THE ROLE OF ANIONS IN CORROSION PROTECTION OF IRON AND ZINC BY POLYPYRROLE

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Le Minh Duc
To my parents

To N. T. Huong, M. Nhat and M. Y with love
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Abbreviations and definitions

$\Delta f$: Change of frequency.
$\varepsilon_F$: Fermi level.
$\Delta m$: Change of mass.
$\rho_q$: The density of the quartz.
$\Delta Q$: Passed charge in electrochemical process.
3-nisa: 3-nitro salycilic.
ACN: Acetonitrile.
$C_{dl}$: Capacitance of double layer.
$C_f$: Sensitive factor of the crystal.
$C_{PM}$: Capacitance of polymer film.
CV: Cyclic voltametry.
DMF: n,n-dimethylformamide.
DMSO: Dimethysulfoxide.
$E_{corr}$: Corrosion potential.
EDX: Energy Dispersive X-ray.
EIS: Electrochemical impedance spectroscopy.
EQCM: Electrochemical quartz crystal microbalance.
$f_o$: Resonant frequency.
$i_{corr}$: Corrosion current.
ICP: Intrinsic conducting polymers.
IR: Infrared spectroscopy.
MeOH: Methanol.
N(Bu)$_4$Br: Tetrabutylammoniumbromide.
OCP: Open Circuit Potential.
Pani: Polyaniline.
Ppy: Polypyrrole.
Ppy(MoO$_4$): Polypyrrole doped with MoO$_4$.
Ppy(X)/Y: Polypyrrole doped with X on substrate Y.
Pss: Polystyrenesulfonate.
R$_{ct}$: Resistance of charge transfer.
R$_e$: Resistance of electrolyte.
$R_{PM}$: Resistance of polymer film.
SEM: Scanning electron microscopy.
SERS: Surface enhanced Raman spectroscopy.
SHE: Standard hydrogen electrode.
SKP: Scanning Kelvinprobe.
THF: Tetrahydrofuran.
t$_q$: Thickness of the quartz.
$V_c$: Volta-potential difference.
v$_q$: Velocity of the acoustic wave in the quartz.
W: Molar mass of anion.
XPS: X-ray photoelectron spectroscopy.
z: Electric charge of anion.
1. Introduction and objective

1.1. General aspect

Metals and alloys, depending on their mechanical, chemical and physical properties, are chosen for variety of applications. They are used not only in industry but also in our daily live as utensils. Metals are present in all products from complicated equipment such as airplanes, autos, etc. to simple things as toys, cooking tools etc.

All metal products are in contact with wet atmosphere or another aggressive medium such as seawater. Therefore, the corrosion process always occurs on the metal surface. This is also a challenge for scientists to control and reduce the enormous damages due to corrosion. But in many cases, the questions ‘What is the mechanism of corrosion’ and ‘How can we prevent metal products from corrosion?’ have no answers.

The term ‘corrosion’ refers to deterioration of materials due to the chemical reactions with the environment. This concept is applicable for metallic and non-metallic materials. Corrosion is involved in the conversion of the surface of metals in contact with corrosive medium into another insoluble compound. Corrosion is also defined as 'the undesirable deterioration' of a metal or an alloy i.e. an interaction of the metal with its environment affecting the main properties of the metal. Corrosion protection is required for a long life and economical use of equipment in technical processes.

Corrosion preventing technology has many options, for instants cathodic protection, anodic protection, use of corrosion inhibitor, forming the precipitates on the metal surface and acting as passive layer, organic coating etc.

Among the methods to prevent corrosion of metals, protection by conducting polymers has been investigated extensively in the recent years. This is considered as a possible alternative for friendly-environment coating because an electrochemical process could eliminate the use of toxic chemicals. The advantage of an electrochemical technique is also the combination of in-situ passivation with polymer coating.

There are many publications related to conducting polymer in corrosion protection. Conducting polymer can decrease the corrosion rate of many metals such as iron, mild steel, aluminium, magnesium and others. However, the mechanism of corrosion protection for the metal surface is not yet clear.

Understanding of the mechanism of corrosion protection by conducting polymer may be beneficial for the application of this mechanism of corrosion protection in industry.
1.2. Objectives
The objectives of this PhD are:
* Synthesis and characterisation of the polypyrrole (Ppy) films doped with inhibitor anions molybdate, hexafluorotitanate on mild steel and 3-nitro salicylate on zinc or galvanised steel.
* Study of the role of inhibitor anions in the corrosion process.
* Development of a mechanistic model of corrosion protection by polypyrrole with inhibitor dopants on active metal substrates.
* Investigating the possible applications of core-shell particles in corrosion protection.

1.3. Contents of the thesis
The thesis is contained in six main parts:
* Introduction and objectives
* ‘Theoretical background’ where the fundamentals of conducting polymers and their applications in corrosion protection using polypyrrole (Ppy) are reviewed. This review focuses on the most recent research of Ppy in corrosion protection of active metals especially mild steel.
* ‘Analytical methods’ lists and describes the main employed methods: Electrochemical Impedance Spectroscopy (EIS); galvanostatic, potentiostatic, and cyclic voltammetry; Electrochemical Quartz Crystal Microbalance (EQCM); and Scanning Kelvinprobe (SKP). The basic principles of these methods are also presented.
* ‘Experimental procedures’ describes the experimental set up, the reaction conditions and lists all chemicals used in the current work.
* ‘Results and discussions’ presents all experimental results. The properties of polypyrrole films on platinum are described in part 5.1. The anion exchange ability of polypyrrole is discussed extensively. The important properties of the polypyrrole film such as the conductivity, pH depending, anion release behaviour are presented. The polypyrrole films doped with molybdate (Ppy(MoO₄)) on Pt and mild steel are described in parts 5.2 and 1.1. These results prove the role of molybdate as inhibitor dopant in corrosion protection of mild steel. The effects of substrates (Pt and mild steel) on polypyrrole films are also discussed. The initial results of Ppy doped with TiF₆²⁻ are shown in the part 5.4. In part 5.5, results with 3-nitro salicylate as dopant anion of Ppy on zinc and galvanised steel and the properties of the Ppy film on Zn are presented. The application of these inhibitor anions in corrosion protection
is discussed in part 5.6. EIS results to test the potential of corrosion resistance of polymers containing core-shell particles are also shown.

* ‘Conclusion’ summarises the main results achieved and remaining problems that should be investigated in future work will be discussed.

These experiments were carried out mainly in the laboratories of The Institute of Physical Chemistry and Electrochemistry. The Scanning Kelvinprobe and XPS experiments were carried out in The Max-Planck Institute-Düsseldorf. Chemetall GmbH prepared the polymer film containing core-shell particles on mild steel and galvanised steel. The work was financed within the BMBF project named ‘Release-Systeme für die Selbstheilung von Polymer/Metal Grenzflächen’.
2. Theoretical background

2.1. Conducting polymers

2.1.1. History

In daily life, polymers such as common plastics are insulators. The term ‘electrical conduction’ is usually assigned to metals or alloys. The discovery of conducting polymers has opened a new branch in material research.

In 1910 Green and Woodhead reported that the electrical conductivity of polyaniline (Pani) was improved when the polymer was treated in acetic acid. However, this new discovery was forgotten. In the succeeding decades, chemists and physicists repeatedly tried to synthesise polymers with metallic conductivity. In the late 1950s and early 1960s, Nattaetal and Luttiger synthesised polyacetylene but the product did not exhibit any conductive properties. Dall’Olio et al. prepared polypyrrole from aqueous sulphuric acid in 1969, but the product had poor in mechanical and electrical properties. In 1979, Diaz and co-workers at IBM in San Jose reported that polypyrrole (Ppy) could be obtained as a freestanding film by electrochemical oxidation of pyrrole in acetonitrile [1, 2].

A very important result was obtained in 1977, when the Chem. Comm. published a paper named “Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)x”. The conductivity of the polyacetylene film increased markedly by exposure to halogen vapour. A new field of chemistry - conducting polymer - was born. The award of the Chemistry Nobel Prize to Shirakawa, MacDiarmid, and Heeger recognised this discovery of conducting polymer in 2000.

Over 25 years the fundamentals of conducting polymers were studied but only fewer commercial applications based on conducting polymers were developed [3]. In the future the impact of conducting polymers in new technologies will increase.

2.1.2. Basic characteristics of conducting polymers

Electro active polymer materials are usually classified in two main groups based on the electric transport. The first group includes polymers of ionic conducting. They are often called ‘polymer electrolytes’ or ‘polymer ionics’. A polyethylene oxide, in which lithium ion is mobile, is a typical example. The second group of intrinsically conducting polymers or conjugated polymers is electronic conductors [4]. This type of polymeric material is discussed
extensively in this thesis. Polyaniline (Pani), Polypyrrole (Ppy) and Polythiophene (Pth) are examples of this class of materials.

2.1.2.1. Common structure of conducting polymer

The principal structure of conducting polymers is the conjugation of carbon $p_z$ orbitals. In other words, there is an alternation of single bonds and double bonds in a carbon-carbon chain. The structures of some common conducting polymers are shown below.

![Polyacetylene](image1)

Polyacetylene

![Polythiophene](image2)

Polythiophene

![Polypyrrole](image3)

Polypyrrole

![Polyaniline](image4)

Polyaniline

2.1.2.2. Electronic structure and conductivity of conducting polymer

The principal structure of conducting polymers is a band structure. The overlap of bonding orbitals produces the valence band. Non-bonding states form the conduction band. For instance, extended-overlap of $\pi$-bands forms the valence band and $\pi^*$ bands the conduction band. The bands are separated by a bandgap. The energy of the bandgap determines the conductivity of materials: conductive (overlapping bands), intrinsically semiconductive ($< 1$ eV) and isolating ($> 3-5$ eV).

Intrinsically semiconductors are materials with thermal excitation of electrons from the valence band to the conduction band [2, 5]. In the special case of conducting polymers oxidation is possible (doping) creating vacancies (holes or radical cation) in the polymer chain. For charge compensation anions diffuse into the polymer networks. The holes are
partially delocalised leading to the deformation of the polymer structure. Two forms ‘polaron’ and ‘bipolaron’ are used for this process depending on the degree of oxidation. The process creates new bands localised in the formerly neutral polymer.

Polaron is a radical cation that is localised over some segments of the polymer. Bipolaron has two charges associated with the structural polymer segment. The bipolaron formation is the result of removing the second electron of the polaron.

Both polaron and bipolaron are mobile and can move along the polymer chain by the rearrangement of C-C bonds of the conjugated system in the electric field [1, 4]. The mobility of polarons and bipolarons is one part of the mechanism of charge transfer in conducting polymer.

The conductivity of conducting polymers is generated by chemical or electrochemical oxidation process of the monomers. The oxidation of conducting polymer leads to positive charges on the polymer chain. These positive charges are compensated by anions diffusing from solution into the polymer network. This process is called doping.

The doping level is a measure of the oxidation or reduction degree of conducting polymer. It is defined as the ratio of charges and monomer units. The electrically conducting form is obtained when the polymer is doped. The electrical conductivity is strongly dependent upon the polymer’s doping level. The doping level is normally higher for electrochemically formed polymers than for chemically formed polymers.
2.1.2.3. The synthesis of conducting polymer

Conducting polymer synthesis can be classified in two main groups:

* Chemical polymerisation:
This method is rather simple, involving monomer, oxidant and dopant in an organic or aqueous solvent. In some special cases, the dopant can act as oxidant. The polymerisation usually occurs in the range of temperatures 20 – 80°C. The product is obtained after filtration and drying. The mechanism proposed assumes that the radical cation is formed in the bulk of solution by oxidation of the monomer. The coupling between radical and monomer and its oxidation produces a bi-radical cation. Coupling and oxidation continue until the polymer chain becomes insoluble.

* Electrochemical polymerisation:
This method is more used by electrochemists. The polymer deposits on the electrode surface. The thickness of film, morphology and other properties can be controlled [6] Electropolymerisation of pyrrole is reviewed in more detail as a typical example in the next part.

2.2. Polypyrrole

2.2.1. Properties

Polypyrrole (Ppy) is a heterocyclic, conjugated conducting polymer. Its structure is shown below [7].

```
N
H
H
N
```

The Ppy rings are mainly linked in the \( \alpha, \alpha' \) positions giving planar geometry. An extended \( \pi \) system of conjugated \( \pi \)-bonds is the origin of the electrical properties of the polymers. Ppy is studied extensively because of its following properties:

* Unlike polyaniline, the pyrrole monomer is a non-carcinogenic compound, the polymer has higher conductivity.

* It can be synthesised by electrochemical polymerisation at rather low oxidation potential, electropolymerisation can be carried out in aqueous media as well as organic solvent.
* Its characteristic properties can easily be modified by changing the dopant anion that is incorporated into the material during synthesis.

* Ppy in oxidised state is stable in air at room temperature as well as at high temperature (250°C).

2.2.2. Factors affecting the electropolymerisation of pyrrole

2.2.2.1. Solvent

Important properties of the solvent are its solubility for the monomer and its nucleophilicity. The nucleophilic character of solvent must be low. The nucleophilic reactions interrupt the polymerisation of pyrrole monomers. The interaction between solvent and monomers or radicals should minimize this effect. In other words, the solvent must keep monomer pyrrole stable during electropolymerisation.

2.2.2.2. Anions

The oxidation potential of dopant anions contained in the electrolyte should be higher than that of pyrrole monomer. It guarantees that pyrrole monomer is oxidised before the oxidation of the dopant anions [1, 4, 6].

The nature and concentration of dopant anions decide the quality of polymer film such as the microstructure, porosity etc. During the redox process, the diffusion of anions into polymer to compensate the positive charges depends on the mobility and the size of anion. Moreover, the interaction between anions and positive charges in the polymer affects the conductivity of Ppy film. The higher the basicity of the anions the lower conductivity of Ppy film.

Concentration of dopant anions should be in the range from 0.1 to 1 M. Above 1 M, no improvement in the quality of the Ppy film was observed.

2.2.2.3. The electropolymerisation methods

There are some typical methods which can be used to synthesise Ppy.

* Constant current or potential: The oxidation is made at constant current or at potential in the oxidation process.

* Scanning voltammetry: The Ppy film can be formed by potential scanning in a small potential window of about 0.6 – 0.65 V (vs. SCE).
2.2.2.4. Mechanism of electropolymerisation

Among the suggested mechanism, Diaz’s mechanism is most often used to illustrate the polymerisation of pyrrole. This mechanism consists of eight steps [6].

+Step 1: the oxidation of monomers to cation radicals.

\[
\begin{align*}
\text{Cyclic monomer} & \xrightarrow{-e} \text{Cyclic monomer}^+ \\
& \xrightarrow{E} \text{Cyclic monomer}^+ \\
\end{align*}
\]

+Step 2: coupling between two cation radicals in the α-position.

\[
\begin{align*}
\text{Cyclic monomer}^+ & + \text{Cyclic monomer}^+ \rightarrow \text{Coupled dimer} \\
\end{align*}
\]

+Step 3: dimer formation by the loss of two protons (stabilisation step).

\[
\begin{align*}
\text{Coupled dimer} & \xrightarrow{-2H^+} \text{Dimer} \\
\end{align*}
\]

+Step 4: oxidation of the dimer.

\[
\begin{align*}
\text{Dimer} & \xrightarrow{-e} \text{Dimer}^{++} \\
& \xrightarrow{E} \text{Dimer}^{++} \\
\end{align*}
\]

+Step 5: trimer formation by reaction of dimer and cation radical

\[
\begin{align*}
\text{Dimer}^{++} & + \text{Cyclic monomer}^+ \rightarrow \text{Trimer} \\
\end{align*}
\]
+Step 6: electro oxidation of the trimer

+Step 7: continuation of oxidation, coupling, deprotonation.

+Step 8: doping process.
2.3. Corrosion protection by polypyrrole

2.3.1. Introduction of corrosion

Corrosion at metal surfaces is a severe industrial problem. A large amount of metal is wasted by corrosion. It can cause tremendous economic damages. Minimising this corrosion can save substantial money and prevent accidents due to equipment failure. Corrosion has and continues to be the research object of scientists [8, 9].

Corrosion is an electrochemical process in nature. An anode (negative electrode), a cathode (positive electrode), an electrolyte (environment), and a circuit connecting the anode and the cathode are required for corrosion to occur. For simplicity, the corrosion process of iron in aqueous environment is discussed as a typical example.

