Nanocomposite Coatings for Corrosion Protection

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Abstract

This thesis describes technical and scientific aspects of new types of composite films/coatings for corrosion protection of carbon steel, composite films with nanometer thickness consisting of mussel adhesive protein (Mefp-1) and ceria nanoparticles, and polymeric composite coatings with micrometre thickness consisting of conducting polymer and ceria nanoparticles in a UV-curing polyester acrylate (PEA) resin.

The influence of microstructure on corrosion behaviour was studied for a Fe-Cr-V-N alloy containing micro-sized nitrides with different chemical composition spread in martensitic alloy matrix. The Volta potential mapping suggested higher relative nobility for the nitride particles than the alloy matrix, and the nitrides with higher amounts of nitrogen and vanadium exhibited higher nobility. Potentiodynamic polarization measurements in a 0.1 M NaCl solution at neutral pH and ambient temperature showed passivity breakdown with initiation of localized corrosion which started in the boundary region surrounding the nitride particles, especially the ones enriched in Cr and Mo.

Mefp-1/ceria nanocomposite films were formed on silica and metal substrates by layer-by-layer immersion deposition. The film formation process was studied in situ using a Quartz Crystal Microbalance with Dissipation (QCM-D). The film grows linearly with increasing number of immersions. Increasing Mefp-1 concentration or using Mefp-1 with larger size leads to more Mefp-1 being deposited. Peak Force Quantitative Nanomechanical Mapping (Peak Force QNM) of the composite films in air indicated that the elastic modulus of the film increased when the film deposited had a higher Mefp-1 concentration. It was also noted that the nature of the outermost layer can affect bulk morphology and surface mechanical properties of the film.

The QCM-D study of Mefp-1 on an iron substrate showed that Mefp-1 adsorsbs at a high rate and changes its conformation with increasing
adsorption time. The QCM-D and in situ Peak Force QNM measurements showed that the addition of Fe$^{3+}$ ions causes a transition in the single Mefp-1 layer from an extended and soft layer to a denser and stiffer layer. In situ ATR-FTIR and Confocal Raman Microscopy (CRM) analyses revealed complex formation between Fe$^{3+}$ and catechol groups in Mefp-1. Moreover, optical microscopy, SEM and AFM characterization of the Mefp-1/ceria composite film formed on carbon steel showed micron-size aggregates rich in Mefp-1 and ceria, and a nanostructure of well dispersed ceria particles in the film. The CRM analysis confirmed the presence of Mefp-1/Fe complexes in the film. Electrochemical impedance microscopy and potentiodynamic polarization measurements showed that the Mefp-1/ceria composite film can provide corrosion protection for carbon steel, and that the protection efficiency increases with exposure time.

Composite coatings of 10 μm thickness composed of a UV-curing PEA resin and a small amount of conductive polymer and ceria nanoparticles were coated on carbon steel. The conductive polymer (PAni) was synthesized with phosphoric acid (PA) as the dopant by chemical oxidative polymerization. The ATR-FTIR and SEM analyses confirmed that the added particles were well dispersed in the coatings. Electrochemical measurements during long exposure in 0.1 M NaCl solution, including open circuit potential (OCP) and EIS, were performed to investigate the protective performance of the coatings. The results showed that adding ceria nanoparticles can improve the barrier properties of the coating, and adding PAni-PA can lead to active protection of the coating. Adding PAni-PA and ceria nanoparticles simultaneously in the coating can improve the protection and stability of the composite coating, providing excellent corrosion protection for carbon steel.

**Key words:** corrosion protection, nanocomposite, coating, tool alloy, layer-by-layer, polarization, passivity, nanomechanical, topography, Mefp-1, ceria nanoparticle, PAni, UV-cure, AFM, Peak Force QNM, EIS, SEM, CRM, QCM-D, ATR-FTIR.
List of Papers

**Paper I** - Microstructure Influence on Corrosion Behaviour of a Fe-Cr-V-N Tool Alloy Studied by SEM/EDS, Scanning Kelvin Force Microscopy and Electrochemical Measurements
Majid Sababi, Sebastian Ejnermark, Jörgen Andersson, Per M. Claesson, Jinshan Pan.

**Paper II** - Structural and Nanomechanical Properties of Paperboard Coatings Studied by Peak Force Tapping Atomic Force Microscopy
Majid Sababi, John Kettle, Hille Rautkoski, Per M. Claesson, Esben Thormann.

**Paper III** - Nanostructured Composite Layers of Mussel Adhesive Protein and Ceria Nanoparticles
Olga Krivosheeva, Majid Sababi, Andra Dedinaite, Per M. Claesson.

**Paper IV** - In situ Investigations of Fe$^{3+}$ Induced Complexation of Adsorbed Mefp-1 Protein Film on Iron Substrate
Fan Zhang, Majid Sababi, Tore Brinck, Dan Persson, Jinshan Pan, Per M. Claesson.

**Paper V** - Thin Composite Films of Mussel Adhesive Proteins and Ceria Nanoparticles on Carbon Steel for Corrosion Protection
Majid Sababi, Fan Zhang, Olga Krivosheeva, Mattias Forslund, Jinshan Pan, Per M. Claesson, Andra Dedinaite.

**Paper VI** - The Influences of Conducting Polymer and Ceria Nanoparticles Additives on Corrosion Resistance Behavior of UV-cure Coatings
Majid Sababi, Jinshan Pan, Per-Erik Augustsson, Per-Erik Sundell, Per M. Claesson.
Submitted.
The author’s contribution to the papers

Paper I. Part of the experimental work, all AFM and polarization experiments, and major part of planning, evaluation, and writing of the first version.

