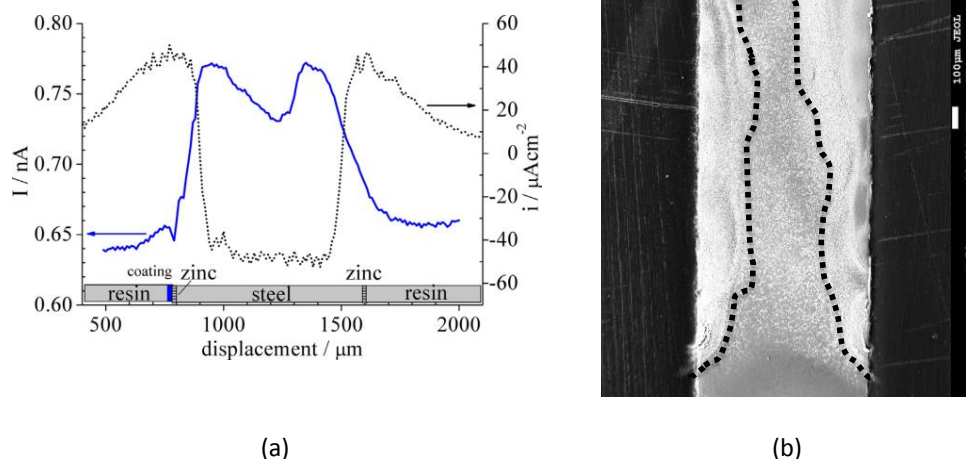


Figure 7.9. SECM amperometric profiles for the cut edge immersed in neutral (pH=5) solutions with the tip biased at +0.45V and (b) SEM micrograph of the cut edge taken at the end of the experiment with dashed lines delimiting the corrosion products.

The position of the SVET microprobe, 100 μm above the surface, together with its large size (20 μm) results in some attenuation of the signal. Therefore heterogeneities on the steel surface due to the accumulation of zinc corrosion products could not be resolved. Comparatively, the SECM uses a smaller probe and the distance to the substrate was only ~20 μm. Attenuation is therefore smaller and the fluctuations on surface reactivity become more significant. The size of the UME is similar to that of the zinc electrodes and about ten times smaller than the steel, therefore the information on the zinc cannot be satisfactorily resolved as the feedback current measured at the sides of the cut edge will be masked by the higher currents measured close to its centre. Therefore the measured currents correspond to the steel (almost) exclusively. This is a difficulty when studying the cut edge configuration, compared to a galvanic couple with cathode/anode separation. For this reason, research on model systems, with physically separated anodes and cathodes (Chapters 5 and 6) was performed to clarify the microscopic processes occurring on the steel in the vicinity of the anode.

7.3 Study of a model cut edge

Concerning the resolution of scanning electrochemical techniques, it is possible to distinguish between the spatial resolution, related to how small of a feature on the sample can be imaged; and electrochemical resolution, which defines the sensitivity to the response of different electrochemical processes. The accuracy and resolution of SECM and LEIS are determined by several factors: the potentiostats, the positioning system, the probe size, the probe-to-sample distance, the tilt/geometry/roughness of the sample and the diffusion of species.

- The potentiostat influences the electrochemical resolution. The experiments performed during this research were made under potentiostatic control and therefore the accuracy is related to the lowest current which can be detected by the probes. For SECM, the UME current has an accuracy error corresponding to less than 0.5% of the measured current; for LEIS, accuracy can be given as the variance in results at 90% confidence, corresponding to less than 10% selecting a short integration time in the FRA. In this sense, it is possible to understand that the sensitivity of these techniques is very different.