The general reaction that occurs at the anode is the dissolution of metal atoms as ions:

\[
Fe = Fe^{2+} + 2e
\]

Electrons from the anode flow to the cathode area through the metallic circuit and force a cathodic reaction (or reactions) to occur. Depending on the pH of the electrolyte, different cathodic reactions can occur. In alkaline and neutral aerated solutions, the predominant cathodic reaction is

\[
O_2 + 2H_2O + 4e \rightarrow 4OH^{-}
\]

In aerated acids, the cathodic reaction could be

\[
O_2 + 4H^+ + 4e \rightarrow 2H_2O
\]

In deaerated acids, the cathodic reaction usually occurs is

\[
2H^+ + 2e \rightarrow H_2
\]

The corrosion product formed on iron surface in the presence of oxygen is:

\[
Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2
\]

This hydrous ferrous oxide (FeO.nH₂O) or ferrous oxide Fe(OH)₂ composes a diffusion barrier layer on the surface. This layer is green to greenish black in colour. In the presence of oxygen Fe²⁺ is oxidised to Fe³⁺. Ordinary rust is the product of this step. The formal reaction equation is

\[
4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3
\]

Hydrous ferric oxide is orange to red-brown in colour. It exists as nonmagnetic Fe₂O₃ (hematite) or as magnetic Fe₂O₃. Fe₃O₄.nH₂O often forms a black intermediate layer between hydrous Fe₂O₃ and FeO. Hence, rust films can consist of up to three layers of iron oxides in different states of oxidation [10].
2.3.2. The present research on corrosion protection by Ppy

Corrosion protection by conducting polymers is a really new approach. In the last years, many researchers have studied the anti-corrosion activity of conducting polymers. Polyaniline (Pani) and Polypyrrole (Ppy) have been investigated intensively. The following part presents in more detail an overview of corrosion protection using Ppy.

2.3.2.1. Electropolymerisation of pyrrole on steel and zinc

The electropolymerisation of pyrrole in aqueous solution has been investigated intensively because this process is favourable from a practical point of view.

In 1989, Schirmeisen and Beck [11] found that a smooth, adherent Ppy coating was obtained on iron at KNO$_3$ concentration of 0.01 – 1 M and at current densities 0.5 – 10 mA cm$^{-2}$. Dissolved oxygen did not interfere, and an adherent, smooth layer could be formed on large surfaces.

Ferreira et al. passivated the surface before electropolymerisation [12]. A treatment with 10% aqueous nitric acid reduced the iron dissolution without preventing the oxidation of pyrrole. In this way, polypyrrole films could deposited on iron in various aqueous solutions containing Na$_2$SO$_4$, K$_2$C$_2$O$_4$, and KNO$_3$.

Fraoua et al. explained the strong adhesion of polypyrrole on iron pretreated in diluted HNO$_3$ acid. With X-ray photoelectron spectroscopy (XPS) and surface enhanced Raman spectroscopy (SERS) evidence was found that a triply iron-nitrogen bond was formed on the surface. In addition, the reaction of pyrrole radicals with the nitrides formed covalent bonds between polypyrrole and iron [13].

Recently, Ocon et al. [14] obtained the Ppy films on mild steel in aqueous solution by a substrate pretreatment in HNO$_3$. In corrosion tests, the electrode potential was shifted towards more positive potentials but below the potential of passivation.

Polypyrrole films could also be formed electrochemically on mild steel in sodium sulphate solution without pretreatment of the substrates (Troch-Nagels et al. 1992 [15]). By polarising the sample anodically in 0.01 M H$_2$SO$_4$, the dissolution was 15 times slower than that of bare mild steel. However, the mechanical properties of the Ppy film were bad.

The electropolymerisation of pyrrole on iron or mild steel in aqueous oxalate solution was investigated by Beck et al. [16, 17]. The electrochemical process proceeded at a constant current density of 2 mA cm$^{-2}$. A short induction period was observed in the potential-time
The theoretical background

The curve of the polymerisation. The properties of the polymer coating were explained by an iron (II) oxalate interlayer. The work of Krstajic et al. [18] showed that the Ppy film was also formed on mild steel in oxalic acid at constant current density of 1 mA cm\(^{-2}\). A corrosion protection mechanism of Ppy on mild steel was suggested.

A series of publications of Wencheng Su and Jude O. Iroh concerned the polymerisation of pyrrole on steel in oxalic acid [19, 20, 21, 22, 23]. The results showed that a layer of \(\text{Fe}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O}\) was formed and passivated the steel substrate. This precipitated layer was further oxidised into soluble product when the oxidation potential of pyrrole was reached [24]. Uniform, smooth and strongly adherent Ppy coatings were obtained in low pH reaction medium at low applied current density.

The electrodeposition of pyrrole on steel was also investigated in organic media. Ferreira et al. [25] investigated the electropolymerisation of pyrrole on iron electrodes in various organic electrolytes such as acetonitrile (ACN), propylene carbonate (PC), methanol (MeOH), tetrahydrofuran (THF), n,n-dimethylformamide (DMF) and dimethlysulfoxide (DMSO). They found that Ppy films could be formed only if the iron dissolution was slower than that of pyrrole polymerisation. THF and MeOH fulfilled this requirement.

H. N. T. Le et al. published results related to corrosion protection of the Ppy film doped with oxalate as inhibitor anions. The Ppy film was formed in 0.05 M potassium tetraoxalate and 0.1 M pyrrole solution at a current of 1 mA cm\(^{-2}\) [26]. The results showed that Ppy coating provided substantial corrosion protection to iron. The corrosion protection of the Ppy film was improved when a bi-layer film was formed, namely, Ppy(oxalate) as inner layer and Ppy(polystyrenesulfonate) as outer layer [27]. The anion of the outer layer was dodecyl sulfate [28]. By Garcia et al. the protection of Ppy films was improved by forming composites with oxalate and oxide particles (Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\)) [29].

A Ppy film was formed in the presence of tartrate (\(\text{C}_4\text{H}_6\text{O}_4^{2-}\)) or of malate (\(\text{C}_4\text{H}_4\text{O}_5^{2-}\)) in aqueous solution on iron surfaces [30, 31]. The film was characterised by SEM, XPS, IR. The Ppy film had the same structural features and elementary composition as that deposited on noble metals.

There are many attempts to use Ppy as protective layer for zinc. In 1998, Zaid et al. obtained the Ppy films on zinc pretreated anodically at 0.35 mA cm\(^{-2}\) in 0.2 M Na\(_2\)S for about 3 minutes [32]. A polypyrrole film was synthesised in 0.9 M pyrrole + 0.1 M Na\(_2\)C\(_2\)O\(_4\) aqueous solution. The pretreatment of zinc electrode was necessary for electropolymerisation of pyrrole. By the same procedure, zinc could be coated with Ppy in some organic solutions. The
best films were obtained in CH$_3$CN with para-toluen sulfonate anions [33]. Petitjean et al. found that Ppy could be prepared in salicylate salt solutions [34]. Salicylate salts passivated zinc without preventing the electropolymerisation of pyrrole.

An inhibitor of iron in aqueous solution is molybdate similarly to chromate and nitrite in the presence of air but cannot prevent corrosion in deaerated solution [35]. The inhibition by molybdate anions was also observed on stainless steel in pure water containing chloride [36] and on iron in 0.01 M NaCl [37]. Hangovan et al. [38] studied the properties of the Ppy(MoO$_4$) films on Pt by CV, SEM and XPS. Their redox properties were investigated in Ref. [39]. It was found that during the cycling of the polymer film, molybdate anions were removed from the Ppy films but were stable in Pani film.

2.3.2.2. Corrosion protection mechanism

Beck et al. suggested a model of corrosion protection by Ppy [40]. The initial fast corrosion was a superposition of cathodic film reduction and anodic oxidation. Cathodic process was the driving process. The second step was caused of nucleophilic molecules dissolved in the solid. Both processes were of pseudo-first-order.

Jude O. Iroh et al. suggested a corrosion protection mechanism of iron by Ppy on the basis of EIS results [22]. The double bonds and the polar –NH group in the ring caused the strong adsorption of Ppy and improved corrosion protection. Ppy coating was acting as diffusion barrier and was inhibiting charge transfer.

Su and Iroh reported a large shift of the corrosion potential ($E_{\text{corr}}$) nearly 600 mV for Ppy(oxalate) on steel compared to bare steel [22]. Reut et al. also recorded this shift of corrosion potential. The different shifts of $E_{\text{corr}}$ could be explained by the different pretreatment of the substrate [41]. It was concluded from these results that Ppy produced the significant ennobling of steel.

But controversial results were published by Krstajic et al. [18]. It was found that Ppy(oxalate) did not provide anodic protection of mild steel in 0.1 M H$_2$SO$_4$. Ppy was undoped in a short time. The dissolution of the steel continued in the pores of the coating.

The mechanism of corrosion protection of steel by Ppy is not yet fully understood and it is likely to change with the corrosion conditions [41].
2.3.2.3. The role of dopant anion

Conducting polymer has been investigated extensively for corrosion protection of metal. It is observed that a conducting polymer film alone cannot protect an unnoble metal completely. With a galvanic coupling experiment it could be shown that the polymethylthiophene film did not act as a redox mediator, passivating the steel substrate within the defect and reoxidising itself by dissolved oxygen [42]. Ppy could not provide anodic protection for iron. Conducting polymers like polyaniline, polypyrrole etc. can improve the corrosion protection of unnoble metals but it is impossible that the porous films protect the metal surface completely [18, 43]. It is expected that protective properties of Ppy can be improved by dopant anion [44]. Counter anions, the so-called dopant anions play an important role in the development of physical properties and morphology. These actions of the anions could be:
- Electroneutralising: dopant anions neutralise the positive charges on the polymer backbone during synthesis of conducting polymer.
- Changing the morphology: the size of the dopant anion can control the microstructure and the porosity of the polymer film.
- Improving the conductivity: the interaction between the positive charges of polymer and anions can influence the conductivity of the polymer film.
- Stabilising the polymer film.
- Compatibility with other polymeric matrices.
- Corrosion inhibition: small dopant anions can be released from the polymer coating when the coating is reduced. If these anions have some inhibiting properties they can provide for some additional protection.

In most studies on the corrosion protection of mild steel by Ppy, the role of the dopant anion as corrosion inhibitor has not been investigated so far. The use of large anions such as polystyrenesulfonate, dodecyl sulphate could improve the corrosion protection of the Ppy film by preventing the penetration of chloride [27, 28]. Corrosion is not inhibited if the coating has small defects. The defect is protected only if inhibitor anions can diffuse to the defect. Thus, the mobility of dopant anions is one of the important parameters. The release of dopant anions from the Ppy film is the first step of corrosion inhibition. Further studies are necessary to understand the role of dopants in Ppy film for corrosion protection.
3. Electrochemical methods

3.1. Cyclic Voltammetry
Cyclic voltammetry (CV) is used both to polymerise the monomers and to characterise the polymers electrochemically. A potential sweep controlled by a potentiostat is applied. The potential is cycled within a given potential range at a constant rate and the current is measured as a function of the potential [8].
The potential rises at a constant rate until it reaches a chosen maximum, and then decreases again at the same rate. The current starts to rise as the potential enters the area where oxidation or reduction can occur. Peaks of oxidation and reduction can be observed. From peak currents and peak potentials rate constants of oxidation or reduction and doping or undoping for the polymer film can be determined.

3.2. Chronoamperometry
The variation of the current as a function of time after a potential step is measured in chronoamperometry. This technique is used mainly to monitor the growth of the polymer film.

3.3. Electrochemical impedance spectroscopy
3.3.1. Fundamentals
Electrochemical Impedance Spectroscopy (EIS) is a powerful tool to investigate chemical and physical processes at liquid/solid interfaces. EIS is becoming increasingly popular for a number of applications such as: characterisation of batteries, fuel cells, organic coatings, ceramics, semiconductors, sensors, and conducting polymers as well as for corrosion studies [45, 46, 47, 48].

In dc theory, the applied potential $E$ (Volt) is related to the current $I$ (Ampere) by Ohm’s law defining the resistance $R$ (Ohm):

$$E = I.R$$

In ac theory, in the analogous equation of $R$ the impedance $Z$ is defined:

$$E = I.Z$$

Impedance $Z$ is measured at a single-frequency by applying an ac voltage to the electrochemical system and measuring the phase shift and the amplitude of the resulting current at that frequency. The frequency is scanned through the frequency range. The spectra are then analysed by simulation of an equivalent electrical circuit. This step is called ‘fitting
procedure’. The circuit is built up of electrical elements such as resistors, capacitors and inductors, representing basic elements of the system.

The excitation signal that is applied to the cell has the form:

\[ E_t = E_o \sin (\omega t) \]

\( E_t \): potential at time \( t \); \( E_o \): amplitude of signal; \( \omega \): angular frequency \((\omega = 2\pi f)\)

For the linear system, the resulting current is given by the equation:

\[ I_t = I_o \sin (\omega t + \phi) \]

Here \( \phi \) is the phase difference between the voltage and the current.

The perturbation potential and the current respond can be written as complex function:

\[ E_t = E_o \exp (j \omega t) \]
\[ I_t = I_o \exp (j \omega t - \phi) \]

The impedance is defined as the ratio between potential and current:

\[ Z(\omega) = \frac{E_o}{I_o} \exp(j \omega) = |Z| \exp(j \omega) = |Z| (\cos \phi + j \sin \phi) = Z' + jZ'' \]

In the complex plane the impedance of a single frequency can be represented by a vector of length with argument \( \phi \) (angle between the real axis of the impedance \( Z' \) and the vector). \( Z'' \) is the imaginary part of the impedance.

The \(|Z|\) and \( \phi \) are related to \( Z' \) and \( Z'' \) by the equation

\[ |Z| = \sqrt{Z'^2 + Z''^2} \]

And the phase angle is defined:

\[ \tan \phi = \frac{Z''}{Z'} \]
3.3.2. Data presentation

The measured data are represented in two types of plots: Nyquist and Bode plot. A simple equivalent circuit and its impedance data used to illustrate the different representations. It consists of solution resistance, double layer capacitance and charge transfer or polarisation resistance (Figure 3.1).

![Equivalent Circuit Diagram](image)

Figure 3.1: The equivalent circuit for a simple electrode reaction. \( R_e \): resistance of electrolyte; \( R_{ct} \): resistance of charge transfer; \( C_{dl} \): capacitance of double layer

![Nyquist Plot Diagram](image)

Figure 3.2: Nyquist plot of the impedance of a simple electrode reaction

3.3.2.1. Nyquist Plot

The Nyquist plot of the impedance of the simple electrode reaction is a semicircle (Figure 3.2). The intercept of the plot with the axis (high frequency) is \( R_e \). The other intercept at low frequency is the sum of \( R_e \) and \( R_{ct} \). The Nyquist plot has some advantages and disadvantages.

*Advantages:
- A simple representation of the \( R_e \).
- The shape of plot does not change when the Ohmic resistance is changed.
Analytical methods

-A simple representation of the charge transfer resistance as diameter of the semi circle.

*Disadvantages:
-Indirect representation on frequency.

3.3.2.2. Bode Plot

Figure 3.3 is a typical Bode plot. Impedance $Z$ and phase angle $\phi$ are presented as a function of frequency (in logarithmic form). The $R_e$ and $R_e+R_{ct}$ value can be taken from the value of $|Z|$ for $\omega \to \infty$ and $\omega \to 0$. At intermediate frequencies, the plot of log$Z$ should be a straight line with slope $-1$. Extrapolating this line to $\omega \to 1$ gives the value of $1/C_{dl}$

$$|Z| = \frac{1}{C_{dl}} ; \omega = 1$$

The phase angle is nearly zero for $\omega \to \infty$ and $\omega \to 1$. It has the maximum for medium frequencies. The Bode plot provides a clear description of the frequency-dependence of the electrochemical parameters.

3.3.3. Interpreting the EIS

EIS spectra can be represented by electrical equivalent circuits. An alternative method and more general is the determination of the transfer function.
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The elements and model’s parameter (i.e. resistant value) decide the degree which the proposed model matches the measured EIS spectrum. The choice of model is based on the understanding of the electrochemical cell in study.

There are commercial programs to simulate the EIS spectrum such as Zahner Software. However, it is difficult to connect the different components in the equivalent circuit with physical process. Mostly, an EIS spectrum but it can be simulated by several equivalent circuits. An example is shown in Figure 3.4. This spectrum shows two semi circles and can be modelled by the equivalent circuits shown below.