Paper II. All the experiments and major part of planning, evaluation, and writing of the first version.

Paper III. Part of the experimental work, all AFM experiments, part of planning, evaluation, and writing.

Paper IV. Part of the experimental work, all AFM experiments, part of planning, evaluation, and writing.

Paper V. Part of the experimental work, all EIS and polarization experiments, part of planning, evaluation, and writing.

Paper VI. Part of the experimental work, all EIS and ATR-FTIR experiments, and major part of planning, evaluation, and writing of the first version.
Summary of Papers

In Paper I, corrosion behaviour of a new nitrogen-based tool alloy (Fe-Cr-V-N) was studied and compared with traditional carbon-based tool alloys. The focus was to find a correlation between composite structure and localized corrosion of the alloy. For this purpose, a new mode of scanning Kelvin force microscopy (KFM) was used in combination with other microscopic methods like SEM/EDS as well as electrochemical methods.

In Paper II, nanomechanical properties of composite coatings which have ideal composite structure (paperboard coatings) have been studied with a new Atomic Force Microscopy (AFM) method known as Peak Force QNM. The aim of this work was to use this technique to analyse nanomechanical properties of a well-defined composite coating. This technique was later used to analyse the Mefp-1/ceria nanocomposite coatings and understand the effect of different factors on mechanical properties.

The main aim in Paper III was to investigate the structure of nanocomposite coatings of mussel adhesive protein (Mefp-1) and ceria nanoparticles. The layer-by-layer formation of Mefp-1/ceria nanocomposite was studied on a model silica surface with a quartz crystal microbalance with dissipation (QCM-D). The effect of different factors like protein concentration and number of layers, adsorbed mass and thickness of the surface layer was studied. Peak Force QNM was used to analyse the nanomechanical properties of these composite coatings and effects of the different factors on the physical and mechanical properties of the coatings. A combination of controlled contact mode AFM and tapping mode AFM was used to measure scratch resistance properties of these nanocomposite coatings.
The main purpose of developing the *Mefp-1/ceria* nanocomposite film coating was to produce a thin film coating for corrosion protection of mild carbon steel. Thus, it was important to understand how the nanocomposite coating can be formed on the mild carbon steel surface. The interaction of *Mefp-1* with model iron surfaces was studied in detail in **Paper IV**. The effect of the Fe$^{3+}$ ion on complexation and properties of the layer were studied *in situ* with QCM-D and Peak Force QNM. Also, spectroscopic methods like ATR-FTIR and Confocal Raman Microspectroscopy (CRM) were used to monitor chemical structure changes in the protein film due to interaction with the iron surface.

In **Paper V**, layer-by-layer formation of *Mefp-1/ceria* nanocomposite coatings was investigated on stainless steel model surfaces in order to compare composite formation on more representative metal surfaces. The *Mefp-1/ceria* nanocomposite formed on mild carbon steel was studied with AFM, SEM and CRM. Afterward, the corrosion performance of the coated mild carbon steel was compared with uncoated mild carbon steel as a reference and with *Mefp-1* as an inhibitor using electrochemical impedance spectroscopy (EIS) and polarization techniques.

The protective ability of a UV-cure polyester acrylate coating (PEA) for mild carbon steel was studied in **Paper VI**. Different additives like conducting polymer and ceria nanoparticles were added to a PEA coating to create a composite coating with the aim of improving the corrosion protection for mild carbon steel. The composite structure and chemical composition of the coatings were investigated with SEM and spectroscopic methods. The EIS method was used to study corrosion performance of the coatings as function of time and to understand the protection mechanisms of the coating.
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1 Introduction

1.1 Metal corrosion

Normally, in order to use metals as an engineering material they need to be extracted from nature with expenditure of energy. Therefore metals are not thermodynamically stable in the open environment and tend to return to their lower Gibbs free energy forms as oxides, hydroxide, etc. All of the chemical and electrochemical reactions by which metals go back to their lower Gibbs free energy states are known as corrosion. Electrochemical reactions are a major part of the corrosion phenomena, where in electrons pass between two half cell reactions. In one of the half cell reactions known as anodic or metal oxidation reactions, electrons are produced [1, 2]:

\[ M^0 \rightarrow M^{n+} + ne^- \]  \hspace{1cm} (1)

where \( M \) represents metal. In the other half cell reaction, known as cathodic or reduction reaction, electrons are consumed. Cathodic reactions depend on pH and availability of different components. The most common cathodic reactions are hydrogen and oxygen reduction under acidic conditions:

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm} (3)

and in neutral or alkaline environments are water or oxygen reduction reactions [1, 2]:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \hspace{1cm} (4)

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  \hspace{1cm} (5)
In general, corrosion is a slow and steady process which destroys metallic structures and causes enormous direct and indirect cost for our society. A partial study of corrosion cost in Sweden by Trädgåidh in 1964 showed costs to be 300-400 million kronor per year. Nowadays in developed countries, the total corrosion cost is 1-4 percents of GDP. Therefore it is important to protect metals from corrosion [3, 4].

1.2 Corrosion protection

It is possible to reduce or stop corrosion by using any means which can decrease or inhibit anodic or cathodic reactions or eliminate the conductive pathway between anodic and cathodic sites. There are lots of practical ways to reduce the corrosion rate for metallic structures. One way is by using more noble materials, e.g. stainless steels instead of mild carbon steel which can naturally create a protective layer (passive layer) on the surface [5-7]. But using noble materials is not always the solution for reasons such as price and processing challenges. Using coatings is another way to control corrosion. Protective coatings can be composed of different materials and act as an artificial protective layer on the metal surface in order slow down anodic and cathodic reactions [8-11].

