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Electrochemical Impedance Spectroscopy for Characterization of Coatings with Intrinsically Conducting Polymers

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Summary: The method of electrochemical impedance spectroscopy (EIS) was applied to investigate the behaviour of a thin intrinsically conducting polymer film (ICP) deposited on a metal substrate. Especially the conductivity, the redox properties, the anion release properties, and the corrosion protection of a coating with and without ICP film on an iron or steel substrate were studied. Combined with other electrochemical methods, the reactions taking place at an injured surface area of the coated iron were studied. The corrosion protection mechanism of polythiophene could be explained.

Keywords: intrinsically conducting polymer, electrochemical impedance spectroscopy, corrosion protection, mild steel

I. Introduction

The application of intrinsically conducting polymers (ICP) for corrosion protection of metals was suggested and very intensive studies were done in recent years. However, the protection mechanism is unclear and even the question, is there a protection, is not yet answered.

In this paper results are presented of an investigation of thin conducting polymer films (polythiophene, polymethylthiophene) with and without topcoat. The questions related to the corrosion protection mechanism of such systems are:

- Is the oxygen reduction catalyzing the reversible oxidation/reduction behaviour of the ICP [1-5]
- Can a defect be repaired by formation of a passivating oxide film [3-5]
- How can the properties of conducting polymer films be changed under the coating in contact with an electrolyte [6-8]

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To answer the above questions, a serie of measurements was made using the method of electrochemical impedance spectroscopy (EIS) combined with other electrochemical methods like cyclic voltammetry and open circuit potential measurements. Based on the results, models of the corrosion protection mechanism of coatings with polythiophene were diccussed.

The equivalent circuit of an electrode covered with a film of an ICP and a topcoat

An electrode with the described coating is completely inert except if the coating has a defect. With a defect, the corrosion reaction of iron on the defect is measured additionally. An organic coating with defect can be modelled with an equivalent circuit shown in Fig.1. The parameters C_c and R_c measured at high frequencies correspond to the organic coating, whereas the parameters C_{dl} and R_{ct} measured at low frequencies are related to the electrochemical corrosion reaction at the metal substrate. The coating capacitance C_c depends on the properties of the coating (thickness, composition, structure, dielectric constant), the coating resistance R_c is determined by the defect area. The larger the defect area the smaller R_c. Due to the corrosion process taking place at the interface metal/coating, the adhesion of the coating decreases. The coating is gradually delaminated. The area of the defect is enlarged, R_c decreases. [9-10]

The conducting polymer itself is not explicitly represented in the equivalent circuit, but the elements of the equivalent circuit are influenced by the conducting polymer, especially the double layer capacitance C_{dl} and the charge transfer resistance R_{ct}. If the conducting polymer protects the iron in the defect area, R_{ct} is very high and the potential of the electrode is shifted to more positive values. In case a passive layer is formed, R_{ct} and C_{dl} correspond to the resistance and the capacitance of the oxide layer.

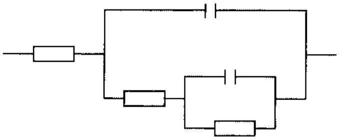

Figure 1. Equivalent circuit of a polymer coated metal according to [10]

Equivalent circuit of an electrode with an ICP film

The ICP film can be analyzed using a transmission line model introduced by Pickup et. al [11. This model can be simplified, if only the change of the conductivity is observed. A simplified equivalent circuit is given in Fig. 2

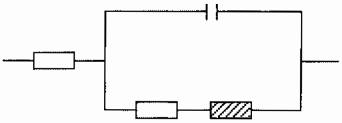

Figure 2. Simplified equivalent circuit of an electrode with a conducting polymer film

The polymer capacitance C_{CP} is related to the redox process taking place in the polymer film and the conductivity is reflected by the resistance R_{CP}, Z is a complex impedance mostly related to a diffusion process in the ICP.

II. Results and discussion

1. Film formation with adhesion promoter

The coating process is based on the pretreatment of the substrate surface with 10^{-3}M 2(3-thienyl)ethylphosphono acid used as adhesion promoter. The synthetic details and the characterisation of the adhesion promoter were described elsewhere [12]. Then a polymethylthiophene (PMT) film is built up galvanostatically in a solution of the monomer. The adhesion promoter forms an ultrathin film with a structure like a self assembled monolayer (SAM). This SAM layer is covalently bond to the substrate, on which PMT can be deposited by electropolymerisation without any metal dissolution [13].