![EIS spectrum and equivalent circuits](image)

**Figure 3.4:** EIS spectrum (left side) and equivalent circuits simulating this spectrum (right side)

There is not a unique model that describes the spectrum. Exact fitting of a spectrum is no proof for the suggested equivalent circuit.

So it is necessary to check the process which takes place at the electrode with other methods or with additional parameters (impedance data in dependence of time, applied dc potential, temperature etc.).
3.4. Electrochemical Quartz Crystal Microbalance

3.4.1. Introduction

The Quartz Crystal Microbalance (QCM) is a piezoelectric device that is extremely sensitive to changes of mass. QCM comprises a thin quartz crystal evaporated on both sides with Au layers that can be charged to establish an electric field across the disk. If an AC voltage is supplied it causes vibrations the resonant frequency of the crystal (Figure 3.5). This resonant frequency is shifted to lower values if the mass of crystal and electrode is changed by the surface process like adsorption, film formation etc. Commercial systems measure mass changes up to 100µg and down to one ng cm⁻² [49].

![Figure 3.5: Orientation of QCM disk. 1: quartz crystal; 2: gold layer](image)

Johnes and Meiure [50] demonstrated the application of QCM to measurements of mass changes in electrochemical system. They investigated the metal deposition with QCM. Nomura and co-workers were the other pioneers of in-situ application of QCM in electrochemistry. This method is now named Electrochemical Quartz Crystal Microbalance (EQCM).

The Coulombic efficiency of electrodeposition can be determined by EQCM. EQCM experiments can provide information of fundamental processes of metal deposition. Under potential deposition of metals, the composition and the morphology of the film or the kinetics of film growth can be investigated by EQCM [51, 52, 53].

In recent years, EQCM has also been used to study conducting polymer deposition. The work of Kaufman et al. [50] was considered as the first application of EQCM to study conducting polymers. This work activated studies of a wide variety of conducting polymer films and the exchange of molecules and ions between film and electrolyte. Recently, mechanical properties of the polymer film were studied by EQCM by measuring the viscoelastic effects in addition to the resonance frequency shift.
3.4.2. Basic principles of the method

3.4.2.1. The piezoelectric effect

In 1980, Jacques and Pierre Curie have found that a mechanical stress applied to the surfaces of various crystals created electrical potential across the crystal proportional to the applied stress. This behaviour was called piezoelectric effect [47, 50].

Later the same authors discovered that application of a voltage across the crystal created a mechanical strain. This inverse piezoelectric effect is the basis of the QCM.

The heart of microbalance is a piezoelectric wafer sliced from a single crystal of quartz. AT-cut (the crystallography orientation) quartz crystals are often used in QCM because they have a low temperature coefficient at room temperature and so the resonance frequency changes only minimally with temperature.

Application of an electric field across the crystal re-orientates the dipoles of crystal (Figure 3.6). The resulting strain of the lattice leads to shear vibration [52].

![Figure 3.6: Schematic representation of converse piezoelectric effect and the generation of shear motions](image)

The vibrations of the quartz crystal generate transverse acoustic waves that spread across the quartz (thickness $t_q$) and are reflected on the crystal surfaces (Figure 3.7).

Standing acoustic waves can be established in the quartz crystal with nodes in the centre of the disk and antinodes at the two surfaces of the disk.
The resonant frequency is related to the thickness of the quartz disk by the following equation:

\[ f_0 = \frac{v_q}{2t_q} = \frac{\lambda}{2} \]

Where \( v_q \): the velocity of the acoustic wave in the quartz; \( f_0 \): the resonant frequency; \( t_q \): the thickness of the quartz and \( \lambda \): the wavelength of the acoustic wave in the quartz.

When there is a film on the surface of the crystal, the acoustic wave will go through this layer. It is assumed that the acoustic wave is continuous across the interface, so that the acoustic property of the film is identical to those of the quartz. Then, the presence of the film on the quartz disk is considered as an increase of quartz thickness. Consequently, the change of thickness or the mass of the quartz (\( \Delta m \)) results in a change of frequency (\( \Delta f \)).

### 3.4.2.2. EQCM interpretation

An electrical equivalent circuit can model the mechanical properties of the quartz resonator. A network analyser is used to measure the impedance of this system. The equivalent circuit of an AT-cut crystal is shown in Figure 3.8.

\( C_0 \) is the electrical capacitance of the quartz resonator; \( R_1 \) corresponds to the dissipation of oscillation energy due to the mounting structure and the medium surrounding the crystal; \( C_1 \) represents the stored energy; \( L_1 \) corresponds to the inertial component during vibration [50]. The equivalent A is represented by the measurable system in B.
Figure 3.8: Equivalent circuit of QCM behaviour (A) and equivalent representation of the circuit (B) of A.

The network analyser measures the reactance ($X_e$) and the resistance ($R_e$). The value of $C_1$ in equivalent circuit A is calculated:

$$C_1 = (f_r - f_s)(2\pi^2 f_s^3 C_o R_1^2)^{-1}$$

$f_s$ is the resonant frequency of conductance. $f_s$ is obtained at $\theta = 0$. $f_i$ is the frequency of zero phase (assuming that the current through crystal and the applied voltage have the same phase angle). $R_1$ is approximately equal to $R_e$ at a frequency at which $X_e$ is zero. $C_o$ is measured at any frequency sufficiently far from the resonant frequency.

$C_1$ is known, and then $L_1$ is calculated from the equation

$$f_s = \left(2\pi(L_1 C_1)^{1/2}\right)^{-1}$$

### 3.4.2.3. Mass-frequency correlation

Sauerbrey was the first to recognise the mass-frequency relation. This equation is now known as the Sauerbrey equation:

$$\Delta f = \left(\frac{2nf_o^2}{A\sqrt{\rho_q\mu_q}}\right)\Delta m = \left(\frac{f_o^2}{N\rho_q}\right)\Delta m = -C_f \Delta m$$

In this formula, the change of frequency $\Delta f$ is proportional to the change of mass ($\Delta m$) per area unit (A). $f_o$ is the oscillation frequency of the fundamental mode of QCM, $n$ is the harmonic number of the vibration; $\rho_q$ (2.648 g cm$^{-3}$) is the density of quartz, $\mu_q$ (2.947 $10^{11}$ g cm$^{-1}$ s$^{-2}$) is the shear modulus of quartz and $C_f$ is the sensitive factor for the crystal. $C_f$ depends on the thickness, and therefore the fundamental frequency.

$\Delta m$ is mass change per unit area with the unit g cm$^{-2}$. The negative sign shows that increases in mass correspond to decreases in frequency. The mass sensitivity per unit area should not
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depend on the electrode geometry. In other words, the frequency change corresponds to the thickness of the film, not to the total mass.

Approximately, Sauerbrey assumed the change of mass at some distances from the centre of the quartz disk is proportional to the shift of frequency. Moreover, the film should be of uniform thickness.

3.5. Scanning Kelvinprobe measurements at polymer/metal interfaces

3.5.1. Principles

The delamination of polymeric coatings on metals is an electrochemical reaction. It has assumed that the delamination is caused by the cathodic oxygen reduction in the defect of the polymer film and the migration and diffusion of ions to the delamination front. To understand delamination, the reactions taken place at defect of metal/polymer interfaces should be studied. However, it is impossible to measure the corrosion current or the distribution of corrosion potentials at the defect with conventional electrochemical techniques [54, 55, 56].

The scanning Kelvinprobe (SKP) is considered to be a new method to measure the corrosion potential of the delamination zone. The Kelvinprobe measures the work-function of the sample using the vibrating condenser method. The work-function is influenced by the electrode potential; therefore the Kelvinprobe is able to measure the local corrosion potentials. Stratmann et al. has employed SKP in corrosion research [57].

The work function is the minimum work required to expel an electron in vacuum from the Fermi level $\varepsilon_F$ of a metal or conducting phase. Since the electron has to move through the surface region, its energy is influenced by the electrical properties of the surface. Therefore, the work function is extremely sensitive to changes of these properties.

The reference electrode and the sample have work functions and Fermi levels of $E1, \phi1$ and $E2, \phi2$, respectively (Figure 3.9). If two metals have no electrical contact, the Fermi levels are different (Figure 3.9 A).
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Figure 3.9: Work function and Fermi level of two electrodes: no contact (A), after contact (B) and with applied potential power (C)

After connection of the two metals, there is a flow of charge to equalise the Fermi levels, charging the surface and building up potential difference $V_c$. Volta-potential difference (Figure 3.9 B). If a potential $V_b$ is applied then the surface charge will be null. $V_b = -V_c$ is the work function difference of the two electrodes. This is the basic principle of Kelvinprobe measurements [58, 59, 60, 61, 62].

In order to make a continuous measurement, a vibrating capacitance probe was developed (Figure 3.10).

The reference electrode is forced to vibrate in a mean distance $\bar{d}$. Sample and reference electrodes form a condenser. The change of capacitance is given by:
\[
C = \varepsilon \varepsilon_0 \frac{A}{d + \Delta d \sin(\sigma f)}
\]
\(\varepsilon, \varepsilon_0:\) dielectric constant of the medium and the vacuum, respectively; \(\sigma:\) frequency of vibration; \(A:\) surface area of the reference plate.

The current of the external circuit is:
\[
i = \Delta \Psi_{\text{sample}} \frac{dC}{dt}
\]
If an external potential \(V\) is applied, the current will be
\[
i = (\Delta \Psi_{\text{sample}} - V) \frac{dC}{dt}
\]
\(V\) is changed until \(i = 0\), giving \(\Delta \Psi_{\text{sample}} = V_{i=0}\).

### 3.5.2. Volta-potential difference and corrosion potential

After the working and reference electrodes are connected by external circuit, their Fermi levels are identical and the sum of energies needed for transfer the electron from working electrode through the interfaces to the reference electrode will be zero.

The energy of an electron in the working electrode is
\[
\tilde{\mu}_e^M = \mu_e^M - F \phi^M
\]
\(\tilde{\mu}_e^M:\) Electrochemical potential of the electron; \(\mu_e^M:\) chemical potential of the electron; \(\phi^M:\) Galvani potential.

The work function of the reference electrode is:
\[
\alpha_{\text{ref}} = - (\mu_{e}^{\text{ref}} - F \chi_{\text{ref}})
\]
\(\mu_{e}^{\text{ref}}:\) Chemical potential of the electron in the reference metal; \(\chi_{\text{ref}}:\) dipole potential of the reference phase.

The energy \(\Delta E_1\) to transfer an electron from the working electrode to the polymer can be expressed by:
\[
\Delta E_1 = - (\mu_{e}^M - F \phi^M) + (\mu_{e}^{\text{poly}} - F \phi^{\text{poly}})
\]
\(\mu_{e}^M, \mu_{e}^{\text{poly}}:\) chemical-potentials of electrons in the metal and the polymer.
\(\phi^M, \phi^{\text{poly}}:\) Volta potential of the metal and the polymer.

The energy \(\Delta E_2\) to transfer an electron from the polymer to the gas phase is given by:
\[
\Delta E_2 = - (\mu_{e}^{\text{poly}} - F \phi^{\text{poly}}) = -(\mu_{e}^{\text{poly}} - F \chi_{\text{gas}}^{\text{poly}} + F \Psi^{\text{poly}})
\]
\( \chi_{\text{gas}}^{\text{poly}} \): Dipole potential at the polymer/gas interface; \( \Psi_{\text{poly}}^{\text{ref}} \): Volta potential of the polymer/vacuum surface.

The energy \( \Delta E_3 \) to transfer an electron from the gas phase to the reference metal:

\[
\Delta E_3 = (\mu_e^{\text{ref}} - F \phi^{\text{ref}}) = -\alpha_e^{\text{ref}} - F \Psi_{\text{poly}}^{\text{ref}}
\]

The sum of three energies must be zero. This condition leads to:

\[
\Delta E_1 + \Delta E_2 + \Delta E_3 = -\frac{\mu_e^{\text{ref}}}{F} + \Delta \phi_{\text{poly}}^{\text{ref}} = \frac{\alpha_e^{\text{ref}}}{F} - \chi_{\text{gas}}^{\text{poly}} + \Delta \Psi_{\text{poly}}^{\text{ref}} = 0
\]

\[
E_{1/2} = \frac{\alpha_e^{\text{ref}}}{F} - \chi_{\text{gas}}^{\text{poly}} + \Delta \Psi_{\text{poly}}^{\text{ref}}
\]

\((-\frac{\mu_e^{\text{ref}}}{F} + \Delta \phi_{\text{poly}}^{\text{ref}} \)) is equal the half cell potential of the metal/polymer interface \( E_{1/2} \).

In the case, the polymeric coating delaminates from metal substrate; the polymer/substrate interface will be replaced by two interfaces: substrate/electrolyte and electrolyte/polymer.

Now, the Galvani potential difference consists of two parts: \( \Delta \phi_{\text{ele}}^{\text{ref}} \) at the metal/electrolyte interface; and Donan potential at electrolyte/polymer interface (\( \Delta \phi_{D} = \phi_{\text{ele}} - \phi_{\text{poly}} \)).

The half-cell potential of the metal/electrolyte interface is:

\[
E_{1/2} = \Delta \phi_{D} + \frac{\alpha_e^{\text{ref}}}{F} - \chi_{\text{gas}}^{\text{poly}} + \Delta \Psi_{\text{poly}}^{\text{ref}}
\]

The electrode potential or corrosion potential \( E_{\text{corr}} \) of the interface is a sum of the half cell potential of the metal/polymer interface and the half-cell potential of reference electrode.

\[
E_{\text{corr}} = E_{1/2} + E_{\text{ref}}^{\text{ref}}
\]

The corrosion potential is presented in some special cases:

* Intact substrate/polymer interface

\[
E_{\text{corr}} = \text{const} + \Delta \Psi_{\text{poly}}^{\text{ref}}
\]

* Delaminated substrate/polymer interface

\[
E_{\text{corr}} = \Delta \phi_{D} + \text{const} + \Delta \Psi_{\text{poly}}^{\text{ref}}
\]

The scanning Kelvinprobe can measure directly the Volta-potential difference \( \Delta \Psi_{\text{poly}}^{\text{ref}} \).
4. Experimental procedures

4.1. Chemicals

The chemicals used in this research are listed in the Table 4.1.

Table 4.1: Chemicals for research

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Producer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrole monomer (kept at 4°C and distilled under vacuum prior to use)</td>
<td>C₄H₅N</td>
<td>Aldrich</td>
<td>98 - 99%,</td>
</tr>
<tr>
<td>Lithium perchlorate</td>
<td>LiClO₄</td>
<td>Fluka</td>
<td>p.a</td>
</tr>
<tr>
<td>Tetrabutylammonium bromide</td>
<td>[CH₃(CH₂)₃]₄NBr</td>
<td>Merck</td>
<td>p.a</td>
</tr>
<tr>
<td>Sodium molybdate</td>
<td>Na₂MoO₄</td>
<td>Aldrich</td>
<td></td>
</tr>
<tr>
<td>Molybdic acid</td>
<td>H₂MoO₄</td>
<td>Acros</td>
<td>p.a</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>J.T.Baker</td>
<td>p.a</td>
</tr>
<tr>
<td>3-Nitro salicylic acid</td>
<td>C₇H₅NO₅</td>
<td>Fluka</td>
<td>97%</td>
</tr>
<tr>
<td>Hexafluorotitanic acid</td>
<td>H₂TiF₆</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>Tetrabutylammonium hexafluorophosphate</td>
<td>[CH₃(CH₂)₃]₄NPF₆</td>
<td>Aldrich</td>
<td>98%</td>
</tr>
</tbody>
</table>

4.2. Equipment

The following equipment was employed:
* EG&G-263A Model potentiostat/galvanostat.
* IM6 impedance measurement system of ZAHNER-Elektrik. The ZAHNER simulation software was integrated in this system. The frequency range used was 100 kHz – 0.1 Hz.
* The network analyser Advantest R3753BH was connected to the EG&G-263A Model potentiostat/galvanostat to measure the impedance of the quartz electrode in EQCM.
* SEM pictures were obtained with Zeiss DSM 982 Gemini microscope (Carl Zeiss, Germany).
4.3. Cell of measurements

4.3.1. Cell for electropolymerisation

The cell was a 15 ml - Teflon container (Figure 4.1). It consisted of two parts which can be screwed together by Teflon screws. The working electrode (WE) was placed between of them. A silicon O-ring (2) was used for sealing. The surface of the WE was 0.64 cm$^2$. The Pt sheet counter electrode (CE) was placed in a narrow slot 3. The distance between anode and cathode was 2.5 cm. The reference electrode was connected with the working electrode through a salt bridge.