*Mefp-1/ceria* nanocomposite coatings are very thin but can effectively protect mild carbon steel from corrosion. The other types of coatings are organic coatings. In general, these types of coatings impede corrosion by acting as a barrier between the corrosive environment and the metal surface. The barrier coatings should be highly impermeable to components which initiate corrosion like water, oxygen and aggressive ions. The protective ability of these coatings can increase by adding fillers to the polymer matrix. Other type of additives function as corrosion inhibiting components which provide protection to the underlying surface after the corrosion process has begun at inherent defects. Conducting polymer is one such component. It is combined with ceria nanoparticles as
a composite polymer coating for protection of mild carbon steel. The main aim of these nanocomposites and polymeric composite coatings is to find an environmental friendly replacement for traditionally hexavalent chromium used in traditional coatings which are known to be harmful to humans and the environment and is banned in a range of industries [12].

1.3  Mussel adhesive protein (Mefp-1)

The blue mussels are known for their incredible ability to attach to a wide range of surfaces such as rock, metal, and wood in a marine environment with both wet and turbulent conditions. No synthetic glue functions well under such conditions. The blue mussel uses a complex organic structure known as byssus, which consists of a stem thread and a plaque. Figure 1 shows schematically the structure of the mussel thread and the way the blue mussel attaches to a surface.

Figure 1. A blue mussel attaching itself to a surface by means of byssus (left), and a schematic illustration of different Mefps distribution in the mussel thread and plaque (right).

Because of this extraordinary property of blue mussels, there has been a lot of studies performed on the structure and chemical composition of the mussel foot. The studies show the mussel foot is mainly composed of collagen and five different proteins, which are named and classified as Mytilus Edulis Foot Proteins (Mefp). Figure 1-right shows the distribution of these five types of Mefp in mussel thread and plaque. Mefp-1 is found
in the coating and functions as a film forming protein; *Mefp*-2 and *Mefp*-4 are in the body of the plaque in the form of a solid foam and *Mefp*-3 and *Mefp*-5 function as adhesive primers between the plaque and the surface [13-15]. These proteins contain different functional groups but all of them contain a post-translational amino acid, 3,4-dihydroxyphenylalanine (DOPA), which is believed to be responsible for adhesion and cohesion via hydrogen bonding, covalent bonding, metal-ligand interaction and cross-linking. Figure 2 shows one of the primary units of *Mefp*-1. The molecular weight of *Mefp*-1 is 110 kDa with 75-85 repeating units and DOPA content of 10-15 mol%. The isoelectric point of *Mefp*-1 is 10.4 due to a lysine content that is around 21 mol% [16].

![Chemical structure of decameric repeating unit of Mefp-1](image)

**Figure 2.** The chemical structure of decameric repeating unit of *Mefp*-1.

### 1.4 Ceria nanoparticles

In recent decades, nanoparticles have been widely studied because of their unique properties and different applications. The surface to mass ratio increases significantly when particle size is reduced to a few nanometers, and radically different properties are created relative to bulk materials [17-19]. Cerium is a rare earth metal and cerium oxide has a lot of applications. It is a semiconductor and can be used as a catalyst, it has high hardness and is used as a polishing material, its ability to store oxygen is used in fuel cells, and its high refractive index and UV absorption ability makes it popular for use as a filler for composite coatings [20-22].
Moreover, cerium salts show a good inhibition effect for metals, especially aluminum alloys. They can slow down cathodic and anodic reactions and improve corrosion resistance for cerium base conversion coatings [23-25]. Also, regardless of other beneficial properties, ceria is not photocatalytically active which means absorption of UV light does not cause free radical production. This is not the case for traditional UV absorbers like titanium oxide and zinc oxide. Moreover, it is reported that ceria nanoparticles are not cytotoxic but instead benefit cells from oxidation insult in contrast to zinc oxide or titanium oxide [26]. All of these properties are motivations to use ceria nanoparticles for improving the physical and mechanical properties of composite coatings. The fact that ceria nanoparticles can prevent degradation of organic molecules such as polymers and proteins also makes it an environmental friendly component.

1.5 Conducting polymers

Conducting polymers or intrinsic conducting polymers (ICPs) were first discovered by MacDiarmid and Heeger at Pennsylvania University in 1977. They showed these polymers have an extended \( \pi \)-conjugated system along their backbones and their conductivity can be controlled from an insulating state to the metallic state by doping with iodine. They won the Nobel Prize in 2000 for this work [27-29]. A lot of investigations have been performed on conducting polymers from the chemistry, physics and material science perspectives. There are several polymers that can be categorized as conducting polymers like polyaniline, polypyrrole, polyacetylene, and polythiophene. Polyaniline which is known as PANi was first prepared in 1862 [30], and developed more than other conducting polymers because of its stability under normal conditions. PANi is a phenylene based polymer with \(-\text{NH}-\) group linked between phenylene rings. In general, polyaniline can be formulated as \([(-B-\text{NH}-B-\text{NH}-)_y(-B-N=Q=N-)_{1-y})_x\] in which B and Q are regarded as benzenoid and quinoid
groups, respectively. As shown in Figure 3, PANi can be in three different oxidation states: leucoemeraldine base which is the fully reduced form \((y=1)\), emeraldine base which is the partially oxidized form \((y=0.5)\), and pernigraniline which is the fully oxidized form \((y=0)\). The leucoemeraldine and pernigraniline bases have very poor conductivity but the emeraldine base has moderate conductivity and its conductivity can be modified by doping and the forming of emeraldine salts. There are many ways to dope polyaniline. One practical and easy way is to use protonic acids to create positive charge carriers. As shown in Figure 4, protonation of imine groups results in radical cations with delocalized \(\pi\)-conjugated bonds which are responsible for the conductivity [31, 32].