The redox properties of the film were investigated with cyclic voltammetry on PMT films grown on steel with SAM monolayer and on Pt. In both cases, the CV peaks show that the characteristic redox property of the PMT film on steel and on Pt are the same [6].

2. Corrosion protection of an ICP film without topcoat

The corrosion of a PMT covered steel electrode was investigated by EIS during immersion in aeraeted 0.1 M NaCl. Comparing the steel samples with and without PMT film, it is shown that the PMT film reduces the corrosion rate of mild steel but cannot completely protect the metal against corrosion. This is in agreement with potentiodynamic curves of steel with and without PMT [13]. The PMT film shifts the corrosion potential to more positive values and reduces the corrosion rate. However, the corrosion potential of PMT coated steel is only 100 mV more noble than that of bare steel and remains within the potential range where iron is dissolved. Passivation of the metal substrate caused by the positive value of the redox potential of PMT, an often discussed protection mechanism [2,14-17], is not observed.

3. Corrosion protection of an ICP film with topcoat

For the corrosion test with topcoat, two standard sample configurations were chosen and exposed in neutral aerated 0.1 M NaCl solution. The first sample was a mild steel with an alkyd coat, the second sample was a mild steel with a PMT film and an alkyd topcoat, for comparison. A small hole was made by a needle in order to simulate a defect. Measuring the open circuit potential, it was observed if the steel substrate was in the passive or in the active state. The PMT, even combined with a topcoat, caused no passivation of the steel substrate, the corrosion potential remained within the active range of iron dissolution. In combination with PMT, only a potential shift of +100 mV was observed.

The results show: the thin PMT film cannot protect mild steel against corrosion. It needs a topcoat to protect the samples. However in many cases the topcoat interacts with the PMT film which is reduced. This can be seen by overcoating a PMT film with conventional clear coating systems. The color of PMT changes from blue (oxidized, conducting state) to red (reduced, non conducting state), (see Table 1).

It means that the electroactivity of the PMT film gets lost by the interaction with the coating. Only with polyurethane (pure or containing an acidic hardener) the blue color of the PMT film shows that no reduction reaction takes place.

Table 1. PMT film overcoated with some conventional coatings

clear coating system	color of the PMT film
epoxy 2K (ZD73-0000) with hardener	red
epoxy 2K (ZD73-0000) without hardener	red
epoxy with acrylic acid as hardener	red
Alkydal F26/60% in xylol	red
alkyd	red
waterborne coating (pH =11)	red
polyurethane 2K + hardener ZH62	red
polyurethane without hardener	blue
polyurethane + acrylic acid as hardener	blue

The influence of the pH of aqueous electrolytes on the electroactivity of PMT films was studied seperately. Figure 3 shows results of EIS measurements of PMT films on Pt in 0.1 M $LiClO_4$ with different pH values.

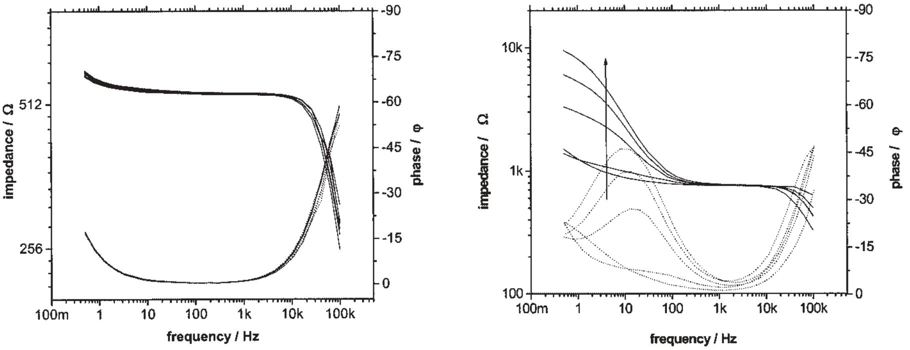

Figure 3. EIS measurements of PMT films on Pt in 0.1 M $LiClO_4$ at different pH values. The phase angle is indicated by dotted lines.

At lower pH (< 9.7) the polymer is still conductive. The resistance is low (about 10 Ω) and it does not change in 90 minutes. At pH=11 the resistance is changed, it increases to 500 Ω after 60 minutes and to 5000 Ω after 120 minutes. It can be seen that the pH value has a strong influence on the conductivity of PMT films. After the 120 minutes immersion at pH = 11, the PMT film is immersed in an acidic electrolyte (pH = 2) in order to verify, whether the PMT film becomes conductive again. The loss of conductivity is irreversible. A change of the pH from 11 to 2 gives only a small decrease of the resistance. The reduced PMT film cannot be reoxidized by oxygen, as was found for PANi [1-2]. The results of EIS measurements are summarized in Figure 4.