![Figure 4.1: The electrochemical cell. 1. Teflon screw; 2. Silicon gasket; 3. Slot for the counter electrode.](image)

4.3.2. Cell for EIS measurement

The photograph of the EIS cell is presented in Figure 4.2. It consisted of two parts which could be fixed to each other with four metal screws at the corners. The working electrode was placed between these parts. A silicon gasket defined the immersion surface of working electrode (0.125 cm$^2$). A glass container was placed on the upper part to hold the electrolyte. Pt net was the counter electrode.
4.4. Pretreatments of substrates

The substrates were pretreated as shown in Table 4.2.

Table 4.2: Conditions of pretreatment

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre.1 Mild steel (20 x 20 mm²)</td>
<td>-polishing with emery paper No 600.</td>
</tr>
<tr>
<td></td>
<td>-rinsing in ethanol in an ultrasonic bath for about 15 minutes.</td>
</tr>
<tr>
<td></td>
<td>-drying in an N₂ stream.</td>
</tr>
<tr>
<td>Pre.2 Passive film on mild steel (20 x 20 mm²)</td>
<td>-treating in Pre.1 as described.</td>
</tr>
<tr>
<td></td>
<td>-immersion in 0.1 M Na₂MoO₄ for 60 minutes, 30°C.</td>
</tr>
<tr>
<td></td>
<td>-potentiostatic passivation at 0.5 V (vs. SCE) for 1 hour.</td>
</tr>
<tr>
<td></td>
<td>-rinsing in distilled water and drying in an N₂ stream.</td>
</tr>
<tr>
<td>Pre.3 Pure zinc (20 x 20 mm²)</td>
<td>-polishing with emery paper No 2000.</td>
</tr>
<tr>
<td></td>
<td>-rinsing in ethanol in an ultrasonic bath for about 15 minutes.</td>
</tr>
</tbody>
</table>

(A Pt sheet was used as electrical contact to the working electrode)
Experimental procedures

4.5. Conditions of electropolymerisation

Electropolymerisation conditions are shown in Table 4.3

Table 4.3: Conditions of electropolymerisation

<table>
<thead>
<tr>
<th>Polymer film</th>
<th>Condition of synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film 1</td>
<td>Ppy(ClO₄) on Pt</td>
</tr>
</tbody>
</table>
|              | -pretreatment under Pre.4
|              | -0.1 M pyrrole monomer, 0.1 M HClO₄, current density 1 mA cm⁻². |
| Film 2       | Ppy(MoO₄) on Pt         |
|              | -pretreatment under Pre.4
|              | -0.1 M pyrrole monomer, 0.01 M MoO₄²⁻, pH=4.8, current density 1 mA cm⁻² or CV with 10 mV s⁻¹ in the range 0.6-0.7 V (vs. SCE) |
| Film 3       | Ppy(MoO₄) on mild steel |
|              | -pretreatment under Pre.1. |
|              | -0.1 M pyrrole monomer, 0.01 M MoO₄²⁻, pH=4.8, current density 1.5 mA cm⁻² |
| Film 4       | Ppy(PF₆) on mild steel  |
|              | -pretreatment under Pre.2 |
|              | -0.1 M pyrrole monomer, 0.1 M PF₆⁻ in acetonitrile, current density 1 mA cm⁻² |
4.6. Electrochemical Impedance Spectroscopy and its interpretation

Electrochemical Impedance Spectroscopy (EIS) primarily characterises a conducting polymer system in terms of electrical properties. The electrochemical behaviour of the polymer film is substituted by an equivalent circuit. The typical Bode plot and the equivalent circuit of a Ppy film are shown in Figure 4.3 and in Figure 4.4, respectively.

![Bode plot of a Ppy film](image)

**Figure 4.3: Bode plot of a Ppy film**
Impedance (solid line) and phase angle (dot line)

![Equivalent circuit](image)

**Figure 4.4: Equivalent circuit for fitting the impedance spectrum of a Ppy film.**

*Re*: resistance of electrolyte, *R_{PM}*: resistance of polymer film; *C_{PM}*: capacitance of polymer film; *R_{ct}*: resistance of charge transfer; *C_{dl}*: capacitance of double layer.
The obtained impedance spectra of the polymer film can be divided in three regions:

-Region 1 (*high frequency* > 1 kHz): characterises the behaviour of the electrolyte. Phase angle is nearly zero (dotted line in Figure 4.3). The resistance of the electrolyte is described by \( R_e \) in the equivalent circuit (Figure 4.4).

-Region 2 (*middle frequency*): shows the properties of the polymer film. The Ppy film behaves as dielectricum with a capacitive impedance. The behaviour is simulated by a capacitance \( C_{PM} \) parallel to the resistance of the polymer film \( R_{PM} \).

-Region 3 (*low frequency*): represents the interface polymer/substrate. \( C_{dl} \) and \( R_{ct} \) are the capacitance of double layer and the charge transfer resistance of the interface, respectively.

The experimental EIS data could be modelled by the equivalent circuit in Figure 4.4 using the fitting procedure of Zahner software. Experiments were repeated three times to prove reproducibility.
5. Results and discussions

5.1. Characterisation of polypyrrole (Ppy) films on Pt

In this section electrochemical properties of Ppy film are described. The dopant anion ClO$_4^-$ was used as small and mobile anion for these experiments. Pt electrode was employed to deposit Ppy on its surface. Doping/undoping was investigated. Cyclicvoltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were two main methods.

5.1.1. Film preparation

The Ppy film was synthesised in 0.1 M HClO$_4$, 0.05 M pyrrole solution at room temperature using the three-electrode cell. The Pt sheet (1 cm$^2$) used as working electrode was cleaned in an ultrasonic bath with ethanol. Electropolymerisation of pyrrole was carried out using galvanostatic or cyclic voltammetry (CV) (Figure 5.1 A and B). When the working electrode was polarised with 0.5 mA cm$^{-2}$, the surface potential increased rapidly and reached the oxidation potential of pyrrole at about 0.7 V (vs. SCE) and then remained constant during the polymerisation process (Figure 5.1A). Ppy covered homogenously the surface.

Figure 5.1B shows the cyclic voltammetric electrodeposition of pyrrole with ClO$_4^-$ as dopant anion. In the first positive cycle, the pyrrole oxidation started around 0.65 V (vs. SCE) with a significant increase in the current density corresponding to the production of the pyrrole radical monomers of pyrrole. In the reverse scan, no cathodic peak was observed. The radicals were consumed rapidly by the follow-up reactions [1]. In the successive scans the current increased steadily indicating the formation of the Ppy film. The redox potential of the Ppy shifted to 0.2 V and -0.2 V (vs. SCE) for oxidation and reduction, respectively.
Figure 5.1: Electropolymerisation of pyrrole in 0.1 M HClO$_4$, 0.05 M pyrrole solution by constant current density 0.5 mA cm$^{-2}$ (A); by CV at 20 mV s$^{-1}$ (B)

5.1.2. Conductivity of Ppy(ClO$_4$)

The conductivity of the Ppy(ClO$_4$) film was investigated by electrochemical impedance spectroscopy (EIS). Figure 5.2 shows the typical Bode plots of Ppy(ClO$_4$) reduced in 0.1 M
LiClO₄ deaerated solution. Every spectrum was recorded after 15 minutes of polarisation at -0.4 V (vs. SCE).

![Bode plots of Ppy(ClO₄) in 0.1 M LiClO₄, from oxidation to reduction](image)

Figure 5.2: Bode plots of Ppy(ClO₄) in 0.1 M LiClO₄, from oxidation to reduction

With the equivalent circuit described in detail in Figure 4.4 (page 38), the conductivity of Ppy could be determined. The fresh Ppy(ClO₄) has a film resistance $R_{PM}$ of about 20 $\Omega$. After 1.5 hours of reduction at -0.4 V (vs. SCE) the resistance $R_{PM}$ increases to about 23 k$\Omega$ as marked by an arrow in Figure 5.2. Ppy is reduced gradually following the reaction:

$$\text{Ppy}^{n^+} (\text{dopant anion})^{n^-} + n\text{e}^- = \text{Ppy} + (\text{dopant anion})^{n^-}$$

This reduction causes the release of dopant anions as is observed by the decrease of $C_{PM}$ in the low frequency range [63].
5.1.3. CV of Ppy(ClO₄) on Pt

The doping/undoping behaviour of the Ppy film was studied in 0.1 M NaCl and 0.1 M tetrabutylammonium bromide (N(Bu)₄Br) aqueous solutions by CV. The results are shown in Figure 5.3.

Figure 5.3: CV of Ppy(ClO₄) in 0.1 M NaCl (A) and in 0.1 M N(Bu)₄Br (B) deaerated solution at scan rate 20 mV s⁻¹. The second cycle is shown.
A Ppy film doped with ClO$_4^-$ and synthesised on Pt (Ppy(ClO$_4$))/Pt was studied. The different shapes of cyclic voltammograms indicate that the electrolyte has some effects on the redox properties of Ppy.

In the cathodic scan of Ppy in NaCl shown in Figure 5.3A, ClO$_4^-$ anions are partially expelled from the film. The remaining negative charge centres are compensated by Na$^+$ ions inserted into polymer film. The insertion of cations results in the negative peak of Ppy reduction at -0.6 V (vs. SCE). It has been also called ‘break-in’ process [64]. In the back scan the polymer film is re-oxidised and Cl$^-$ anions are incorporated into the Ppy film. The oxidation peak is observed at -0.2 V (vs. SCE). Chloride anions which are more mobile take part in the doping/undoping process of the polymer film. After 6 cycles, a constant redox current is observed, the redox process of Ppy(ClO$_4$) has become reversible. There is no evidence for film deformation.

A different CV behaviour of the Ppy film was obtained when the same film was investigated in 0.1 M N(Bu)$_4$Br deaerated solution (Figure 5.3 B). The release of the ClO$_4^-$ anions is predominant in the cathodic scan. In the reverse scan, however, bromide anions are incorporated into the film to compensate the positive charge. Because of the large size, the N(Bu)$_4^+$ cations can not be incorporated into the film.

The redox behaviour or the anion exchange of Ppy films does not only depend on the nature of the anions. It also depends on the type and size of cation in the electrolyte [65, 66]. The incorporation of cations may cause the change of the polymer morphology found elsewhere [67, 68].

5.1.4. pH dependence of conductivity

The conductivity of Ppy was evaluated in 0.1 M LiClO$_4$ solution at different pH-values by EIS. The film was formed on Pt with ClO$_4^-$ as the dopant anions. Figure 5.4 shows the film resistance as a function of the pH.

At pH-values of 5.8 and 9.5, the Ppy film is conductive. Film resistance $R_{PM}$ is about 30 $\Omega$, constant over 90 minutes of immersion. At a pH of 11.1 the resistance of Ppy film increases rapidly with the immersion time to about 1 K$\Omega$. If the Ppy film is then immersed in an acid solution of LiClO$_4$ (pH=2.6), the conductivity of the film is regained. The film resistance gets back to nearly the initial value.
Figure 5.4: The film conductivity of Ppy(ClO$_4$) as function of pH

One explanation may be: the deprotonation and protonation processes occur during the immersion of the Ppy film in the alkaline and the acid solution, respectively [69]. These processes are described in Figure 5.5. The deprotonation leads to expelling of counter anions and the decrease of the $H / C$ ratio in Ppy in the alkaline medium and the decrease of Ppy conductivity. This process is reversible, so that the conductivity of the Ppy film is got back in acid solution. A different behaviour was observed for polymethylthiophene [70].

![Deprotonation and protonation of Ppy in alkaline and acid media](image)
5.1.5. Exchange of perchlorate vs. salicylate

The anion exchange of Ppy film can be studied in four steps: (i) Measuring the EIS spectrum of fresh Ppy(ClO$_4$) films in 0.1 M N(Bu)$_4$Br solution at OCP. (ii) Reducing the film at -0.7 V (vs. SCE) in 30 minutes and measuring again the EIS spectrum. (iii) Rinsing the sample with distilled water and oxidising in 0.1 M salicylate solution at 0.4 V (vs. SCE) for 30 minutes. (iii) Measuring the EIS spectrum of the re-oxidised sample in 0.1 M N(Bu)$_4$Br.

![EIS spectrum](image)

**Figure 5.6:** Exchange of dopant anion perchlorate against salicylate.

1: Ppy(ClO$_4$) after forming, 2: after reduction at -0.7 V, 3: after re-oxidation at 0.4 V

The resistance of the fresh Ppy(ClO$_4$) film is about 89 Ω (Figure 5.6, curve 1). After 30 minutes of reduction, the impedance of the Ppy film increases due to the lower conductivity (curve 2). The film resistance is nearly 1000 times larger than that of the fresh film. Curve 3 represents the impedance of the Ppy film after re-oxidation in 0.1 M sodium salicylate solution. The conductivity of the polymer film is regained but the resistance is now 200 Ω. It is therefore possible to expel ClO$_4^-$ anions during reduction in N(Bu)$_4$Br leading to a Ppy film of high resistance. The size of the cations N(Bu)$_4^+$ prevents its incorporation. In the re-oxidation step, salicylate anions are incorporated into the Ppy film, the film resistance decreases again. The film is now in oxidised state.

A similar behaviour is observed for the exchange of perchlorate and succinate anions (Figure 5.7). The film resistance changes from 82 Ω (oxidation) to 122.2 KΩ (reduction) and falls down to 303 Ω after re-oxidation.
Obviously, the anion exchange of Ppy is possible using polarisation. In this manner Ppy can be doped with different anions and can be used as a storage for these anions.

5.1.6. The rate of anion release

It is known that Ppy is reduced when the negative potential is applied on a Ppy film previously immobilised on a Pt electrode in solution. The release of dopant anion can be determined by the reduction level of Ppy in general. The change of film’s capacitance, which can be obtained using EIS, in turn is a measure to know the release of anions. 

The reduction of Ppy(perchlorate) and Ppy(salicylate) on Pt were investigated using EIS. In order to prevent the insertion of cations into the Ppy at negative potentials, 0.1 M N(Bu)₄Br solution was used as electrolyte. After polarisation at –0.7 V (vs. SCE), spectra of EIS were recorded as a function of time.

Figure 5.8 shows the change of the film’s capacitance after 1-hour reduction. The capacitance of Ppy(ClO₄) is small and decreases in the first minutes. The capacitance of Ppy(salicylate) is larger and decreases more slowly with time. That means that Ppy(ClO₄) is reduced easier than Ppy(salicylate). The reduction time depends on the size of the dopant anions.
Figure 5.8: The film capacitance depends on the reduction time. Reduction at −0.7 V (vs. SCE) with the dopant anions ClO$_4^-$ (●) and salicylate C$_7$H$_5$O$_3$ (■).
5.2. Characterisation of Ppy(MoO₄) on Pt

5.2.1. Electropolymerisation of pyrrole

The platinum electrodes (1 x 1 cm²) were cleaned with ethanol ultrasonically. The electropolymerisation was performed in a conventional three-electrode cell consisting of a Pt plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt working electrode. The polypyrrole (Ppy) films were generated galvanostatically at a current density of 1 mA cm⁻² in aqueous solutions of 0.1 M pyrrole and 0.01 M sodium molybdate (pH = 4.8).

After formation of the film, the sample was rinsed with distilled water and dried in nitrogen atmosphere. The film thickness was about 1-1.2 µm estimated from the electropolymerisation charge assuming 0.4 C cm⁻² µ⁻¹ [71].

5.2.2. The release of anions from Ppy(MoO₄)/Pt

5.2.2.1. Redox properties of Ppy(MoO₄) film

The redox behaviour of Ppy(MoO₄) studied by CV in 0.1 M N(Bu)₄Br is shown in Figure 5.9.

Figure 5.9: CV of Ppy(MoO₄)/Pt in 0.1 M N(Bu)₄Br, N₂ atmosphere, scan rate 20 mV s⁻¹

In the first cathodic scan, the Ppy film is reduced at about –0.3 V (vs. SCE). Because the incorporation of the cation is inhibited, the release of molybdate could take place. The re-oxidation peak of the film is observed at 0 V (vs. SCE) when the scan is reversed. This oxidation peak is explained by the incorporation of bromide from the electrolyte. The
behaviour of the first cycle and the successive cycles are different. The new cathodic peak shifts in the positive direction and keeps constant in the successive cycles. The film remains its redox properties until the 10th cycles. There is no evidence of film decomposition. This result is in good agreement with the work published by T.V.Vernitskaya [39].