![Chemical structures of different oxidation states of polyaniline.](image)

Figure 3. Chemical structures of different oxidation states of polyaniline.
Figure 4. Doping and dedoping of emeraldine base to intermediate emeraldine salt.

Conducting polymers were used for corrosion protection purposes for the first time by MacDiarmid in 1985, and after that extensive work has been done to study corrosion inhibition on mild carbon steel by using different polyaniline and polypyrrole coatings [28, 29, 33-41]. Nevertheless, the corrosion protection mechanism of conducting polymer is not very well understood. One of the most suggested mechanisms is that conducting polymers have higher oxidation potentials than metals, and can react with metals and create a passive layer on the metal surface, which protects the metal by the barrier-like passive layer or changing the electrochemical potential of the metal to a level in the passive range [23-25]. This mechanism is similar to the way that hexavalent chromium-containing coatings protect the metal surface and therefore it is an attractive idea for replacing chromate used in the coatings, which are known to be harmful to people and the environment.
2 Materials and Methods

2.1 Materials

2.1.1 N-based tool alloy (Fe-Cr-V-N)

Fe-Cr-V-N is a nitrogen based tool alloy produced by powder metallurgy processing and was provided by Uddeholms AB, Sweden. The chemical composition of this material is given in Table 1. The amount of carbon is reduced and replaced with nitrogen to eliminate chromium carbide precipitation during heat treatment process as the latter can reduce corrosion resistance and mechanical properties dramatically. Nitrogen makes conditions favourable for producing alloys which contain nitride phases in the alloy matrix. The Fe-Cr-V-N alloy has extremely good corrosion resistance as well as high hardness (around 60 HRC) [42, 43].

Table 1. Chemical composition of the test materials (in wt%), Fe is the balance.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Cr-V-N</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>4.2</td>
<td>0.05</td>
<td>21.2</td>
<td>1.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>

2.1.2 Mussel adhesive protein (Mefp-1)

The mussel adhesive protein, Mefp-1, was supplied by Biopolymer AB, Gothenburg, Sweden. The extraction and purification was explained in details by Qvist [44]. The purity of the supplied Mefp-1 was from 92 to 97 wt%. Mefp-1 was supplied in a 1 wt% citric acid solution as a preservative and was stored at +5°C in the dark.

2.1.3 Ceria nanoparticles

The ceria nanoparticles, NANOBYK-3810, were supplied by BYK Additives and Instruments (Wesel, Germany). Ceria nanoparticles were
dispersed in water at a concentration of 180 mg mL\(^{-1}\) and the particle size was around 10 nm with a narrow size distribution according to the supplier and confirmed by dynamic light scattering measurement. Ceria nanoparticles were negatively charged, with Z-potential of -10 mV as measured with a Zetasizer Nano Instrument.

### 2.1.4 UV-cure polymer coating

Polyester acrylate (PEA), UV-cure base resin for primer coating applications was provided by Cytec for primer coating applications. This formulation was based on chlorinated polyester diluted with hexanediol diacrylate. The combination of three parts 1-hydroxy-cyclohexyl-phenylketone (Additol CPK, Cytec Surface Specialties) with two parts 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO-L, BASF) was used as a photo initiator to induce radical polymerization during exposure to UV light. The photo initiator was 5 wt% of the whole formulation. The 5 wt% of phosphorus-containing acidic methacrylate (Ebecryl 171, Cytec Surface Specialties) was used as adhesion promoter.

### 2.1.5 Conducting polymer (PAni-PA)

Conducting polymer, polyaniline, doped with phosphoric acid was synthesized by oxidation polymerization with a rapid mixing method. The synthesis method has been explained in detail elsewhere [45]. Briefly, aniline in the presence of phosphoric acid with molar ratio of 2:1 was polymerized with ammonium peroxodisulfate as oxidant. The reaction temperature was controlled with ice to be within the range of 0 to 5°C for around five hours. Changing colour from dark blue to dark green indicated polyaniline’s transition from a non-conductive state to a conductive state. The PAni-PA powders were washed and filtered with MilliQ water several times, and finally washed with ethanol to remove non-polymerized monomers. The powders were dried at room temperature in a desiccator. The aniline, phosphoric acid and ammonium peroxodisulfate were
purchased from Sigma-Aldrich with purity around 99%. Aniline was used without additional purification.

2.2 Methods

2.2.1 Kelvin probe force microscopy (KFM)

The Kelvin probe force microscopy [46] is a widely used method to study the electrical properties of metal surfaces and to map electric potential between a conductive tip and a metal surface [46-51]. The Kelvin probe measurement works based on Contact Potential Difference ($V_{CPD}$) which was first revealed by Sir William Thomson, better known as Lord Kelvin, in 1898 [52]. He discovered that plates of copper and zinc develop electrical charge when brought into close proximity and electrically connected. Then he explained that the potential difference created between surfaces of two dissimilar metals brought in close proximity while electrically connected is the result of the exchange of electrons from the metal with the higher Fermi level to the other metal, until they reach the same Fermi level and the two surfaces become equally and oppositely charged, like a charged capacitor. This phenomenon is shown in Figure 5-A and Figure 5-B. The contact potential value can be explained by the metal’s work function which is shown in equation (6). The work function of a metal is the minimum energy required to extract an electron from its Fermi level to free vacuum.

$$V_{CPD} = \frac{\Phi_2 - \Phi_1}{|e|}$$  \hspace{1cm} (6)

where $\Phi_1$ and $\Phi_2$ are the work functions for metal 1 and 2, respectively, and $e$ is the unit charge of an electron. It is possible to measure the $V_{CPD}$ potential by applying an external potential (which is called the backing potential) until surface charges disappear. At this point the external potential is equal to $V_{CPD}$, as shown in Figure 5-C. Different
Kelvin probe microscopies have been developed based on how to detect this charge-free state. The dual-pass lift up scan and single-pass scan are the two basic scanning modes developed for this purpose.