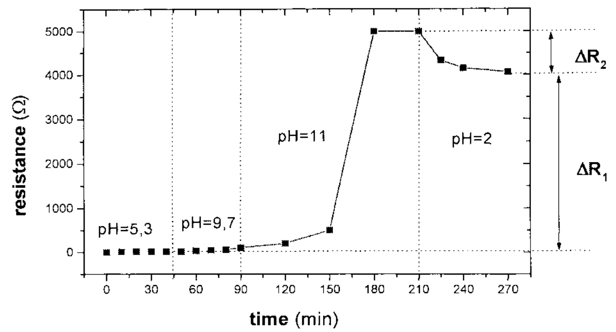

Figure 4. Resistance of PMT films on Pt at pH = 5.3, 9.7, 11.0 and 2.0 obtained from impedance measurements

A possible explanation is given by Wang [8]. According to these studies, PMT is attacked by nucleophilic anions and water. The formation of C=O bonds in aromatic rings disturbs the conjugated system of the polymer, so that the polymer is deactivated. The structure is irreversibly changed by the nucleophile attack. The higher the concentration of nucleophile in the electrolyte, the faster the polymer is deactivated. The concentration of nucleophiles depends on the pH value of the electrolyte.

For further studies of the influence of PMT electroactivity on the corrosion protection of mild steel an experiment was developed where the reaction on the steel surface and the reaction in the conducting polymer film could be observed separately. The principal electrode configuration is shown in Fig.5. The conducting polymer film was formed on a platinum electrode. A separate mild steel electrode could be connected or disconnected with the platinum electrode. This electrode was covered by an insulating epoxy film, which was scratched in order to simulate a small defect. The behaviour of both electrodes was investigated under various conditions by EIS.

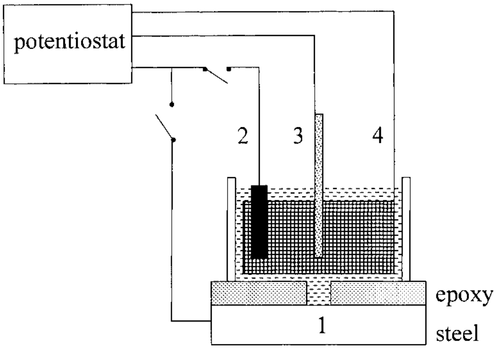

Figure 5. Scheme of the electrochemical cell:(1) mild steel/epoxy, (2) Pt/PMT, (3) SCE reference electrode, (4) Pt counter electrode, exposure in 0.1 M $LiClO_4$, aerated and deaerated.

The behaviour of the Pt/PMT electrode is shown in Figure 6. In deaerated solution the resistance of the PMT film is very low (approx. 50 Ω) and remains nearly constant after coupling with the steel/epoxy electrode for 120 minutes, i.e. PMT is in the conductive state but does not oxidize the steel. After 2 hours the solution is saturated with air and now the conductivity of PMT decreases, if the Pt/PMT electrode is connected with the steel/epoxy electrode. A second time constant is observed in the frequency range of 1 kHz to 10 Hz and the resistance increases to 5 kΩ. The reduction of PMT is caused by iron corrosion in the O_2 containing solution.

PMT remains conductive in aerated $LiClO_4$ solution, if the Pt/PMT electrode is not connected with the steel/epoxy electrode [18]. After connection the resistance increases very fast and rises continuously up to 22 hours. It means that in the hole O_2 reduction takes place as cathodic process causing iron dissolution and, simultaneously, reduction of PMT.

The behaviuor of the mild steel/epoxy electrode is shown in Figure 7. The high frequency part is related to the coating parameters (C_c, R_c). The low frequency part can be attributed to the electrochemical corrosion reaction taking place at the steel substrate (R_{ct}, C_{dl}). The value of C_c is not changed during exposure in deaerated and aerated solution. The value of R_c is about 400 kΩ and remains nearly constant during coupling with the Pt/PMT electrode in deaerated solution (Fig. 7a). In contrary, in aerated solution R_c is decreased to 20 kΩ after 30 minutes due to the corrosion of mild steel in the hole (Fig.7b). The size of the hole is markedly increased and the bottom of the hole is covered with the corrosion products. In the high frequency range, the double layer capacitance C_{dl} increases because of the increasing defect area. The charge transfer resistance decreases significantly indicating the strong dissolution of iron in the defect.