It is expected that MoO$_4^{2-}$ anions can be incorporated into the Ppy film during electrodeposition and that they can be released from the Ppy film under the conditions of potential cycling. When MoO$_4^{2-}$ is expelled from the Ppy film, bromide anions can be incorporated. During cycling the Ppy(MoO$_4$)/Pt films remain their redox properties.

### 5.2.2.2. Studies of Ppy film reduction by EIS

The release of the anion MoO$_4^{2-}$ under polarisation can be also monitored by EIS. Figure 5.10 shows the typical Bode plots of Ppy(MoO$_4$)/Pt as a function of the potential in 0.1 M NaCl (A) and in 0.1 M N(Bu)$_4$Br (B).

In both cases, the resistance of the film $R_{PM}$ increases with the reduction of the polymer (as marked by an arrow in Figure 5.10). At the same time, the capacitance $C_{PM}$ of the polymer decreases at high frequencies. It indicates that the polymer film changes from the conductive state to the semi-conductive state at -0.2 V (vs. SCE) as a consequence of the anion release.

As long as the anion molybdate is not released from the polymer film, the capacitance $C_{PM}$ does not change because the film is saturated with electrolyte [63]. Using the equivalent circuit shown in Figure 4.4 (page 38), the values of the Ppy resistance and of the Ppy capacitance are calculated and presented in Figure 5.11.
Figure 5.10: Reduction of Ppy(MoO$_4$)/Pt in 0.1 M NaCl (A) and in 0.1 M N(Bu)$_4$Br (B), N$_2$. Impedance (solid line), phase angle (dotted line)
Figure 5.11: The change of film capacitance $C_{PM}$ (■) and resistance $R_{PM}$ (○) during reduction in 0.1 M NaCl (A) and 0.1 M N(Bu)$_4$Br (B)
As expected, $R_{PM}$ and $C_{PM}$ are changed with potential monotonously in both electrolytes. The reduction of Ppy(MoO$_4$) films results in the increase of $R_{PM}$. It is observed, however, $R_{PM}$ decreases at negative potentials (< -0.6 V) in NaCl. This decrease can be attributed to the decrease of ionic resistance of Ppy film due to the moving of Na$^+$ cations into the film. The film is saturated by the electrolyte.

In addition, the changes of $C_{PM}$ are observed during the reduction process. In NaCl solution, the values of $C_{PM}$ decrease from 2.5 µF to 0.65 µF. Whereas in N(Bu)$_4$Br solution the values of $C_{PM}$ sharply decrease to 19 nF. The smaller values of $C_{PM}$ are obtained when the Ppy film is reduced in a large cation solution. The incorporation of cations in the Ppy film can be reflected by the smaller values of film resistance $R_{PM}$ and larger capacitance $C_{PM}$.

In NaCl solution anion and cation transport takes place during the reduction. Molybdate can release from the polymer but at more negative potentials Na$^+$ insertion is preferred.

5.2.2.3. Electrochemical quartz crystal microbalance experiment

In principle, the release of anions from polymer films results in the change of its mass. EQCM is a reliable method to control this process.

The EQCM investigations were performed with a lab-build set-up. The electrical admittance of the quartz crystal was measured with a network analyzer (model R3753BH, Advantest, Tokyo) near the resonance frequency. From the fitting procedure the resonance frequency $f$ and the damping $w$ are obtained. Polished 10 MHz AT-cut quartz crystals (KVG, Neckarbischofsheim, Germany) with Au electrodes (ca. 100 nm) on a Cr adhesion layer (ca. 5 nm) were used. The electrical potential of the Au electrode facing the solution was controlled with an EG&G 263A potentiostat, the other electrode faced the air. The potentials were measured versus a saturated calomel electrode (SCE). The counter electrode was a Pt foil. The whole EQCM setup was controlled by lab-made software. Further details concerning the experimental setup are described in Refs [72, 73].

The Ppy film was grown on a gold quartz used as working electrode by applying a constant potential 0.7 V (vs. SCE) in an aqueous solution containing 0.1 M pyrrole and 0.01 M sodium molybdate. After deposition, the film was rinsed with distilled water and dried in N$_2$ atmosphere. Figure 5.12 shows the variation of the frequency as a function of charge passed during electropolymerisation of pyrrole in the presence of molybdate.
The almost linear negative frequency shift (Δf) versus the charge passed (Q) during the oxidation of Ppy(MoO$_4$) indicates that the Ppy film is homogenous on the Au/quartz electrode under these experimental conditions [74].

The conversion of the frequency shift to the mass change is calculated from the Sauerbrey equation.

$$\Delta m = -C_{SC} \cdot \Delta f$$

Where Δf is the frequency shift, Δm is the mass change, the Sauerbrey constant is $C_{SC} = 226.01 \text{ Hz cm}^2 \mu\text{g}^{-1}$ for a 10 MHz quartz [52, 75].

To investigate the ion flux – in and out of the film, a fresh Ppy(MoO$_4$) film was deposited on a Au/quartz electrode immersed in 0.1 M N(Bu)$_4$Br deaerated solution. The mass change of Ppy was recorded during the potential sweep from 0.5 V to -0.6 V against SCE of 20 mV s$^{-1}$. The typical mass and current response (recorded simultaneously) is presented in Figure 5.13. The Ppy mass decreases in the first cathodic scan. It is possible that molybdate anions are expelled from the polymer during reduction causing the mass decrease. Then, in the reverse scan, small bromide anions from the solution are incorporated into the polymer film to compensate the charge. It results in the mass increase in anodic direction. However, it is
observed that the polymer mass does not go back to the initial value. This mass change may be due to the difference in the molar mass between molybdate and bromide.

Figure 5.13: The change of Ppy mass in deaerated solution of 0.1 M N(Bu)_4Br, scan rate 20 mV s\(^{-1}\) (CV-dotted line, mass-solid line)

The damping change (\(\Delta w\)) of the Ppy film obtained during the reduction is shown in Figure 5.14. It can be seen that the damping change (\(\Delta w\)) is small and has not the same order with frequency change (\(\Delta f\)). It means that the mass change is caused by the release of anions and can be calculated by Sauerbrey equation. The viscoelastic properties and/or the surface morphology of the film do not change so much. The break-in effect may not occur [76].
To elucidate the behaviour of the Ppy film during the first cathodic scan, the plot of mass change ($\Delta m$) is plotted versus the density of charge passed ($\Delta Q$). The apparent molar mass of anions involved in the reduction of the Ppy film can be determined. Using data of Figure 5.13, one can determine the $\Delta m$-$\Delta Q$ graph in the region of the potential for the release of anions (Figure 5.15). From the slope of the plot, the molar mass of the charged species can be calculated using the following equation:

$$W = -zF\left(\frac{\Delta m}{\Delta Q}\right)$$

Where $W$ is molar mass of anion (g mol$^{-1}$); $F$ is Faraday constant; $z$ is electric charge of anion; $\Delta m$ is mass change (g cm$^{-2}$) and $\Delta Q$ is charge passed (C cm$^{-2}$).
Figure 5.15: The change of Ppy mass vs. charge passed (solid line) for reduction in 0.1 M N(Bu)$_4$Br, N$_2$, scan rate 20 mV s$^{-1}$. Dotted line is the linear fitting curve.

In the cathodic scan, the insertion of the cation N(Bu)$_4^+$ is hindered because of the large size. The mass decrease is only possible due to the release of dopant anions. The molar mass of dopant anion is:

$$W = -96500 \times (-2) \times 6.8 \times 10^{-4} = 131 \text{ g mol}^{-1}$$

Theoretically, the molar mass of MoO$_4^{2-}$ is 159.94 g mol$^{-1}$. The different mass indicates that there is an amount of solvent (H$_2$O) transported during the first negative scan. The number of solvent can be calculated [74, 77, 78]:

$$W' = W + x.W_{H2O}$$

$W$ is the calculated molar mass; $x$ is the number of hydrated water molecules; $W_{H2O}$ is the molar mass of the solvent.

The $x$ value will be 1.5. It means that 1.5 moles of solvent are incorporated into the film by anion release from the Ppy film.

The release of molybdate from the Ppy film was also investigated by EQCM in a small cation solution. The film was formed in the same conditions as described above. The plot of mass change vs. potential during the redox process in 0.1 M KCl is shown in Figure 5.16.
An irreversible mass change is observed after the first cycle of the reduction (Figure 5.16). Probably, part of heavy molybdate anions is replaced by more light-weight chloride anions. The damping changes are large. The Ppy(MoO₄) film morphology may be changed by potential cycling. The application of Sauerbrey equation for molar mass calculation of molybdate is not possible [76].

The incorporation of cation K⁺ causes the increase of the film mass at below -0.5V (vs. SCE). The damping is small in the range of potential from -0.4 V to -0.7 V in cathodic scan, the molar mass of cation K⁺ can be determined by Sauerbrey equation. Relating this mass change to charge passed one obtains apparent molar mass of cation $M_{app}=97 \text{ g mol}^{-1}$. This value means that each K⁺ ion (39 g mol⁻¹) carries approximately three water molecules (54 g mol⁻¹) into the film. The incorporation of hydrate cations results in the strong increase of the mass of Ppy [76]. This behaviour was observed by Yang [64].

In conclusion, Ppy films doped with molybdate were synthesised in molybdate salt solution electrochemically. The redox properties of Ppy(MoO₄) were investigated by CV. Because of the different types of anions in the polymer and in the electrolyte, the cyclic voltammograms are different in the 1ˢᵗ cycle and in successive cycles. After 10 cycles, the film is still stable as
demonstrated by the constant behaviour of CVs. There are no evidences of film decomposition.

Molybdate anions are released from polymer film by polarisation as confirmed by EIS and EQCM. The release of MoO\(_4^{2-}\) results in the increase in film resistance \(R_{PM}\) and decrease in film capacitance \(C_{PM}\) simultaneously. This behaviour can be observed both in a small and a large cation solution. The film capacitance \(C_{PM}\) decreases during the reduction of the Ppy(MoO\(_4\)) film in NaCl solution but not so much as in N(Bu)\(_4\)Br. In NaCl solution, the release of molybdate is relative slow because the moving of Na\(^+\) into the film is faster. The size of cation in electrolyte had some effects on the redox reaction of the film or the release of anions from the Ppy film.

These results are confirmed by EQCM experiments. Cycling a Ppy(MoO\(_4\)) in a large cation solution results in the small damping. Therefore, the mass change can be attributed to the replacement of MoO\(_4^{2-}\) and Br\(^-\). The anion exchange reaction is accompanied by the exchange of solvent molecules. A large damping is observed when the film is cycled in small cation solution. The incorporation of hydrate cations may cause the change of film morphology (so-called ‘break-in’ process) and influence the release of molybdate from the film.

The results of EIS and EQCM are in excellent agreement.
5.3. Electropolymerisation of pyrrole on mild steel

Electropolymerisation of pyrrole on metals such as Fe, Zn, Al, and Mg is prevented by the oxidation of these metals because the oxidation potentials are lower than that of pyrrole. The dissolution of metals is so large that the Ppy film has no adhesion to the substrate. This problem can be overcome by many methods [79], one of them is the proper selection of the electrolyte.

The role of molybdate as an inhibitor stored in the Ppy film as well as the use of the Ppy to protect mild steel from corrosion is discussed in this chapter.

5.3.1. Behaviour of mild steel in molybdate solution

Figure 5.17 shows the open circuit potential (OCP) vs. time curves of the mild steel electrode immersed in aerated and deaerated aqueous solution of 0.01 M Na$_2$MoO$_4$. The mild steel electrode (0.64 cm$^2$) was polished with 600 grit emery paper, then cleaned in an ultrasonic bath in ethanol and finally dried in a nitrogen stream.

![Figure 5.17: OCP-time curve of mild steel in aerated (■) and in deaerated (•) 0.01 M Na$_2$MoO$_4$ solution](image)

In both cases, the OCP shifts rapidly to positive potentials towards the passive region of mild steel. This potential rise can be ascribed to the reaction between molybdate anions and mild
steel as soon as the electrode is immersed into the solution. The insoluble product can block the surface and make the surface potential more positive [80]. This effect can be seen in deaerated medium. In the presence of oxygen, however, the OCP shift is faster and achieves larger positive potentials. In other words, MoO$_4^{2-}$ compound acts as an oxidant and passivates the surface of mild steel surface shortly even if without oxygen. Surface analysis of mild steel exposed to molybdate by XPS, AES and an electron microprobe confirms the presence of FeO.OH in combination with MoO$_3$ [81]. In contrast, the passivation of mild steel needs oxygen in solutions containing inhibitor such as oxalate, succinate, and phthalate [82].

5.3.2. Electropolymerisation of pyrrole on mild steel

The electropolymerisation was performed in a conventional three-electrode cell consisting of a Pt plate as counter electrode and the saturated calomel electrode (SCE) as reference electrode. A mild steel working electrode (4 cm$^2$) was polished with 600 grit emery papers, cleaned in ethanol in an ultrasonic bath and dried in a nitrogen atmosphere. The polypyrrole (Ppy) films were generated galvanostatically at a current density of 1.5 mA cm$^{-2}$ in an aqueous solution of 0.1 M pyrrole and 0.01M sodium molybdate (pH=4.8). The total charge passed was 0.9 C cm$^{-2}$. After formation, the sample was rinsed in distilled water and dried in nitrogen atmosphere. The potential-time curve for galvanic deposition of Ppy(MoO$_4$) on mild steel is shown in Figure 5.18. The polymerisation starts at a constant current of 1.5 mA cm$^{-2}$ for which the potential increases rapidly and then decreases slowly. After 100 seconds, the potential is stabilised at about 0.9 V (vs. SCE) which corresponds to the oxidation potential of pyrrole. This behaviour indicates that the dissolution of mild steel is prevented. Pyrrole can be oxidised on mild steel. However, the oxidation potential of pyrrole is higher than normal. The reasons may be: i) the barrier effect of the passivating layer of molybdate on the surface ii) the lower conductivity of the electrolyte.
Polypyrrole doped with molybdate on mild steel

Figure 5.18: Electropolymerisation of pyrrole on mild steel, \( i = 1.5 \text{ mA cm}^{-2} \), 0.01 M MoO\(_4^{2-}\), pH= 4.8, 0.1 M pyrrole

Figure 5.19: Potential-time curve for the electrodeposition of Ppy on Pt (1) and on mild steel (2) from 0.1 M \( \text{H}_2\text{C}_2\text{O}_4 \), 0.1 M pyrrole, at 1 mA cm\(^{-2}\)

It should be noted that the polymerisation in presence of molybdate on mild steel occurs without an induction period. This is in contrast to other procedures which have been reported [17, 21, 27]. The electropolymerisation of pyrrole in oxalate aqueous solution is a typical
example to elucidate the role of molybdate in the polymerisation. An induction time is present during the polymerisation as shown in Figure 5.19.

Obviously, the surface of mild steel needs nearly 200 seconds to be passivated in oxalic acid (H$_2$C$_2$O$_4$). The induction time is attributed to the active dissolution of mild steel. This active range is assigned at the negative potential. Next, the formation of Fe-oxalate results in the potential shift towards positive potentials high enough for oxidation of pyrrole. Finally, the positive potential levels off until the end of polymerisation. The behaviour is different from that of the electropolymerisation on Pt. Pyrrole can be oxidised immediately on Pt after applying the current through the cell.
5.3.3. Characterisation of Ppy(MoO₄)/mild steel film

5.3.3.1. Film morphology

Figure 5.20: SEM pictures of Ppy(MoO₄) on mild steel (A) and on Pt (B)

Figure 5.20 shows SEM micrographs of Ppy films doped with MoO₄²⁻ on mild steel (A) and on Pt (B). The total consumed charge for deposition was about 0.9 C cm⁻². The films formed
on mild steel are homogenous, compact, but thinner than on Pt. The typical cauliflower structure of Ppy films on mild steel is observed.

5.3.3.2. Thickness of Ppy films on mild steel
A Ppy film was formed on mild steel at the condition mentioned above, and then covered by conducting resin. A cross-section of the sample was made by cutting and polishing with 1200 emery paper. SEM and Energy Dispersive X-ray (EDX) measurements were carried out to determine the thickness of the Ppy film.