Figure 5. Electronic energy levels for two conducting specimens in which $\Phi_1$ and $\Phi_2$ are the respective work functions. (A) two specimens are separated, with distance $d$ with no electrical connection, (B) two samples are in electrical contact, and (C) external backing potential ($V_b$) has nullified the CPD potential ($V_{CPD}$). $E_{vac}$ is the vacuum level energy, and $E_{F1}$ and $E_{F2}$ are the respective Fermi level energies for the two conducting specimens.

In Kelvin probe force microscopy, a conductive tip acts as one of the metals, and the sample is another metal, as illustrated in Figure 5. Energy stored in a parallel capacitor is $U = \frac{1}{2} C \Delta V^2$, where $C$ is local capacitance between AFM tip and the sample, and $\Delta V$ is the voltage difference between the two surfaces. The force between tip and sample is the rate of energy change with separation $Z$:

$$F = -\frac{dU}{dZ} = -\frac{1}{2} \frac{dC}{dZ} \Delta V^2$$

(7)
The voltage difference, $\Delta V$, in the surface potential measurement consists of both DC and AC components: DC components like $V_{CPD}$ due to differences in work function, $V_{DC}$ (externally applied DC voltage) and an applied AC voltage $V_{AC}$ at a frequency $\omega$:

$$\Delta V = V_{DC} - V_{CPD} + V_{AC} \sin(\omega t)$$  \hspace{1cm} (8)

Combining equations (7) and (8):

$$F_{\omega} = \frac{1}{2} \frac{\partial C}{\partial Z} (V_{DC} - V_{CPD})^2 + \frac{1}{2} V_{AC}^2 + \frac{\partial C}{\partial Z} (V_{DC} - V_{CPD}) \sin(\omega t) + \frac{1}{4} \frac{\partial C}{\partial Z} V_{AC}^2 \cos(2\omega t)$$  \hspace{1cm} (9)

According to equation (9), the electric force applied to the tip consists of three different terms: $F_{DC}$ results in a static deflection of the tip, $F_{\omega}$ with frequency of $\omega$ is used to measure $V_{CPD}$, and $F_{2\omega}$ can be used for scanning capacitance microscopy (SCM) [53]:

$$F_{\omega} = \frac{\partial C}{\partial Z} (V_{DC} - V_{CPD}) V_{AC} \sin(\omega t)$$  \hspace{1cm} (10)

Equation (10) indicates that if the tip is driven with an applied DC voltage of $V_{DC}$ and an applied AC voltage of $V_{AC}$ with frequency of $\omega$, its oscillation will be affected by $V_{CPD}$. Then, $V_{CPD}$ can be measured by changing the applied DC potential until the point $F_{\omega}$ equals zero. Therefore, the surface contact potential difference can be acquired from equation (10) when $V_{DC} = V_{CPD}$.

In dual-pass lift-up Kelvin probe force microscopy (known as KPFM) the measurements are performed with two scans for each scan line. In the first scan the topographic information of the sample is recorded in the
normal Tapping Mode. Later, the tip is lifted up a defined distance (around 50 nm) and follows the topographic information which is recorded in the first scan in order to maintain the tip-sample distance constant during the second scan and oscillated at resonance frequency ($\omega_r$). A lock-in amplifier is used to extract the electrical force component ($F_{\omega r}$) with resonance frequency, $\omega = \omega_r$. The output signal of the lock-in amplifier is directly proportional to the difference between $V_{CPD}$ and $V_{DC}$ according to equation (10) and $V_{CPD}$ can be measured by applying $V_{DC}$ to the tip to nullifying the output signal of the lock-in amplifier, i.e., $F_{\omega r} = 0$. Consequently, the value of $V_{CPD}$ is measured for each point on the sample and the surface potential image of the whole area is produced. Figure 6 illustrates the dual scan mode operation principle [46, 47, 54].

![Diagram](image_url)

**Figure 6.** Dual scan mode for surface potential measurements (KPFM). The tip is oscillated with an AC bias voltage ($V_{AC}$) at resonance frequency ($\omega_r$), and the surface potential is measured by using a DC bias voltage.

In single-pass Kelvin probe force microscopy (known as KFM) the measurements are performed in one scan but at two very different
frequencies. By using a lock-in amplifier, the first resonance frequency $\omega_r$ of the cantilever is used for recording topography information in intermittent contact mode (Tapping Mode). Simultaneously, an AC bias voltage (3-5 V) is applied at a frequency ($\omega_e$, around 10 KHz) which is well below the resonance frequency of the cantilever. By using a second lock-in amplifier and an added DC voltage bias to nullify $F_{\omega_e}$ and measure $V_{CPD}$ for each point of the sample surface, the same way as for the dual-pass mode. Figure 7 illustrates the single scan mode operation principle [55, 56].