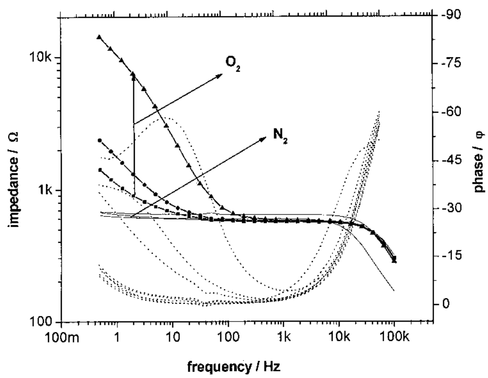

Figure 6. EIS measurements of a Pt/PMT electrode coupled to a steel/epoxy electrode after (—) 0, 30, 60, 90, 120 minutes in deaerated solution and then after (■)30, (●)60 minutes, (▲)22 hours in aerated solution. The phase angle is indicated by dotted lines.

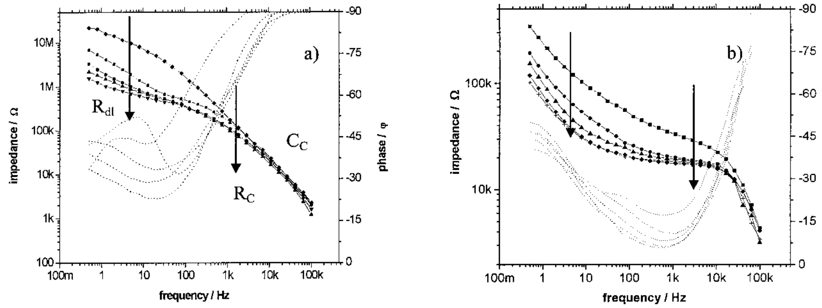

Figure 7. Bode plots of a mild steel/epoxy electrode in 0.1 M $LiClO_4$, a) deaerated, b) aerated after coupling with a Pt/PMT electrode. The phase angle is indicated by dotted lines.

The process could be principally described as follows:

anodic reaction $Fe \rightarrow Fe^{2+} + 2e$ (1)

cathodic reaction $\frac{1}{2} O_2 + 2e + H_2O \rightarrow 2\ OH^-$ (2)

additionally $PMT_{ox} + 2e \rightarrow PMT_{red} + 2A^-$ (3)

$2OH^- + Fe^{2+} \longrightarrow Fe(OH)_2 \xrightarrow[+O_2]{} Fe(OH)_3 \xrightarrow[-H\ O]{} Fe_2O_3$ (4)

The reaction (3) is irreversible, because the resistance of PMT increases continuously, i.e. the reduced PMT film provides no electrons for the oxygen reduction. After 22 hours connection between both electrodes, rust is observed in the hole of the epoxy covered steel electrode and the potential of the steel electrode changes from +0.3 V to –0.6 V(vs.SCE), immediately after disconnection. The bare steel surface within the hole cannot be passivated by the PMT film in O_2 containing solution.

4. Possible protection of ICPs

The results have shown that ICP films shift the electrode potential towards more positive potentials, but the shift does not lead to passivation. But, a noteworthy synergism exists between PMT film reduction, oxygen reduction and iron dissolution. The experiments have demonstrated that there is no catalytic effect of the conducting polymers, neither for the oxygen reduction nor for the metal passivation, contrary to statements in the literature. The potential of iron is remaining in the active dissolution region. A passive oxide layer cannot be formed under these conditions.

Combination of the adhesion promoting SAM layer and a film of conducting polymers as a primer coating, increases the corrosion protection of secondary coatings, because this combination gives good protection against delamination.

Recently a possible protection mechanism was suggested in the literature [19-20]: The layer of the conducting polymer is separating the process of metal dissolution from the process of oxygen reduction. This would prevent the local pH increase at the metal surface and the subsequent delamination.

IV. Conclusion

It was shown that EIS is an useful method to investigate the corrosion protection of a combination of organic coatings with conducting polymer films.

An ultrathin adherent ICP film like PMT could reduce the corrosion rate of mild steel and improve the corrosion protection by a topcoat. The electroactivity of PMT gets lost if the topcoat is reducing the PMT.

An experiment was performed separating the PMT film and the mild steel/epoxy electrode. The experiment showed, that the ICP film (more specific, the polymethylthiophene) could not passivate the mild steel electrode. Only by a complex combination of oxygen reduction, iron dissolution and ICP reduction an interaction between ICP film and mild steel was observed.

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