As seen in Figure 5.21, three parts can be distinguished clearly. The Ppy film is determined in the middle part. The thickness of the Ppy film was estimated to about 1.2 µm, the charge consumed was 0.9 C cm\(^{-2}\). The result is reproducible.

![Cross-section SEM of Ppy(MoO\(_4\))/mild steel total charge passed is 0.9 C cm\(^{-2}\)](image)

Figure 5.21: Cross-section SEM of Ppy(MoO\(_4\))/mild steel total charge passed is 0.9 C cm\(^{-2}\)

It has been known that total charge for electropolymerisation of pyrrole is about 0.4 C cm\(^{-2}\) µ\(^{-1}\) on inert electrodes such as platinum. The value obtained in the current experiment is 0.75 C µ\(^{-1}\) cm\(^{-2}\). The reason of this difference may be: a part of charge is used for the passivation of mild steel with molybdate.
5.3.3.3. XPS analysis

![Figure 5.22: XPS spectra for molybdate in Ppy(MoO$_4$) on mild steel [83]](image)

Figure 5.22 shows the XPS surface analysis of the Ppy(MoO$_4$) on mild steel. Ppy was electrodeposited under similar conditions mentioned above.

The complex spectra of Mo 3d peaks correspond to the chemical states. The peaks are assigned: Mo$_{13d5}$ (231 eV), Mo$_{13d3}$ (233 eV), Mo$_{23d5}$ (234.5 eV) and Mo$_{23d3}$ (236 eV) [84]. The XPS spectra are supposed that molybdate should be in two compounds: [MoO$_4$]$^{2-}$ (62%) and [Mo$_7$O$_{24}$]$^{6-}$ (38%). Both types of molybdate are doped in Ppy.

One should take into account the fact that molybdate exist in different forms depending on the pH of solution [39]. This relation can be presented:

\[
[\text{MoO}_4]^{2-} \leftrightarrow [\text{Mo}_7\text{O}_{24}]^{6-} \leftrightarrow [\text{Mo}_8\text{O}_{26}]^{4-} \leftrightarrow [\text{Mo}_{36}\text{O}_{112}]^{8-} \leftrightarrow \text{MoO}_3\cdot2\text{H}_2\text{O}
\]

\[
pH=6.5 - 4.5 \quad pH=2.9 \quad pH<2 \quad pH=0.9
\]

In this condition of electropolymerisation (pH about 4.8), the presence of [MoO$_4$]$^{2-}$ and [Mo$_7$O$_{24}$]$^{6-}$ in polymer film is obvious.
5.3.4. Anion release from Ppy(MoO₄)/mild steel

Electrochemical behaviour of Ppy on mild steel was characterised by EIS combined with cyclic voltammetry. Figure 5.23 shows the change of the resistance $R_{PM}$ and the capacitance $C_{PM}$ of Ppy(MoO₄)/mild steel with the potential.

![Graph showing change of $R_{PM}$ and $C_{PM}$ with potential](image)

In the potential range from 0.6 V - 0.2 V (vs. SCE), the Ppy film is conductive; $R_{PM}$ is small (about 20 Ω). Following the negative scan, $R_{PM}$ increases gradually. The reduction of the Ppy film begins at 0.2 V (vs. SCE). The behaviour is reversible (see reverse scan) i.e. $R_{PM}$ decreases nearly to the original value. The Ppy(MoO₄) film is now in the oxidised state.

The change of the film capacitance $C_{PM}$ is inversely proportional to that of $R_{PM}$. It decreases in the negative scan and increases in the positive scan gradually. It is observed, however, that the film capacitance does not return to the original value. The explanation for this phenomenon is that the transport of solvent (water) accompanies by the anion exchange. It leads to the conformation changes of the conducting polymer. Hence, it can be concluded that:

- Ppy(MoO₄) can be synthesised electrochemically on active metals like mild steel, in a one-step process. The dissolution of mild steel can be prevented with molybdate. The film is homogenous and adhesive on mild steel.
- Ppy(MoO₄) film formed on mild steel has the same redox property as on Pt. During reduction in N(Bu)₄Br solution the decrease of film capacitance is observed. It means that molybdate releases from the film.
- There is no evidence of film decomposition. Corrosion test of Ppy(MoO₄) on mild steel

5.3.4.1. Polarisation curves

![Polarisation curve diagram](image)

Figure 5.24: The potentiodynamic curve of Ppy(MoO₄)/mild steel film (1) and bare mild steel (2) in 0.1 M NaCl, 1 mV s⁻¹

The protective effect of Ppy(MoO₄) film on mild steel was examined in aerated 0.1 M NaCl. The corrosion potential E₉₉ and corrosion current density i₉₉ were determined by extrapolation of anodic and cathodic Tafel lines.

Figure 5.24 indicates that E₉₉ shifts towards positive potentials (about 500 mV) and i₉₉ decreases about one order in magnitude as compared to the bare mild steel electrode. The polymer film can prevent the metal surface from corrosion. The inhibiting efficiency E of Ppy(MoO₄) is obtained by equation:

$$E = \frac{i^0 - i}{i^0} \times 100\%$$

Where $i^0$, $i$ denote the corrosion current of bare mild steel and Ppy(MoO₄)/mild steel, respectively. The inhibiting efficiency E is about 98% for Ppy(MoO₄) on mild steel.
5.3.4.2. OCP measurement

![OCP-time curve of Ppy(MoO₄)/mild steel (about 1.5 µm) in 0.1 M NaCl](image)

The corrosion behaviour of mild steel covered by Ppy(MoO₄) films was investigated by OCP-time measurements. The samples were immersed in a 0.1 M NaCl solution as corrosive medium and the OCP was recorded versus time. The protection time is characterised by the time during which the OCP of the covered electrode remains in the passive state of mild steel before it drops down to the corrosion potential of unprotected mild steel.

The OCP-time curve of Ppy(MoO₄) coated on mild steel in NaCl is presented in Figure 5.25. The OCP is initially positive at about 0.35 V (vs. SCE) which corresponds to redox potential of Ppy. The mild steel electrode maintains in its passive state for about 7 hours. Then, the potential sharply decreases to a second plateau at about -0.2 V (vs. SCE) and is stable there for about 5 hours. In this plateau, chloride anions have reached the metal surface through the pores of Ppy film. The anodic reaction can take place and the polymer is reduced partially. This reduction causes the molybdate anion release which is needed to slow down the corrosion rate. This may be a reason why OCP is stable at plateau 2. The release of molybdate from the Ppy film in this second plateau was confirmed by EIS measurement shown in Figure 5.26. The reduction of Ppy film causes the increase of the film resistance (marked by an arrow) and the release of molybdate causes the decrease of the film capacitance.
Figure 5.26: EIS spectra of the Ppy(MoO$_4$) film in the second plateau of the OCP in 0.1 M NaCl solution. Impedance (solid line), phase angle (dotted line)

Finally, OCP decreases towards the corrosion potential of the mild steel because of the large concentration of chloride in the polymer/mild steel interface, Ppy cannot protect mild steel any longer.

This second plateau is only observed if the dopant anions of the conducting polymer have some ability to inhibit the corrosion reaction of mild steel [18, 27]. If the anions cannot give this protection, the second plateau is missing and the potential falls down to the corrosion potential of mild steel at the end of the first plateau [85].

Ppy(MoO$_4$) has shown the protective ability for mild steel. The corrosion potential is kept at the second plateau where mild steel is in a passive state.

5.3.4.3. The role of molybdate passive layers in corrosion protection

It is clear that a passive layer of molybdate is formed on mild steel during the electropolymerisation process. This layer can reduce the oxidation of mild steel and facilitates the polymerisation of pyrrole. In order to clarify the role of molybdate in this passive layer in corrosion protection, a Ppy film with the non-inhibitive anions ClO$_4^-$ was electrodeposited on mild steel passivated with molybdate. The corrosion test was carried out in 0.1 M NaCl solution.

A mild steel electrode was passivated in molybdate solution with the following procedure: immersion in 0.1 M Na$_2$MoO$_4$ for 60 minutes, 30°C; potentiostatic passivation at 0.5 V (vs.
SCE) for 1 hour; rinsing in distilled water and drying under N\textsubscript{2} stream [86]. The Ppy(ClO\textsubscript{4}) film was electrodeposited under these conditions: 0.1 M LiClO\textsubscript{4}, 0.1 M pyrrole monomer, \textit{i} = 1 mA cm\textsuperscript{-2}. The OCP of Ppy(ClO\textsubscript{4}) was recorded in 0.1 M NaCl.

![OCP-time curve of Ppy(ClO\textsubscript{4})/passive layer/mild steel in 0.1 M NaCl](image)

Figure 5.27: OCP-time curve of Ppy(ClO\textsubscript{4})/passive layer/mild steel in 0.1 M NaCl

Figure 5.27 shows the OCP-time curve of Ppy(ClO\textsubscript{4})/passive layer/mild steel in 0.1 M NaCl. At the beginning, the OCP is still in the passive range of mild steel. Ppy(ClO\textsubscript{4}) can protect the substrate from corrosion. Nevertheless, this protection only remains for a short time (about 100 seconds). The penetration of chloride through the film is very fast and breaks down the passive film of molybdate formed in the pretreatment procedure. The OCP decreases sharply to the active potential range.

This OCP measurement indicates that the passive film of molybdate on the mild steel cannot prevent the penetration of chloride and cannot reduce the corrosion rate. Molybdate in a passive layer under the polymer film does not play any role for corrosion protection.

5.3.4.4. The possibility of self-healing with Ppy(MoO\textsubscript{4}) film on mild steel

The self-healing action of Ppy(MoO\textsubscript{4}) film was investigated. On a fresh Ppy(MoO\textsubscript{4})/mild steel film, a small defect (about 0.04 mm\textsuperscript{2}) was made with a needle. OCP–time curve was recorded in aerated 0.1 M NaCl as seen in Figure 5.28.
After immersion, the potential decreases immediately and then levels off at a potential of about -0.1 V for 4 hours. This observation could be explained as follows: the dissolution of mild steel at defect occurs immediately after the Ppy film contacts with the corrosive environment. Because of the galvanical connection with mild steel, Ppy will be reduced to compensate the redox process. This reduction is a driving-force for molybdate anions to be released from the Ppy near the defect. A passive compound Fe$_x$Mo$_y$O$_z$ is produced and it acts as inhibitor in the defect. It results in the maintenance of the potential for a certain time. The fluctuation of the OCP, numerous small spikes of potential are observed, is explained as the breakdown of the passive film by chloride and the re-passivation by MoO$_4^{2-}$ in the defects. A small defect of the Ppy film is protected from corrosion by the Ppy(MoO$_4$) film.

The same experiment was carried out with a Ppy film doped with PF$_6^-$ as non-inhibitive anion. After passivating with molybdate, a mild steel electrode was covered with Ppy in 0.1 M N(Bu)$_4$PF$_6$, 0.1 M pyrrole in dichloromethane at 1.5 mA cm$^{-2}$. A small defect was made with a needle (0.04 mm$^2$) on the fresh film. As corrosive medium 0.1 M NaCl was also used.
Figure 5.29: Fe/molybdate passive layer/Ppy(PF₆⁻), i=1.5 mA cm⁻², in dichloromethane, about 1.5 µm, 2: Fe/ Ppy(MoO₄²⁻), ca. 1.5 µm, after dipping 4 hours
Experiment: with defect ca. 0.04 mm², in 0.1 M NaCl, scan rate: 0.5 mV s⁻¹

The polarisation curves shown in Figure 5.29 are obtained on two Ppy films with different dopant anions, namely PF₆⁻ (curve 1) and molybdate (curve 2). Although there is a molybdate passive layer, the corrosion potential of Ppy(PF₆⁻) is still in the active range at the beginning of the experiment. No shift of the corrosion potential is observed here. This behaviour shows that the defect is attacked continuously by chloride. Ppy(PF₆⁻) film cannot protect and repair this defect.

On the contrary, a positive shift of the corrosion potential and the decrease of the corrosion current are observed on Ppy(MoO₄²⁻)/mild steel (curve 2). The defect is passivated for 4 hours. The corrosion potential remains in the passive range. The corrosion current for Ppy(MoO₄²⁻) is nearly two orders of magnitude smaller than that of Ppy(PF₆⁻).

These results show that molybdate within a polymer plays an important role in self-healing of a defect. Passive layers containing molybdate on mild steel can reduce the dissolution of the active metal during the polymerisation but cannot act as corrosion inhibitor. The self-healing action for mild steel only takes place on Ppy films doped with corrosion inhibitors such as molybdate.
5.3.4.5. Delamination

The corrosion process of Ppy(MoO$_4$) on mild steel was investigated with the Scanning Kelvinprobe (SKP). The experimental set-up and the SKP measurements were made in MPI Düsseldorf. The artificial defect was prepared on a part of Ppy film shown in Figure 5.30.

![Figure 5.30: Preparation of iron electrode coated by Ppy(MoO$_4$) film for SKP experiments [87]](image)

The used SKP tip had a diameter of 100µm. Top-coat was polyacryl resin (BASF) applied on the film in order to avoid the difficulties resulting from the folding of the film during the delamination experiment. The humid atmosphere (93 – 95%) was controlled during the experiment.

Ppy was formed on mild steel under the following conditions: 0.1 M pyrrole + 0.01 M molybdate aqueous electrolyte; current density 1.5 mA cm$^{-2}$. The SKP measurements were obtained in 0.1 M KCl solution.

Figure 5.31 shows the profile of corrosion potential $E_{\text{corr}}$ as function of the distance to the defect border for different times after contact of the defect with electrolyte. The following features must be mentioned: (i) the region next to the defect where $E_{\text{corr}}$ is similar to the corrosion potential of bare mild steel (-0.45 V vs. SHE). (ii) a region of abrupt increase from low to high values of $E_{\text{corr}}$. This region shifts from left to right i.e. away from the defect border with increasing time; (iii) a region where the adhesion is not yet lost [54].
It can be seen that the delamination of Ppy film is very fast in KCl (about 1600 µm for 2 hours). The corrosion potential of the delaminated area remains in the active range potential of corroding iron (about 0.45 V vs. SHE). The passivation of the defect does not take place. Because of their size, cations K⁺ can move into the Ppy film easier than the release of molybdate from the film during delamination process. The transport of anions in electrochemical experiment is only few micron while the delamination over hundreds micron, that leads to the predominately cation incorporation into the film for charge compensation. The amount of molybdate is not enough to passivate the large defect.

The delamination of Ppy(MoO₄) film on mild steel investigated further in 0.1 M N(Bu)₄Cl solution is shown in Figure 5.32. The delamination is much slower than that in small cation solution. Now the delamination front reaches 1600µm after 33 hours instead of 2 hours in KCl solution. The reduction of Ppy at the defect is slowed down. Obviously, the size of cation in electrolyte had effects on the delamination process. The incorporation of cation N(Bu)₄⁺ is hindered because of their size. The release of molybdate anions is predominant.
Figure 5.32: SKP measurement of Ppy(MoO$_4$)/mild steel in 0.1 M N(Bu)$_4$Cl [87]

The release of molybdate in delamination process is confirmed by the XPS experiment shown in Figure 5.33. After delamination, the Ppy film was peeled off and molybdate was detected by XPS in the film.

Figure 5.33: XPS measurement of Ppy(MoO$_4$) on mild steel after delamination in 0.1 M N(Bu)$_4$Cl [83]
No signals of molybdate were found, only iron was seen in the spectra. The presence of iron may come from the corrosion process. The molybdate has moved to the defect during the corrosion process.

The same SKP experiment was repeated and the amount of molybdate within the Ppy film was measured by XPS at the defect and at the interface polymer/metal. The result is presented in Figure 5.34.

It can be seen that there is a difference of the amount of molybdate at the defect and at the interface polymer/substrate. At the defect, molybdate anions are expelled from the polymer due to the reduction of Ppy when the defect is connected with the substrate galvanically. The amount of molybdate is consumed to form the passive layer and to suppress the cathodic delamination. Nevertheless, the Ppy film is still in the oxidised state in the undelaminated region of Ppy (point 2, Figure 5.34). Molybdate anions still remain in the Ppy film. This is the reason why the quantity of molybdate in the Ppy film at the defect is smaller than at the interface where the Ppy protects the metal.