![Diagram of single-pass mode operation principle](image)

**Figure 7.** Single-pass mode surface potential measurements (KFM), by two excitation frequencies, first resonance frequency ($\omega_r$) of the cantilever for topography measurement and another frequency ($\omega_e$, around 10 KHz) for $V_{CPD}$ measurement.

The single-pass scan mode has advantages in comparison with the dual-pass scan mode. For instance, its resolution is expected to be higher because there is no lifting from the surface which can decrease lateral resolution, and it is faster because there is no need to scan twice to
acquire the topography and surface potential. The main criticism of the single-pass scan mode is possible cross talk between topography and surface potential data because they are collected along the same scan line.

2.2.2 Peak force QNM

Peak Force QNM is another atomic force microscopy technique which has been used in this work, known as Peak Force Quantitative Nanomechanical Mapping (Peak Force QNM) [57, 58]. This technique allows the measurement of physical and mechanical properties of the surface in the vertical direction with nanometre lateral resolution while simultaneously mapping topographical information. This makes it a suitable technique for studying the physical and mechanical properties of nanocomposite coatings.

Peak force tapping operates based on measuring and analysing force curves produced during each tip-sample interaction for every pixel in the mapped image. With a controlled applied force to the surface as feedback force it is possible to provide quantitative mapping of material surface properties [59, 60]. Briefly, the surface position is modulated by a sine wave with an amplitude of 150 nm and a frequency of 2 kHz. During each period of oscillation, the surface is moved into contact with the AFM tip and the feedback electronics adjust the average surface position such that the maximum cantilever deflection (the peak force) equals a predetermined set point value. By calibration of the optical lever sensitivity [61] and the cantilever spring constant [62, 63], the information about cantilever deflection and piezo position can be converted into a force vs distance curve, as shown in Figure 8. It is then possible to extract information like surface deformation at different tip-sample separations, at the peak force and at a given percentage of the peak force. Adhesion is determined by the difference between the zero force and minimum force during retraction. Energy dissipation (energy dissipated during tip-sample
interaction) can be calculated from the area between force curves during approach and retraction. In addition, the elastic modulus of the sample can be determined by fitting the linear part of the retraction force curve using the Derjaguin-Muller-Toporov (DMT) model:

\[
F = \frac{4}{3} E^* \sqrt{Rd^3} + F_{\text{adh}}
\]

(11)

where, \( F \) is the force, \( E^* \) is the effective elastic modulus, \( R \) is the tip radius, \( d \) is the deformation value for a given force, and \( F_{\text{adh}} \) is the maximum adhesion force between AFM tip and sample. The effective elastic modulus in equation (11) is related to the sample elastic modulus, \( E_s \):

\[
\frac{1}{E^*} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_t^2}{E_t}
\]

(12)

where \( \nu_s \) and \( E_s \) are the Poisson’s ratio and Young’s modulus of the sample and \( \nu_t \) and \( E_t \) are the Poisson’s ratio and Young’s modulus of the tip. Normally, the elastic modulus of the tip is selected to be much higher than the elastic modulus of the sample to be able to neglect the second term on the right-hand side of equation (12). Then the elastic modulus of the sample is directly related to the effective elastic modulus. In this method and according to equation (11) we have to determine the tip radius. The tip radius is measured with an indirect method, where the radius was adjusted to achieve the correct value of a sample with known elastic modulus (polystyrene, \( E = 2.7 \) GPa).
Figure 8. Schematic illustration of a force-separation curve generated during one cycle in Peak Force QNM. At position (A) the tip is out of contact and no force is detected. At position (B) the tip is dragged into contact by an attractive force. At position (C) the sample is deformed by a positive applied load. At position (D) the tip and sample are held together at negative load by adhesion. At position (E) the tip is again brought out of contact and the cycle is completed. Sample deformation, tip-sample adhesion, energy dissipation, and elastic modulus are determined from the force-separation curve.

2.2.3 *Quartz crystal microbalance with dissipation (QCM-D)*

The Quartz Crystal Microbalance with Dissipation (QCM-D) is a highly sensitive balance which can measure real-time mass change per unit area with better than ng cm\(^{-2}\) resolution by measuring the change in frequency of a quartz crystal resonator. Also, it can provide information about structural or viscoelastic properties of the layer, such as if an added mass...
has a rigid or soft structure via the dissipation parameter \( D \). Dissipation is measured when the oscillating driving voltage to the crystal is turned off and the energy from the oscillating crystal is dissipated. \( D \) is defined as:

\[
D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}} \tag{13}
\]

where \( E_{\text{lost}} \) is energy lost during one oscillation cycle and \( E_{\text{stored}} \) is the total energy stored in the oscillator. QCM-D is a suitable instrument to study, for instance, in situ formation of the \( \text{Mepf-1/ceria} \) nanocomposite and how adjustment of different parameters can change the properties of the layer.