- The positioning system influences the spatial resolution. The positioning system is a motor-driven device and the Uniscan M370 system, used for both SECM and LEIS, has an open-loop design, i.e., it relies on a factory calibration to determine probe position. Further, the accuracy of the positioning system is also determined by the speed at which the probe is moved. The lower the shift velocity, the better the accuracy, i.e. the sample position is usually more accurately achieved at $1 \mu\text{ms}^{-1}$ than at 1mms^{-1} . A minimum step size of $10 \mu\text{m}$ with a scan velocity of $5.6 \mu\text{ms}^{-1}$, was used for SECM profiles and a step of $127 \mu\text{m}$ with a scan velocity of $8.9 \mu\text{ms}^{-1}$ was used for LEIS. While the step size is well above the 8 nm motor drive resolution for both techniques, the scan speed in LEIS measurements may be a disadvantage when compared to the scan speed in SECM in terms of resolution. In practical terms, it allows to map larger areas in less time thus limiting the effect of system evolution of the results. A drift of the motor results in a gradual shift of the zero position by a few tens of micrometers and because of that the profiles corresponding to different scans had to be corrected so they could overlap. This also limits identification of critical regions of the sample.

- The probe dimensions and geometry has an impact both on the electrochemical resolution and on the spatial resolution. In the limiting scenario of a probe with a large diameter of $100 \mu\text{m}$ scanning over a very small sample in $1 \mu\text{m}$ steps, the probe would see the response from the sample at every step until it had completely passed over it. The amperometric current measured by the SECM results from the interaction of the UMEs diffusion-layer with the sample, and therefore, no topographical feature can appear smaller than the probe diameter itself. In

the case of the local current sensed by the LEIS bi-probe, it results from potential gradients in solution generated by the sample; therefore, it is possible to detect activity for samples smaller than the probe as long as they are sufficiently active. Decreasing the probe dimensions down to the micrometer range, or even less might seem an obvious solution to increase resolution, but it is necessary to take other parameters into account. The signal-to-noise ratio would decrease and the probe would need to be positioned much closer to the surface, requiring perfectly flat and levelled samples, which is certainly not the case of the systems studied during the course of this dissertation. Further, because the corresponding scan step size should be comparable to the tip dimensions, the time required to perform a scan would be too long and for sure the behaviour of the sample would evolve from the first to the last point measured.

- The probe-to-sample distance is an essential parameter in the electrochemical response. In the case of SECM, this parameter is quantified by the approach curve experiments. Ideally, for detection of local effects, the probe should be about 2-4 radius away from the surface of the sample. In LEIS there is no accurate method to determine this distance, further, the optimum probe-to-sample distance depends on the conductivity of the electrolyte, the geometry of the sample and the electrochemical activity of the sample. Bringing the bi-probe closer to the sample may increase the signal-to-noise ratio but decreases sensitivity towards the distribution of the potential fields in solution.

- When it comes to the surface of the sample itself, for a flat sample, the tilt should be considered, although the scan area also plays an important role in the resolution. Over a scan line along a length of 80 mm, a change in 10 μm (slope = 1/8000) may appear very flat and leveled in geometrical terms, but this change in probe-to-sample distance has a pronounced effect on the electrochemical response of the UME. Naturally, before starting the experiments, the necessary time was taken to level the surfaces and assure that the drift in the current was only due to contamination of the disk UME by corrosion products. With smaller probes, because they need to be positioned closer to the surface, the tilt is more critical and crashing can easily happen. An advanced SECM imaging mode, the *constant-distance*, also called *constant-current mode*, it allows in theory the probe to account for topographic changes, adjusting in z as it maps in xy , but is not available in the M370 model. Further, it is only useful if the sample is homogeneous, i.e. purely conductive or purely insulating, which again is certainly not the case of the systems under study in the current dissertation.

Even in ideally designed systems, with optimized accuracy and resolution from the positioning system, probe and potentiostat, the electrochemical nature of the system under study can also limit the resolution. This is related to the diffusion region formed at the sample

interface in solution. Diffusion is a mass-transfer mechanism resulting from the gradients in chemical potential of a species and in practice it smoothes the concentration gradients. Diffusion is random and is three-dimensional, meaning that products do not diffuse in strict paths from the solution to the sample, from the sample to the probe or from the probe to the sample; the products from the reactions always spread through a larger volume than the reaction site itself. For this reason, local electrochemical techniques cannot be used to estimate corrosion rates although they are very useful to provide insight into the corrosion mechanisms.