5.3.4.6. **Raman spectroscopy of Ppy(MoO₄)₂**

During the corrosion process, Ppy will be reduced because a galvanic cell is established between Ppy and mild steel. Raman spectroscopy was used to characterise the state of Ppy, oxidised or reduced.
Ppy(MoO$_4$)/mild steel was prepared in aqueous solution of 0.1 M pyrrole + 0.01 M molybdate at 1.5 mA cm$^{-2}$. Three states of Ppy (fully oxidised, partially reduced and totally reduced) were determined through the OCP obtained by dipping samples in 0.1 M NaCl. Raman spectra of these samples are shown in Figure 5.35.

Several bands are representative for the oxidised state. The band 1600 cm$^{-1}$ belongs to the inter-ring (C=C) of oxidized Ppy (0.1 V). It shifts towards low wavenumbers in more negative potential (1597 cm$^{-1}$ at –0.4 V and 1594 cm$^{-1}$ at –0.6 V). The bands 1052 cm$^{-1}$, 1083 cm$^{-1}$ are assigned to the C-H in plane deformation [88, 89]. They are also shifted to lower wavenumbers during the corrosion process. The Raman peaks of the dopant anion shift from 931 cm$^{-1}$ to 920 cm$^{-1}$ in the reduced state [90].

![Figure 5.35: Raman spectra of Ppy in different states: 1. complete oxidation (after formation); 2. partial reduction; 3. complete reduction](image)

The Ppy(MoO$_4$)/mild steel film is in the oxidised state while it protects mild steel substrate and is progressively changed to the reduced state during the protection progress.

The properties of Ppy(MoO$_4$) can be summarised:

- Ppy(MoO$_4$) films covered on mild steel have the effect of corrosion inhibition. The $E_{corr}$ is in the passive range of potential in chloride solution. The potential shift is nearly 500 mV (vs. SCE) compared to bare mild steel. At the same time, $i_{corr}$ decreases one order of magnitude
when Ppy(MoO$_4$) covers on mild steel. The protective efficiency is fairly high (about 98%, see chapter 5.3.4.1), indicating a good property of Ppy(MoO$_4$) in corrosion protection for mild steel.

- The self-healing effect of Ppy(MoO$_4$) film can be observed by OCP measurement. In contrast, Ppy(PF$_6$) cannot prevent corrosion of mild steel even with no defect. Molybdate in corrosion protection of mild steel is acting as anodic inhibitor.

- The release of the molybdate is necessary for self-healing of defect by Ppy. The reduction of the Ppy film during the corrosion process is the driving-force to release inhibitor anions. Raman experiments show that Ppy changes from the oxidised state to the reduced state during the corrosion process. This observation is reported elsewhere [88, 91]. XPS results confirm this observation.

- The EQCM and EIS results in aqueous solution indicate that the reduction of Ppy(MoO$_4$) is accompanied by a mixed anion/cation transport and by water uptake. However, it is possible to show that the medium size molybdate anion can be released from the film to improve the protective properties of Ppy film deposited on mild steel.

- The Scanning Kelvinprobe experiments of Ppy(MoO$_4$) film show that the release of molybdate can be found when the film is reduced in a large size cation solution. The delamination can be stopped. On the contrary, the delamination of Ppy(MoO$_4$) film is fast in a small cation solution. The incorporation of cations is predominant. Therefore, the delamination cannot be hindered.

- The release behaviour of molybdate from the Ppy film depends much on the size and mobility of cations in the electrolyte.
5.4. Investigation of Ppy film doped with TiF₆⁻ anion

Titanium and its alloys are extensively employed in aircraft industry due to mechanical strength and high corrosion. Origin of the corrosion resistance is a film of TiO₂ passivating the surface [81].

Attempts were made to develop a corrosion protection system for Fe, Al and other metals based on the formation of a conversion layer containing Ti. In the literature a layer of Ti-Zr for Al was described [92, 93]. The concept should be transferred to a Ppy film if TiF₆⁻ is used as dopant anion. Some results with this anion are described in this part.

5.4.1. Synthesis of Ppy(TiF₆⁻) film

Ppy film doped with TiF₆⁻ was electropolymerised at a constant potential of 0.7 V (vs. SCE) in 0.1 M H₂TiF₆ + 0.1 M pyrrole solution at room temperature on platinum electrodes (1cm²).

The electropolymerisation was performed in a conventional three-electrode cell containing a Pt sheet as counter electrode and the saturated calomel electrode (SCE) as reference electrode. The thickness of the Ppy film was about 1 µm.

5.4.2. The reduction of Ppy(TiF₆⁻) film

The behaviour of anion release from the Ppy(TiF₆⁻) film during the reduction was investigated by EIS in the solution containing large and small cations, namely N(Bu)₄Br and NaCl. The EIS spectra of Ppy(TiF₆⁻) were recorded in the potential range from 0.1 V to -1 V (vs. SCE).

In both cases, the release of dopant anions is observed. The reduction of Ppy film results in the increase of polymer resistance Rₚₚ. Simultaneously, the decrease of the film capacitance Cₚₚ (at high frequencies) with increasing cathodic potential indicates that dopant anions are expelled from the Ppy film. The release of dopant TiF₆⁻ from Ppy film seems to be independent on the size of the cation in solution. The anion exchange process of Ppy(TiF₆⁻) is predominant during the reduction.
Figure 5.36: The reduction of Ppy(TiF₆)/Pt in 0.1 M N(Bu)₄Br. Impedance (solid line), phase angle (dotted line)

Figure 5.37: The reduction of Ppy(TiF₆)/Pt in 0.1 M NaCl. Impedance (solid line), phase angle (dotted line)

Using the equivalent circuit shown in Figure 4.4 (page 38), the values of the film capacitance and of the film resistance are calculated and presented in Figure 5.38 A and B.
Values of the film resistance $R_{PM}$ and the capacitance $C_{PM}$ in both cases are changed with potential. These values are in the same order. It means that the behaviour of the Ppy(TiF$_6$)
film is similar in the different electrolytes. It is found that there is a little bit difference of $C_{PM}$ in NaCl (110nF) and in N(Bu)$_4$Br (60nF). The similar values of $C_{PM}$ in small and large solution reflect that TiF$_6^{2-}$ anions can release from Ppy film during reduction not depending on the type of cations in electrolyte.

5.4.3. Redox property of Ppy(TiF$_6$/Pt
The redox property of Ppy(TiF$_6$) was investigated by CV. The film was formed on Pt under the condition mentioned above. Reversible potentiodynamic cycling of Ppy(TiF$_6$) film can be achieved in 0.1 M N(Bu)$_4$Br solution as shown in Figure 5.39.

![Figure 5.39: CV of Ppy(TiF$_6$/Pt in 0.1 M N(Bu)$_4$Br, 20 mV s$^{-1}$](image)

The first cathodic cycle is connected with the release TiF$_6^{2-}$ anions from the polymer. The maximum of the reduction is observed at 0 V (vs. SCE). In the next cycles, bromide anions replace TiF$_6^{2-}$ anions.

5.4.4. Preparation of Ppy(TiF$_6$) on mild steel
Attempts failed to prepare TiF$_6^{2-}$ doped Ppy film on mild steel. The dissolution of the substrate is much greater than the electropolymerisation of pyrrole. But it was possible to prepare Ppy(TiF$_6$) film by indirect method of anion exchange. The anions were exchanged by the following procedure: Ppy(MoO$_4$) was formed on mild steel and then held at a potential of -0.4 V (vs. SCE) in 0.1 M N(Bu)$_4$Br for about 30 minutes. The
molybdate anions were released from the film. Then, Ppy film was re-oxidised in 0.1 M H₂TiF₆ at the constant potential of 0.4 V (vs. SCE) for 10 minutes, rinsed in distilled water and dried in an N₂ stream. The process of anion exchange was controlled by EIS measurements (Figure 5.40).

![Figure 5.40: 1) Ppy(MoO₄)/mild steel in oxidised state; 2) Ppy(MoO₄)/mild steel in reduced state, 3) Ppy(TiF₆)/mild steel after exchange anion. The impedance spectra were measured in 0.1 M N(Bu)₄Br. Impedance (solid line), phase angle (dotted line)](image)

In the oxidised state, the Ppy film is conductive (curve 1, Figure 5.40). The film resistance $R_{PM}$ is about 50 Ω. After reduction, the Ppy film is non-conductive (curve 2). The film resistance increase rapidly ($R_{PM} = 10$ KΩ). The decrease of the film resistance after re-oxidation in H₂TiF₆ solution (curve 3) indicates that molybdate anions are replaced by TiF₆²⁻ anions. The conductivity of the Ppy film is partially regained ($R_{PM} = 200$ Ω).

5.4.5. Corrosion test of Ppy(TiF₆) film on mild steel

After anion exchange, Ppy(TiF₆)/mild steel was immersed in 0.1 M NaCl. The OCP-time dependence is shown in Figure 5.41.

After a fast decay a first plateau at 0.1 V is observed. A second plateau in the OCP-time curve is found at about -0.3 V (vs. SCE) for two hours. This second plateau might be connected with the penetration of chloride to the substrate surface during the immersion. Inhibitive TiF₆²⁻ anions released from the polymer film stabilise the OCP. The fluctuation of the OCP

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points to passivation/re-passivation phenomena. After 3 hours the OCP falls down to the corrosion potential of bare mild steel.

![OCP - time curve of Ppy(TiF₆)/mild steel in aerated 0.1 M NaCl solution](image)

Figure 5.41: OCP – time curve of Ppy(TiF₆)/mild steel in aerated 0.1 M NaCl solution

The OCP measurement of Ppy(TiF₆)/mild steel was repeated *with a small defect*. Results are presented in Figure 5.42. Ppy(TiF₆)/mild steel was synthesised indirectly by anion exchange of MoO₄²⁻ versus TiF₆²⁻. The small defect was made by a needle (about 0.04 mm²).

The initial OCP, observed with Ppy in the oxidised state, decreases for 1.5 hours. After 1.5 hours, the OCP increases again to the value of the second of Figure 5.41 at -0.3 V (vs. SCE). At this potential similar oscillations are observed.

The sharp fall of the OCP at the beginning of the OCP measurement is explained by the dissolution of the iron in the defect as a result of the attack by chloride anions.
Figure 5.42: OCP – time curve of Ppy(TiF₆)/mild steel in 0.1 M NaCl, O₂, with a defect of ca. 0.04 mm²

Ppy(TiF₆) has shown a protective effect on mild steel. The dissolution in a defect of the film on mild steel is inhibited.
5.4.6. *Scanning Kelvinprobe experiment*

The delamination of Ppy(TiF$_6$) was also investigated by SKP experiments in 0.1 M KCl solution. The film was formed on Au/glass electrodes by applying a constant potential of 0.7 V (vs. SCE) in 0.1 M H$_2$TiF$_6 + 0.1$ M pyrrole aqueous solution.

The experimental set-up was constructed in The Max Planck Institute for Iron Research and described in detail in Ref. [87]. The sample was connected with iron plate to perform the delamination (Figure 5.43). The same experimental conditions shown in the section 5.3.4.5 (page 74) was used. The time dependence of the delamination of a Ppy film doped with TiF$_6^{2-}$ is shown in Figure 5.44. Three regions are observed:

- the region next to the defect where $E_{corr}$ is similar to $E_{corr}$ of mild steel
- the region of sharp increase of $E_{corr}$ corresponding to the defect border
- the undelamination region with a positive potential

![Figure 5.43: Preparation of SKP experiment for Ppy(TiF$_6$)/Au/glass electrode](image)

At the beginning of the immersion, no delamination occurs. The measured potential is still in positive region and equal to the redox potential of Ppy. With increasing time, the delamination starts and is progressing, the defect gets larger.

After 15 hours of experiment, the defect is still not larger than 250 $\mu$m. This shows that the presence of TiF$_6^{2-}$ anion effectively reduce the delamination.
From these results of Ppy(TiF$_6$), it can be concluded that:

- The release of TiF$_6^{2-}$ anions from the Ppy film can be observed in EIS experiments. TiF$_6^{2-}$ anions are mobile enough to release from Ppy film during the reduction process. This is shown with the increase of the film resistance $R_{PM}$ and decrease of the film capacitance $C_{PM}$. Cations in the electrolyte have no effects on the release of TiF$_6^{2-}$ anion from the Ppy film. This behaviour cannot be observed on Ppy(MoO$_4$) film. Obviously, TiF$_6^{2-}$ anions are more mobile than molybdate anions.

- The corrosion of mild steel is inhibited by Ppy(TiF$_6$). In the presence of TiF$_6^{2-}$ anions the defect can be passivated. Ppy(TiF$_6$) film may provide anodic protection for mild steel. In addition, Ppy(TiF$_6$) can reduce the cathodic reaction shown in the SKP experiments. The delamination of a polymer film is lowered significantly in despite of the presence of small cations in the electrolyte.
5.5. The Ppy film on Zn

5.5.1. Passivation of Zn in solutions of nitro compounds

Some nitro compounds: 5-nitro salicylic acid, 3,5-nitro salicylic and 3-nitro salicylic acid were studied as corrosion inhibitors for Zn. The pure Zn sheets were immersed in these solutions in certain time. Their surfaces were compared before and after immersion by visual inspection. The results were compared with Zn immersed in salicylic acid and KNO₃.

![Figure 5.45: Photographs of pure zinc after 4 days of immersion in](image)

Figure 5.45 shows photographs of pure Zn after 4 days of immersion in different solutions. Four samples (a, b, c, d) have different colours as compared with pure Zn. The colour changes come from corrosion products of Zn. The colour of sample e was not changed. Corrosion products were not observed on this sample.

3-nitro salicylic acid (3-nisa) might be the candidate for corrosion protection for Zn. The effect was observed in alkaline (pH=8) and in acid solution (pH=2.5). Further experiments were made in acid solution because the electropolymerisation of pyrrole is only possible in acid.

5.5.2. The behaviour of Zn in 3-nitro salicylate solution

Figure 5.46 shows the OCP recorded when a pure Zn electrode was immersed in different aerated solutions.
Figure 5.46: Behaviours of pure Zn in 3-nisa (1); 5-nisa (2); 3,5-nisa (3); KNO$_3$ (4) and salicylic acid (5). All solutions with concentration of 0.01 M and pH=2.5.

The effect of 3-nitrosalicylic acid is observed. The OCP of pure zinc is shifted at about 0.45 V to more positive values compared with salicylic acid without nitro-group (Figure 5.46, curve 1). Müller and Langenbucher [94] have found that nitrosalicylic acids which have a nitro-group ortho to a hydroxy-group are effective inhibitors for zinc flakes used as pigments in water-borne paints. The inhibiting effect can be explained with the formation of chelate complexes with Zn (II). The complex is shown below.

5.5.3. Electropolymerisation of pyrrole on Zn

A pure Zn electrode (2 x 2cm$^2$) was polished with 1200 emery paper, and then cleaned ultrasonically in ethanol. The electropolymerisation was performed in a conventional three-electrode cell consisting of a Pt plate as counter electrode and the saturated calomel electrode (SCE) as reference electrode. The Ppy films were generated galvanostatically at a current...
density of 1.5 mA cm\(^{-2}\) in an aqueous solution of 0.3 M pyrrole and 0.01 M 3-nisa (pH = 2.5). After film formation, the sample was rinsed in distilled water and dried in a nitrogen stream.

![Graph showing potential-time curve](image)

Figure 5.47: Electropolymerisation of pyrrole on Zn in 0.01 M 3-nisa + 0.3 M pyrrole aqueous solution, current density=1.5 mA cm\(^{-2}\)

Figure 5.47 shows the potential-time curve for galvanostatic electropolymerisation of pyrrole on Zn. After a very short time (about 50 seconds) the potential increases abruptly, then decreases slowly and levels off at 0.85 V (vs. SCE). At this potential the polymerisation reaction takes place.

There is no induction period, characteristic for primary metal dissolution. The chelate complex layer prevents the Zn dissolution, but promotes the polymerisation of pyrrole. The oxidation of pyrrole is facilitated.

In the presence of 3-nisa, Ppy can be prepared on Zn electrochemically in a 1-step procedure. It is also to note that Zn must not have any special treatment before electro- polymerisation. No dissolution of Zn at the oxidation potential of pyrrole occurs.

5.5.4. Morphology of the Ppy film of Zn

The morphology of a Ppy(3-nisa) film on Zn was investigated by SEM as shown in Figure 5.48.
The black film of Ppy is homogenous and adherent. SEM reveals the characteristic cauliflower morphology. The quality of the polymer film is excellent, no cracks or detachments are observed.
5.5.5. Corrosion test

5.5.5.1. Potentiodynamic measurements

The corrosion resistance of Ppy doped with 3-nisa on Zn was determined by potentiodynamic polarisation measurement in 0.1 M NaCl. A Pt counter electrode and a SCE reference electrode were used.