Detailed information about QCM-D operation is provided by Rodahl et al. [64]. Briefly, applying a voltage to the quartz crystal causes it to oscillate at its resonance frequency. Changes in mass on the quartz surface leads to changes in the resonance frequency of the crystal which can be related through physical models like the Sauerbrey relationship:

\[
\Delta m = -C \frac{\Delta f_n}{n} \tag{14}
\]

In this equation, the mass change \( \Delta m \) is directly related to the frequency change \( \Delta f_n \) of the quartz crystal at the \( n \)th overtone. The overtone (harmonic) order has the value 1, 3, 5 .... \( C \) is the mass sensitivity constant and depends on the physical properties of the quartz crystal which in our case was 0.177 mg m\(^{-2}\) Hz\(^{-1}\). If the added mass follows equation (14) then normalization of frequency change at all of the overtones should lead to a constant value. Normally this condition is valid for added mass with high rigidity which does not change the dissipation value of the quartz crystal (\( \Delta D \approx 0 \)). On the other hand, for soft layers (\( \Delta D >> 0 \)), the Sauerbrey equation does not fit the data very well and underestimates the mass change due to the added layer because the
frequency change not only depends on the mass but also on the mechanical properties of the film (including shear modulus and viscosity). In this case the change in energy dissipation is a key factor for characterizing the surface film [65, 66]. One viscoelastic model describing properties of these types of layers is explained in detail by Voinova [67]. In this model the layer is characterized by an elastic spring constant and a viscous dashpot connected in parallel (Voight element). The added layer is characterized by a frequency-dependent complex shear modulus:

\[ G = G' + iG'' = \mu + i2\pi f\eta \]  

(15)

where \( G' \) and \( G'' \) describe energy storage and energy dissipation, respectively. \( \mu \) is the elastic shear (storage) modulus, \( f \) is the oscillation frequency and \( \eta \) is the shear viscosity (loss modulus).

2.2.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance microscopy (EIS) is an electrochemical technique which has been widely used to study real time corrosion resistance or protection efficiency of coatings for underlying materials [68, 69]. EIS does not cause damage of the sample in comparison to other electrochemical techniques like potentiodynamic polarization; therefore it can be used in situ for long term evaluations [70, 71].

As shown in Figure 9, EIS usually works by applying an AC potential to the sample via a reference electrode, and then measuring the current passing through the sample and a counter electrode. A potentionstat is used for applying the potential and collecting the current, the impedance calculation is done with a Frequency Response Analyzer (FRA), and the procedure is controlled by software in a computer.
Figure 9. Setup for Electrochemical Impedance Spectroscopy (EIS) measurements.

A spectrum is generated by sweeping the AC potential frequency and measuring impedance over a wide frequency change. Also, the perturbation AC potential amplitude is kept small to restrict the system to the linear regime, which means that the applied potential should not cause irreversible change of the sample condition. In the linear regime, the current response to a sinusoidal potential is a sinusoid with the same frequency but shifted in phase as shown in Figure 10.

Figure 10. Sinusoidal current response in a linear system.
Simultaneous analysis of the current and potential signals allows calculation of sample impedance. The AC potential signal can be expressed as:

\[ E(t) = E_m \sin(\omega t) \]  \hspace{1cm} (16)

where \( E \) is the potential at time \( t \), \( E_m \) is the amplitude of the potential signal, and \( \omega = 2\pi f \) is the angular frequency in radians per second and \( f \) is the frequency. As it is shown in Figure 10, the current response \( I(t) \), of the system is at the same frequency but shifted in phase (\( \phi \)):

\[ I(t) = I_m \sin(\omega t + \phi) \]  \hspace{1cm} (17)

where \( I_m \) is the amplitude of the current signal. The impedance is defined similar to the Ohms law by dividing the potential by the current in polar coordinate according to:

\[ Z(\omega) = \frac{E(t)}{I(t)} \]  \hspace{1cm} (18)

The modulus of the impedance is \( |Z| = E_m / I_m \) and the phase angle is \( \phi(\omega) \). By using the complex number \( Z = Z' + jZ'' \), the impedance relationship can be presented in Cartesian coordinate. Here, \( j = \sqrt{-1} \), is the imaginary number. The real and imaginary parts of the impedance are:

\[ Z' = |Z| \cos \phi \quad \text{and} \quad Z'' = |Z| \sin \phi \]  \hspace{1cm} (19)

The phase angle \( \phi \) and the magnitude of the impedance \( |Z| \) are given by:

\[ \phi = \tan^{-1}(Z''/Z') \quad \text{and} \quad |Z| = \sqrt{Z'^2 + Z''^2} \]  \hspace{1cm} (20)
The EIS spectra can be displayed in different ways. In a Nyquist plot the imaginary part of the impedance, \( Z'' \), is plotted versus the real part of the impedance, \( Z' \). In a Bode and Phase plot an impedance magnitude \( |Z| \) and phase angle of the impedance \( \phi \) are plotted against frequency, respectively \([72, 73]\). EIS spectra are commonly analyzed by fitting the data with equivalent electrical circuits whose components should define a physical or electrochemical property of the system \([74-77]\).
3 Summary of Key Results

3.1 Corrosion study of a N-based alloy (Fe-Cr-V-N)

3.1.1 Microstructure and chemical composition

The microstructure of the polished surface of the Fe-Cr-V-N alloy is shown in the BSE-SEM image in Figure 11. According to this image, the alloy contains three different phases with three different compositions. It should be noted that there are two dark phases distinguished as a darker nitride and lighter nitride. The chemical composition of these phases was examined with EDS analysis and data are shown in Table 2. The alloy matrix which has the brightest contrast in the BSE-SEM image has the lowest content of chromium, vanadium and nitrogen and the highest content of iron in comparison with the darker phases in Figure 11. The darker nitride contains the highest content of vanadium (34 wt%) and nitrogen (19 wt%). On the other hand, the lighter nitride contains the highest amount of molybdenum and chromium.