In the local impedance measurements, the relative position of the two elements of the bi-probe results in a better measurement of the spreading of the potential field in solution. By comparison, the SVET measures the ionic flow in only two directions, the vertical and the horizontal along the sweep line, although the results published are usually only the vertical component of the ionic current.

The SECM operating in the amperometric mode is quite different from the other scanning electrochemical techniques in this respect. The current at tip results from hemispherical diffusion around the UME and when the tip approaches the sample, a disturbance of the diffusion layer around the UME is measured. If the sample is insulating, negative feedback will always be observed due to blocking of the hemispherical diffusion. If the sample is conductive, or has conductive features, the feedback response will depend on the size of the electroactive features and on the potential of the sample. When a feature is much larger than the tip, any species, e.g. the mediator, produced at the UME, will be regenerated at its surface under diffusion limited conditions. As the electroactive features become of the same size as the probe or even smaller and depending of the potential of the sample, the regeneration of the mediator species may no longer occur under diffusion limited conditions. In this case, the tip current is a measure of the electron transfer rate of the mediator regeneration reaction at the sample or of mass transfer coefficient.

Aimed at improved resolution of the SECM towards identification of the zinc anode and the effect of zinc corrosion products on the cathodic reactions, a model cut edge consisting of a zinc anode and a split iron cathode was used. Another advantage of this model system is its enlarged dimensions, which allows the use of LEIS. However, the factor that limits resolution the most in LEIS is the separation between the electrodes of the bi-probe which is c.a. 1.5mm. This means that the probe has little or no sensitivity to detect variations within the potential field generated in solution caused by a very small heterogeneity in the sample. Further, in the case of electrodes smaller than this separation, the measurement is not really localized as the

response is an average value between that of the feature being analyzed and that of the surrounding matrix. Despite the limited resolution, LEIS has a great advantage towards the SECM and the SVET, it allows the identification of the electrochemical processes occurring at individual electrodes. The local impedance measurements are not normalized to an area. The potential stimulus is applied to the whole substrate and the current resulting from the processes at the interface is measured as an ionic current (or rather, as potential gradient) by the bi-probe at a selected frequency. This means that the area providing current in solution cannot be defined. Further, local impedance spectra are critically affected by geometrical effects that often introduce inductive loops that are still under study. In LEIS, measurements can be performed in two modes: full spectrum at a fixed position and fixed frequency scanning. While the full spectrum is useful to identify the process occurring at each electrode, the admittance line scans give a good idea of the time variation of the processes, although with various limitations. Because profiles are made at a single frequency, care has to be taken to ensure stability of the system during the time of the experiments. The behaviour may shift from resistive to capacitive and therefore full spectra were made at regular intervals to guarantee the nature of the process sensed.

As expected, the free corrosion potential of the galvanic model assumed a fairly stable value around -1.0 V, corresponding to the reversible potential for zinc corrosion in neutral, acidic and alkaline solutions. At any pH, iron is polarized into its thermodynamic region of immunity and therefore it will be the cathode. Nevertheless, the bulk pH resulted in a significant change in the behaviour of the cut edge and the cut edge model. In the acidic solution, the potential vs. time curve presented numerous spikes that revealed hydrogen evolution, which is expected to be the main cathodic reaction on iron, whereas zinc dissolves and remains in solution. After 24h the remaining zinc was insufficient to offer cathodic protection, triggering self-corrosion of iron similarly to what was observed on the real cut edge.

In neutral medium, corrosion of the galvanic couple occurred with precipitation of white corrosion products over iron, forming a semi-circle at some distance from the edge, similarly to the distribution found at the cut edge depicted on Figure 7.9 b. However, in the model configuration the location of precipitates was somewhat surprising; irrespective of the wide insulating surface separating the cathode and the anode, precipitation occurred not over the resin or at the edge of the iron plate. Naturally, the pH and zinc cation concentration dictate the precipitation sites and although it is possible to perform potentiometric mapping of local distributions of Zn^{2+} [44], this technique is still under development particularly when it comes to increase selectivity in the presence of Na^+ . Among the electrochemical techniques available at

the lab, SIET is the only capable of delivering chemical information and therefore is used to perform pH measurements. The bulk pH measurement performed with the ISME confirmed that on zinc there was no sign of acidification that could result from local hydrolysis, whereas strong alkalisation on the cathodes was detected, with the pH reaching 10.5. A slightly lower pH, around 9, was observed at the cathode near the anode, in the region without the zinc corrosion products, due to the consumption of OH^- in the precipitation process. A high pH was also measured in the insulating region between the two cathodes showing the flow of hydroxyl ions from the remote cathode to the anode.