Figure 5.49 shows the potentiodynamic curves for bare Zn (1) and Ppy(3-nisa)/Zn (2) in 0.1 M NaCl.

![Potentiodynamic curves](image)

The corrosion potential \( E_{\text{corr}} \) of Ppy(3-nisa)/Zn shifts by nearly 1 V (vs. SCE) to more positive potentials as compared to bare Zn. The corrosion current is decreased. The Ppy film with 3-nisa as dopant anion inhibits the corrosion of Zn. The protective efficiency of Ppy(3-nisa) for Zn was 98%.

5.5.5.2. OCP-time measurements

OCP-time curve of Ppy(3-nisa)/Zn film was measured in 0.1 M NaCl solution (Figure 5.50). At the beginning, the potential is around 0.1 V (vs. SCE). The Ppy film remains in its oxidised state and can prevent the penetration of chloride. No corrosion occurs. Then, the potential decreases and the plateau at -0.4 V (vs. SCE) is observed. Chloride ions reach the surface through the pores of polymer film. The Zn dissolution reaction is compensated by the
Polypyrrrole film on Zn

reduction of Ppy. But the reduction of Ppy film releases 3-nisa anions that act as corrosion inhibitor. Therefore, that OCP is stabilised at -0.4 V (vs. SCE) for more than 1 hour. After 3 hours, the OCP reaches the active potential of Zn and then the metal surface is no longer protected.

![Graph showing OCP-time in 0.1 M NaCl for Ppy(3-nisa)/Zn](image)

**Figure 5.50: OCP-time in 0.1 M NaCl for Ppy(3-nisa)/Zn**

The protection time which has been previously defined as the time during which the OCP of the covered metal remains in the passive state before it drops down to the corrosion potential of the unprotected metal, is shorter than the protection time of Ppy(MoO$_4$) films on mild steel (Figure 5.25). Compared with Ppy(MoO$_4$) films the short first plateau can be attributed to a relative high porosity of Ppy(3-nisa) films, whereas the shorter second plateau is connected with the low mobility of 3-nisa anions. This may be a reason why the large delamination of Ppy(3-nisa) in KCl solution was observed [87]. However it should be mentioned that 3-nisa as supporting electrolyte is up to now the only system where electrodeposition of pyrrole on zinc can take place without a special pretreatment.

The self-repairing ability of Ppy films doped with 3-nisa was also tested. A fresh film Ppy(3-nisa)/Zn with a small defect (0.04 mm$^2$) was used for OCP-time measurements (Figure 5.51). The defect causes a fast decay of the OCP. A stable condition is reached at -0.65 V (vs. SCE) for nearly 1 hour. Again fluctuations of the OCP are observed explained by the passivation/re-passivation process in the defect.
3-nisa is a prospective compound for the formation of adherent and homogenous Ppy films on zinc in a one-step process. The thin protective layer formed inhibits the dissolution of Zn and facilitates the electropolymerisation of pyrrole. No special pretreatment for Zn before polymerisation is necessary. Protective efficiency is up to 98% when compared to bare Zn.
5.6. Application of core-shell particles in corrosion protection

By chemical oxidation Ppy was formed on nano size inorganic particles (BaSO₄, SiO₂). The final product is called core-shell particle consisting of inorganic core and a Ppy shell. The particles with an oxidised shell containing corrosion inhibiting anion were tested as additives to polymer coatings.

5.6.1. Materials and preparation of core-shell particles

Pyrrole was distilled in vacuum. Inorganic particles were supplied by CHEMETALL (BaSO₄ d< 100 nm; SiO₂ d=10-20 nm). Fe²⁺/H₂O₂ was used as oxidant. The inhibitor anions MoO₄²⁻, TiF₆²⁻, ZrF₆²⁻ and 3-nisa were tested.

In a typical procedure, 0.1 mg ml⁻¹ inorganic particle, 0.5 M pyrrole monomer and 0.5 M dopant anions were mixed in aqueous solution and stirred vigorously for 30 minutes. Then 5.10⁻⁴ M Fe²⁺/H₂O₂ oxidant was added. The polymerisation took place immediately. The solution colour changed to dark green. The stirring was continued for 1 hour to make sure that the polymerisation was finished. The final product was obtained after filtration, drying and grinding.

The core-shell particles were mixed with a so-called matrix polymer. The mixture was applied as a primer on mild steel and galvanised steel. The corrosion protection of these primers was evaluated by EIS. The investigated matrix polymers were PC4601 (pH=8.5), XK68 (pH=4.2) and Worleecryl (pH=5.5).

5.6.2. Corrosion test with EIS

5.6.2.1. Experimental

EIS experiments were carried out in a 3-electrode cell. Pt gauze was used as counter electrode, SCE as reference electrode. The substrate (4 cm x 4 cm) with the coated primer layer was the working electrode. The samples were immersed in 0.1 M KNO₃ (active area 0.94 cm²) and EIS spectra were measured every 10 minutes for 1 hour. Three regions of the EIS spectra can be distinguished:

+ **High frequency range** (50 KHz - 1 KHz) representing the dielectric behaviour of polymer film.
+ **Middle frequency** range (1 KHz - 10 Hz) characteristic for the resistance of the polymer film.
+ **Low frequency** range (<10 Hz) representing the interface polymer film/metal substrate.
The equivalent circuit shown in Figure 4.4 on page 38 was used to simulate all the EIS spectra.

5.6.2.2. Results

The obtained EIS spectra on different samples can be classified in three groups:

*Group 1: matrix polymer without additives

The typical EIS behaviour on mild steel and galvanised steel during immersion in 0.1 M KNO₃ is presented in Figure 5.52.

![EIS spectra of matrix polymer without additives](image)

Figure 5.52: EIS spectra of matrix polymer without additives in 0.1 M KNO₃

The high frequency range (50 KHz - 1 KHz) of the EIS spectra is related to the dielectric behaviour of the polymer film. The increase of polymer capacitance $C_{PM}$ during immersion time indicates that the polymer matrix is not dense enough to prevent the diffusion of water into the polymer film. The incorporation of water is causing the decrease of the polymer resistance $R_{PM}$ in the middle frequency range (1 KHz-10 Hz) in 1 hour of immersion. The presence of electrolyte at the interface is causing the corrosion. The increase of $C_{OX}$ corresponds precisely to this process as shown in the low frequency (< 10Hz) of the EIS spectra.

PC4601, XK68 and Worleecryl, without additives did not inhibit the corrosion of mild steel and galvanised steel.
*Group 2: matrix polymer with additives

Core-shell particles with different dopant anions were used as additives in three matrix polymer films. The influence of core-shell particle additives on the corrosion is shown in Figure 5.53.

Figure 5.53: EIS spectra of matrix polymer + additives in 0.1 M KNO$_3$ solution

Contrary to the case of matrix polymer films without additives, the film with additives has an inhibiting influence on corrosion. After one-hour of immersion, the capacitance values of $C_{PM}$ and $C_{OX}$ remain constant. The diffusion of water into the film is hindered, $C_{PM}$ does not change. $C_{OX}$ representing the interface polymer/substrate is also constant. No corrosion occurred.

The resistance of the polymer $R_{PM}$ increases with time. An explanation for this phenomenon is that Ppy is reduced to produce anions acting as inhibitors of corrosion. Despite the high pH of the matrix polymer, the Ppy film is still active. The results are listed in Table 5.1.

Table 5.1: Matrix polymer+core shell particles with protective effects

<table>
<thead>
<tr>
<th>Matrix polymer</th>
<th>Core</th>
<th>Inhibitor anion</th>
<th>% by weight</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC4601</td>
<td>BaSO$_4$</td>
<td>TiF$_6^{2-}$, ZrF$_6^{2-}$</td>
<td>20</td>
<td>Mild steel</td>
</tr>
<tr>
<td>PC4601</td>
<td>BaSO$_4$</td>
<td>TiF$_6^{2-}$, ZrF$_6^{2-}$</td>
<td>20</td>
<td>Galvanised steel</td>
</tr>
<tr>
<td>Worleecriyl</td>
<td>SiO$_2$</td>
<td>3-nisa</td>
<td>20</td>
<td>Galvanised steel</td>
</tr>
</tbody>
</table>
*Group 3: core-shell particles with no corrosion inhibition

The typical EIS spectra of this group are shown in Figure 5.54. The corrosion occurred after coating the metal surface with the matrix polymer. The corrosion products were visible on the surface.

In KNO$_3$ medium, the resistance of polymer $R_{PM}$ is small and decreases dramatically with time. The capacitance of the interface polymer/substrate increases significantly due to corrosion. On the other hand, the charge transfer resistance is small during the immersion. The corrosion reaction is not inhibited. The results are shown in Table 5.2.

![EIS behaviour of core-shell particle matrix polymer without protective action](image)

Table 5.2

<table>
<thead>
<tr>
<th>Matrix polymer</th>
<th>Core</th>
<th>Inhibitor anion</th>
<th>% by weight</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC4601</td>
<td>SiO$_2$</td>
<td>TiF$_6^{2-}$, ZrF$_6^{2-}$</td>
<td>20-40</td>
<td>Galvanised steel</td>
</tr>
<tr>
<td>XK68</td>
<td>SiO$_2$, BaSO$_4$</td>
<td>MoO$_4^{2-}$, TiF$_6^{2-}$, ZrF$_6^{2-}$, 3Nisa</td>
<td>20-40</td>
<td>Galvanised steel</td>
</tr>
<tr>
<td>Worleecryl</td>
<td>SiO$_2$, BaSO$_4$</td>
<td>MoO$_4^{2-}$, TiF$_6^{2-}$, ZrF$_6^{2-}$, 3Nisa</td>
<td>20, 40</td>
<td>Mild steel</td>
</tr>
</tbody>
</table>

Figure 5.54: EIS behaviour of core-shell particle matrix polymer without protective action
Conclusions:
* Using the matrix polymer without core shell particles no corrosion protection is found.
* Matrix polymer with core shell particles doped with anions TiF$_6^{2-}$, ZrF$_6^{2-}$ inhibits the corrosion of mild steel. 3-nisa was a positive effect on galvanised steel.
* Surprisingly the inhibitive effect of inhibitor anion MoO$_4^{2-}$ is very small, may be the mobility of MoO$_4^{2-}$ is too low.
6. Proposed mechanism of corrosion protection by Ppy

Ppy film doped with inhibitor anions such as molybdate were synthesised on mild steel in a 1-step process. Corrosion tests indicated a significant improvement of the protective performance of Ppy film. Ppy coatings even prevented corrosion in defect of the coating. Now the corrosion protection mechanism of Ppy with small defect on mild steel will be discussed. A defect on Ppy coating deposited on mild steel substrate may be produced either because of manufacturing or due to damage. When this occurs, bare mild steel is exposed to the corrosive atmosphere. The oxidation of substrate occurs. The following corrosion or anodic reaction takes place at the bottom of the defect:

\[
\text{Fe} = \text{Fe}^{2+} + 2e^- \quad (1)
\]

The open circuit potential of the coated sample drops down to the corrosion potential of iron if the sample is immersed in NaCl (Figure 5.25, page 69).

The electrons produced in (1) are consumed in cathodic reactions as followed:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \quad (2)
\]

\[
\text{Ppy}_{\text{OX}}(\text{DOP}) + ne = \text{Ppy}_{\text{RED}} + \text{DOP}^{n-} \quad (3)
\]

Where \(\text{Ppy}_{\text{OX}}, \text{Ppy}_{\text{RED}}\) are the oxidised and reduced states of polypyrrole, respectively. \(\text{DOP}^{n-}\) is a dopant anion.

The Ppy film is reduced (reaction 3) as a result of the galvanically coupling to metal substrate. Reaction (2) takes place within the defect as well as on Ppy film if Ppy is conductive and can mediate the electron transfer [95, 96].

The dopant anions \(\text{DOP}^{n-}\) form insoluble salts or complexes \([\text{Fe}_x\text{O}_y(\text{DOP})_z]\) with iron ions and can prevent further corrosion. In other words, the defect is repaired by the inhibitor anions produced during the reduction of Ppy film. The second plateau in OCP-time curve (Figure 5.25, page 69) and the fluctuation of OCP (Figure 5.28, page 72) reflect the possibility of self-repairing of Ppy film.
Based on the model of Kinlen [97], the proposed mechanism of corrosion protection of Ppy is developed as in the following figure. However, from the results of the OCP and EIS measurement re-oxidation of conducting polymer by oxygen could not be found.
7. Conclusions

Inhibitors used as dopant anions in polymer films are responsible for the anticorrosion behaviour of Ppy. The Ppy film can work as self-repairing for small defects of the film.

* Ppy film doped with MoO$_4^{2-}$ and TiF$_6^{2-}$ showed the role of anions in corrosion protection of iron. Ppy doped with 3-nitro salicylate was used for zinc protection. The films were formed on inert electrodes (gold/glass or Pt), on mild steel and zinc electrodes in acid aqueous solutions.

* Ppy(MoO$_4$):

Molybdate was built-in into the film as dopant anion. The results of XPS revealed that molybdate exist in two types: [MoO$_4$]$^{2-}$ (62%) and [Mo$_7$O$_{24}$]$^{6-}$ (28%). The film was conductive, homogenous, and compact. Cyclic voltammograms have shown that the film was active. By scanning the potential, the Ppy film changed from the oxidised to the reduced state and at the same time the anions were released from the polymer. To support this observation, Electrochemical Impedance Spectroscopy (EIS), Electrochemical Quartz Crystal Microbalance (EQCM) and Raman Spectroscopy were used. EIS has indicated the change of the resistance $R_{PM}$ and the capacitance $C_{PM}$ of the Ppy film during reduction. EQCM has shown: the mass of the Ppy film decreased in the cathodic region and increased in the anodic region. The anion flux was also observed in Scanning Kelvinprobe (SKP) and X-ray Photoelectron Spectroscopy (XPS) experiments. The release of anion is one of the important factors of the corrosion protection property of the Ppy film. However, the release behaviour of molybdate anions depends much on the size of cations in the electrolyte. At negative potentials, the incorporation of cations is predominant. Probably, molybdate is a medium size anion and not mobile enough to compete with the cations in the electrolyte for the moving in or out of the Ppy film.

It should be also noted that Ppy(MoO$_4$) can be electrodeposited on mild steel in a one-step process. No induction period was observed during polymerisation. Ppy(MoO$_4$) shifted the corrosion potential of mild steel into the passive range. The corrosion current decreased simultaneously. The role of molybdate in corrosion protection was also investigated for Ppy films with small defects. The Open Circuit Potential (OCP) showed the fluctuations around -0.2 V (vs. SCE). It means that the defect was passivated / repassivated continuously for 4 hours. It was assumed that molybdate was released from Ppy, move to the defect and act as corrosion inhibitor by forming a complex with iron ion.
Conclusions

* The role of TiF$_6^{2-}$ anions in Ppy films was also investigated. TiF$_6^{2-}$ anions has shown good inhibitor properties. The release of TiF$_6^{2-}$ anions from the film is independent on the size of cations in the electrolyte. This is reflected by the small difference of film capacitance $C_{PM}$ when the film was reduced in small and large cation solution. The delamination of the Ppy film was clearly slowed down also in the presence of small cations as compared to Ppy doped with molybdate. However, the mechanism of this action is not yet known.

* While many inhibitor anions are known for mild steel or iron, only a few are known for zinc or galvanised steel. 3-nitro salicylate (3-nisa) was used as inhibitor dopant for zinc in this work. Ppy film could be formed on Zn without any special pretreatment. The dissolution of Zn decreased dramatically in the presence of 3-nisa.

* The application of Ppy/metal inorganic composites in corrosion protection for mild steel and galvanised steel was also investigated in this work. Nano inorganic particles served as core covered with Ppy doped with inhibitor anions as shell. Mixture of core-shell particles with a polymer was used as primer coatings. The positive effect on the corrosion protection of the coating was illustrated by the increase of the coating resistance and the stabilisation of the film capacitance during immersion in corrosive medium.

* Based on the results presented in this PhD thesis, additional studies may be useful to improve the possibility of application of core-shell particles on corrosion protection. The conditions of chemical polymerisation such as pH, concentrations etc. may be further optimised in order to obtain better properties of composites. The compatibility of core-shell particles with polymer should be investigated so far.
8. References

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Dresden, den 25.07.2005

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