The stability diagram of different zinc species in 10 mM chloride and 5 μM carbonate solution was calculated using Hydra-Medusa® software, assuming a concentration of zinc in solution of 10^{-5} M, Figure 7.10. Thermodynamic predictions are in good agreement with out observations, in which on regions where zinc corrosion products did not precipitated the pH was below 9.5, whereas for higher pH, $\text{Zn}(\text{OH})_2$ and ZnO become stable. The stability diagram highlighted that although zinc hydrolysis doesn't acidify the solution, it has an important buffering effect on the maintenance of pH values below ~ 9.0 in the vicinity of the zinc and at edge of the inner iron cathode, favouring the stability of zinc soluble species (ZnOH^+), whereas closer to the centre of the iron plate the pH is sufficiently high to allow the formation of $\text{Zn}(\text{OH})_2$ and ZnO .

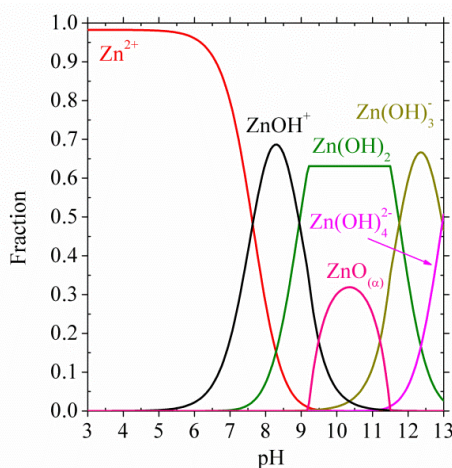


Figure 7.10. Stability diagram of zinc species as a function of pH at 25°C calculated using the Hydra-Medusa® software and considering $[\text{Zn}^{2+}] = 10^{-5}$ M, $[\text{Cl}^-] = 10^{-2}$ M and $[\text{CO}_3^{2-}] = 5 \times 10^{-6}$ M.

The SECM measurements revealed fairly homogeneous regeneration of FcMeOH on the cathode far away from the zinc whereas the precipitation of corrosion products created topographic features that reduce the volume of electrolyte under the microprobe, causing a drop of the feedback current. These results are consistent with the observations performed with the cut edge. The redox competition mode revealed only a slight increase in the tip current,

suggesting a minor barrier effect on the cathodic reaction due to the presence of the zinc corrosion products. Ionic current mapping with the SVET, also did not reveal evidence of cathodic inhibition contradicting previous observations from Ogle et al [33] and even from the previous research on the cut edge. This discrepancy may be explained by the cancellation of positive and negative currents when the electrodes are in very close proximity, i.e., by attenuation of the concentration gradients in a microscopic narrow region in the vicinity of the probe [45]. Although the anode was much larger than in the cut edge and well separated from the cathode, SECM showed little sensitivity for zinc, possibly due to a small efficiency of the metal to the regeneration of the mediator but mostly because of recession of the dissolving surface during the experiment.

In alkaline medium, corrosion of the galvanic couple occurred with precipitation of a very thin layer of zinc corrosion products on the iron plate closer to the zinc. EDS analysis revealed that the distribution of the corrosion products similar to what was observed in neutral medium. Nevertheless, the SECM results were very interesting and very different from those obtained in neutral medium. The feedback current revealed homogeneous regeneration of mediator at the cathode not covered by corrosion products, whereas on the iron plate closer to the anode nearly half of the surface revealed a lower feedback current. This is the region where corrosion products accumulate. The feedback current is affected by both the conductive nature of the substrate and topography and this local current decrease might reveal either of the two. However, in a conducting surface, a decrease of the tip-to-sample distance would result in an increase of the feedback current, and so this sub-step on can only be assigned to the precipitation of zinc oxides. Further, the corresponding profile for the cathodic activity shows significant oxygen depletion at the iron plates except in the region where the corrosion products accumulate. These results reveal local inhibition of the cathodic reaction associated with the presence of zinc insoluble species, i.e. self-healing. Although some authors [46, 47, 48] support the theory that self-healing might result from the stabilization of a FeOOH layer by action of the zinc cations, which would result in a more protective layer, our results indicate that iron is immune and therefore, the zinc corrosion products alone must be responsible for any self-healing.

Despite attempts were made to differentiate and characterize the nature of the corrosion products at neutral and alkaline pH, identification was not achieved. The composition of the solid products seemed complex and the chemistry of the precipitating environments change constantly with time, possibly generating different products not just during the immersion process but also during the drying process. In neutral solution, the growth of the

layer of zinc oxides has been explained by the diffusion of anions in solution towards the anode, followed by their precipitation corrosion products layer and their reaction with the cations zinc complexes, resulting in a porous layer with a $\text{Zn}(\text{OH})_2$ matrix, with some moderate protection, that is, not blocking effectively the cathodic reaction. In alkaline solution the zinc oxide layer is apparently thinner than the one formed under neutral conditions probably due to slower kinetics of zinc dissolution and precipitation, which results in a more compact and protective structure which is effective in blocking the cathodic reaction.

The LEIS, as mentioned as mentioned before, has a comparatively low resolution when compared to the SECM and the SVET, but it provides valuable mechanistic information. The low frequency impedance provides more information on the evolution of the processes at cathodes and anodes than the high frequency impedance. At high frequencies the impedance reveals mostly the resistance of the electrolyte, thus being nearly constant with time and irrespective of the properties of the electrode, while at low frequencies it is the mass transfer processes or the charge transfer resistance that determines the spectrum. The decrease in the admittance above the zinc in acidic medium is consistent with the dissolution of the electrode. At pH 10, the admittance readings over the zinc were fairly stable during the experiment time. At this pH zinc oxides are thermodynamically stable; this means that zinc oxidation takes place in steady-state fashion either through a quasi-passive layer or else in a relatively localised manner, comparable to pitting dissolution. An advantage towards the SECM is that the admittance profile measured at 1 Hz is quite sensitive to the activity at the zinc anode providing some information regarding corrosion kinetics. However, the interpretation concerning the response from the cathodes is not straightforward.

In neutral solution and for shorter exposure times, the cathode closer to the zinc did not produce a response to the excitation signal. A small perturbation in the sample potential should produce fluctuations in the double layer, i.e., on the charged particles at the sample/electrolyte interface which control the flow of ionic currents into bulk solution. The explanation for absence of a.c. current takes into account the reactions occurring above the inner cathode, in bulk solution, i.e. closer to the tip. These reactions, which occur at a high rate, are chemical in nature, and thus do not respond to the small a.c. stimulus applied to the system, thus decreasing the a.c. current below the noise level. At a later stage of the corrosion processes, once a pseudo-steady state is achieved, a higher concentration of free ions is reached over the inner cathode, with a consequent increase of conductivity of the electrolyte and thus an apparent increase of the admittance.

In acidic and alkaline solutions, the a.c. current measured above both cathodes rapidly decreases to noise levels. In acidic solution, fitting of the local spectra to an EEC, revealed that while the zinc is active and protecting the iron, the hydrogen evolution reaction has a high discharge rate which causes the cathodic process to be under mixed activation-concentration transport. In this case the explanation for the absence of response at the cathodes is apparently simple: an a.c. excitation around the mixed potential will not produce an a.c. potential as the cathodic current does not change with potential. At pH2, after 24h immersion the process is no longer under mixed control and in principle it should be possible to measure local potential field. In practice, the impedance of the interface is comparable to the ohmic impedance and thus the measurement is almost at noise level. In alkaline solution, the local spectra did not reveal mass transport limitations but did reveal that the resistance at low frequency is very high. In this situation, the impedance at low frequency is too high to be measured by the bi-probe and the current flows through the path of less resistance that is, through the counter electrode.

Although the local pH has not been determined in this part of the work, the influence of the pH on the corrosion products layer was evident. In a NaCl solution, with nearly neutral bulk pH, the local pH can go up to approximately 11, while the anode remains in a neutral solution. In alkaline environment the pH in the vicinity of the cathodes should also rise but more moderately. Further, zinc hydrolysis is not expected to decrease greatly the pH and zinc becomes quasi-passive while protecting iron, part of its oxides remain on the zinc surface and some part reach the cathode.

SECM operating in the *feedback* and *redox-competition modes*, provided evidence of self-healing, or inhibition of the cathodic reaction in alkaline solutions and it was associated with the blocking effect of the zinc corrosion products. The LEIS showed that in acidic medium, the galvanic corrosion of iron-zinc is limited by a mixed activation-concentration cathodic process. This information could not be extracted from analysis of the real cut edge system because of the close proximity of the metals is below the resolution of the scanning electrochemical techniques.

Despite the limitations presented concerning the resolution of the local scanning techniques and the nature of the systems under study, the LEIS and the SECM have proved valuable tools to provide insight into the study of localized corrosion at EG cut edges. Interpretation is not straightforward and is necessary to take into account side reactions, namely in the case of SECM, and geometry induced artefacts, in the case of LEIS. Apart of the redox-competition mode of the SECM, these techniques do not have chemical resolution and thus complementary analysis with the SVET/SIET and thermodynamic calculations revealed necessary.

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8. General Conclusions

The dielectric properties of a Zn-55Al rich-primer applied on electrogalvanized steel were determined using Electrochemical Impedance Spectroscopy. The primer is characterized by a resistance of $10^7 \Omega\text{cm}^2$, a capacitance of 10^{-8}Fcm^{-2} and a dielectric constant of 40 which agrees with its conductive nature. An electrical equivalent circuit was proposed to model the impedance behaviour of the primer, in which the system is described by three relaxation processes corresponding to the active particles directly exposed to the solution, to the properties of the polymer and to the reactions occurring in the vicinity of the substrate. This model allows a better insight on the dielectric properties of weldable primers and on their degradation. It was the first time that a model is able to simulate the impedance response of a weldable primer as a function of plastic deformation. Three stages of degradation were identified: for the intact, non-elongated samples, only one relaxation process was observed, corresponding to the charge transfer at the conducting particles and the mixed double layer/polymer capacitance; as water penetrates the intact coating, the pore resistance decreases and a second capacitive loop accounting for charge transfer becomes evident. Concerning the elongation, it was observed that small elongations produce an increase in the active area, corresponding to metal particles becoming exposed. For large elongations, the substrate becomes exposed, giving rise to a third relaxation process corresponding to a diffusion limited reaction due to the presence of zinc and aluminium corrosion products.

Imaging of a cut edge under neutral, acidic and alkaline conditions was performed for the first time using both the SECM and the SVET. The anodic activity on the thin zinc anode was identified only by the SVET, whereas the feedback current for the oxidation of FcMeOH, used as mediator, provided information on the steel surface. In acidic solution, the corrosion was highly localized, with oxygen being consumed and Fe^{2+} being released into the solution, in the vicinity of the active anode. In nearly neutral solution, non-uniform conductivity of the steel surface correlated well with the accumulation of zinc corrosion products. Measurements in alkaline medium showed homogeneous conductivity of the steel surfaces until the tip got contaminated by precipitation of zinc oxi-hydroxides on its surface.

The resolution of the electrochemical behaviour of the different regions at the cut edge was found to be poor due to the close proximity of the dissimilar metals. Within this context, the use of an asymmetric three-electrode model cut edge system consisting of a thin zinc anode

and two iron cathodes gave an improved insight of the galvanic corrosion of iron-zinc cut edge systems at the microscopic scale.

In pH 2, the amperometric measurements revealed that although the main cathodic reaction at this pH is hydrogen evolution, the reduction of dissolved oxygen on iron and also over the zinc occurred as a parallel reaction. The local impedance spectra revealed, the cathodic reactions on the iron surface occur under mixed activation-mass transport rate control.

In alkaline conditions, the SECM revealed clear inhibition of the cathodic reaction in the region covered by zinc corrosion products, corresponding to approximately half the width of the cathode in the vicinity of the anode.

In neutral conditions, reduction at the cathode lead to nearly uniform depletion of oxygen, as revealed by the SECM and in good agreement with the SVET. Zinc imposed a strong cathodic polarization on steel shifting its potential into its region of thermodynamic immunity; the solution around steel suffered strong alkalisation, reaching a pH as high as 11.5. The resulting pH gradients determined the region where the zinc oxy-hydroxides precipitated, i.e. at some distance from the cathode edge, at the region at which a critical pH of 9.5 was reached. This distribution of corrosion products was found to be identical whether the iron and the zinc were in physical contact or separated by an insulator. The local impedance distribution provided good spatial information on the remote part of the cathode, whereas the precipitation of corrosion products leads to masking of the cathodic activity in the first stages of immersion. It was the first time the LEIS was used to study this type of system.

The different techniques provided information regarding the physico-chemical characteristics of the iron-zinc system under immersion in chloride solutions of pH 2, 5 and 10. The pH of the electrolyte has a strong influence on the nature of zinc corrosion products and their ability to suppress the cathodic activity. The SECM and the LEIS proved to have adequate resolution to detect the properties of the thin layers of zinc corrosion products formed under the various conditions. Further, the various scanning techniques in combination with thermodynamic predictions provided complementary information which was beneficial in discarding artefacts related to stirring of the solution or interaction of the probes with the surface.

9. Suggestions for Future Work

During the course of this research some topics were found to be worth of further work and clarification. Some of these topics are presented below.

- Characterization of zinc corrosion products

The SECM was able to detect quite clearly the different ability to inhibit the cathodic reactions of zinc corrosion products formed under neutral and alkaline pH. The reason for such and the underlying protection mechanisms are still a topic of discussion in the research community. Analysis of the nature, morphology and the dielectric properties of the corrosion products formed at each pH is therefore vital although hard. Ideally, the characterization of the products would have to be made *in-situ* e.g. with μ -Raman spectroscopy. This was attempted but the results obtained were not sufficiently clarifying to be included in this dissertation. Some more work would be required in this field. The study of the dielectric properties of zinc corrosion products precipitated on both iron and zinc substrates using LEIS could also be interesting.

- Application of SECM and LEIS to the study of primers having defects with controlled geometry

Although the attempts to use the SECM and the LEIS to monitor the evolution of corrosion on elongated primers were not very successful; there are some alternatives that could be attempted. In the case of the SECM, the main problem is related to the roughness of the primer which requires a larger working distance to avoid crashing of the tip on to the surface. Therefore, an UME with a diameter of 25 μm could in principle be able to map activity at the defects without interference of topography as it would operate at a larger distance from the surface. In the case of LEIS, the limitation to the study of elongated primers is related to the resolution of the bi-probe that is not able to distinguish the response from adjacent cracks. The solution to this problem would be either to produce defects with controlled geometry (scribes), which is already described in the literature for other systems, or to fabricate a bi-probe, e.g. made from double-barrel capillaries.

- Assessing the effect of activation/ concentration controlled processes on LEIS admittance profiles

During the course of the research using the LEIS, probably the most controversial result deals with the interpretation of admittance profiles over cathodic regions. The interpretation was based upon the variations of local conductivity of the electrolyte and the existence of mixed activation-concentration reactions but this phenomenon is not described in the literature. It would definitively be worth to do more research in this field. Performing the measurements over the sample polarized at varying cathodic potentials could give an insight into this subject. Deaerating the electrolyte could also be an interesting approach.

- Development of numerical models for cut edge corrosion

Numerical modelling simulation may be used to provide a better insight of the corrosion mechanisms especially when the spatial resolution is inadequate for direct observation of the processes occurring at individual electrodes. In this context, replication of some work in the literature using COMSOL Multiphysics was successful but the development of models for the systems studied in this dissertation would be a whole new research topic.