![BSE-SEM image of Fe-Cr-V-N multi-phase structure.](image)

Figure 11. BSE-SEM image of Fe-Cr-V-N multi-phase structure.
Table 2. Average of at least five analysis points, showing elemental composition (in wt%) of the darker nitride phase, the lighter nitride phase and the matrix.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cr</th>
<th>V</th>
<th>N</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darker nitride</td>
<td>34.0±0.7</td>
<td>34.3±0.8</td>
<td>19.1±0.4</td>
<td>0.9±0.0</td>
<td>13.1±0.7</td>
</tr>
<tr>
<td>Lighter nitride</td>
<td>37.5±0.5</td>
<td>5.5±0.2</td>
<td>8.3±0.3</td>
<td>2.3±0.1</td>
<td>42.3±0.6</td>
</tr>
<tr>
<td>Alloy matrix</td>
<td>19.3±0.4</td>
<td>1.1±0.2</td>
<td>2.5±0.3</td>
<td>1.8±0.8</td>
<td>75.2±0.3</td>
</tr>
</tbody>
</table>

3.1.2 Volta potential

Volta potential measurements were performed on the Fe-Cr-V-N with KFM. Figure 12 shows topography image (Figure 12-A) and Volta potential map (Figure 12-B and C), and Volta potential line profile (Figure 12-D) over a polished surface area. The AFM topography image shows that nitride particles have higher height values than the metal matrix. Volta potential mapping over the same surface shows that the nitride particles have higher Volta potentials than the alloy matrix; also there are two types of nitride particles according to Volta potential values which are more apparent in the image with higher lateral resolution (Figure 12-C). Comparing Volta potential images and the BSE image (Figure 11) shows that the darker nitride phase has a higher content of alloying metals in comparison with the lighter nitride phase which has the highest Volta potential. The average of at least five Volta potential measurements for each phase showed a Volta potential value of 220±3 mV for the darker nitride, 151±6 mV for the lighter nitride, and 68±3 mV for the alloy matrix. The higher nobility of the nitride phase can be related to the higher content of vanadium and nitrogen (Table 2), because vanadium showed high corrosion resistance in a sodium chloride solution and decreased pitting of stainless steels [78, 79]. Also, nitrogen content in stainless steel can improve pitting resistance [80, 81]. Therefore, vanadium and nitrogen can be postulated to improve formation of a stable passive layer on the
surface. The Volta potential results suggest that the nitride phase has higher stability under corrosive conditions.

Figure 12. (A) Topographic image of a polished Fe-Cr-V-N alloy with scanned area 20×20 µm, (B) Volta potential image of the same surface area, (C) Volta potential image over a similar surface area 10×10 µm, (D) Volta potential line profile scan as indicated in (C).

3.1.3 Microstructure influence on corrosion morphology

The Fe-Cr-V-N alloy was examined in an accelerated corrosion test in order to study the influence of microstructure on corrosion behavior of this alloy. The accelerated corrosion test was performed by polarizing the sample in 0.1 M NaCl from -0.2 V vs. OCP to the upward potential until the anodic current density reached 0.1 mA cm², and then reversing the potential down to the OCP. Figure 13 shows BSE-SEM images of the sample after the accelerated corrosion test. The alloy matrix is dissolved where the dissolution rate was high (Figure 13-A). This can be compared with the nitride particles which are stable, in agreement with KFM prediction of the lowest nobility for the alloy matrix. Moreover, Figure 13-B and C show that corrosion starts at the matrix in the boundary adjacent to the nitride particles, and specifically from lighter nitride particles.
Figure 13. BSE-SEM image of the Fe-Cr-V-N alloy after the polarization in 0.1 NaCl solution. (A) dissolution of alloy matrix after passivity breakdown, (B) corrosion initiation in the boundary region of nitride particles, (C) corrosion initiated at the boundary of lighter nitride particles.

3.2 **Mefp-1/ceria nanocomposite for corrosion protection of mild carbon steel**

3.2.1 **Mefp-1/ceria nanocomposite formation on silica surface**

The Layer-by-Layer (LbL) technique involves sequential adsorption of different components by immersion of a surface in solutions with different composition (in this case Mefp-1 and ceria nanoparticles) and rinsing with pure water between steps. The sequential adsorption of Mefp-1 and ceria nanoparticles was studied by QCM-D. Figure 14 shows changes in frequency and dissipation during adsorption of Mefp-1 (0.01 mg mL\(^{-1}\)) and ceria nanoparticles (0.5 mg mL\(^{-1}\)) on a silica surface. First, frequency and dissipation were set to zero for pure water (region I) to establish a base line. In region II, a buffer solution of 1 wt% citric acid with pH≈5.5 was
introduced over the silica surface, and the decrease in frequency and increase in dissipation is due to changes in bulk density and viscosity of the buffer solution [82, 83]. Introduction of 0.01 mg mL\(^{-1}\) Mefp-1 to the buffer solution causes a further decrease in frequency and a moderate increase in dissipation. Once equilibrium is achieved, the surface is rinsed with pure water to remove the excess of Mefp-1 and citric acid. Comparison between regions IV and I indicates that decrease in frequency and increase in dissipation are due to adsorption of Mefp-1 on the silica surface. Introduction of 0.5 mg mL\(^{-1}\) ceria nanoparticles to the Mefp-1 layer causes a rapid decrease in frequency and slight decrease in dissipation (region V). After that, more mass is added to the layer the dissipation decreases, which means the rigidity of the layer increases as ceria nanoparticles deposited. Following rinsing with water no significant effect on frequency and dissipation values could be detected, showing a firm attachment between Mefp-1 and ceria nanoparticles. The increasing mass with sequential adsorption of Mefp-1 and ceria showed that LbL is a good method to build a Mefp-1/ceria nanocomposite.

![Figure 14. Changes in frequency (solid curve) and dissipation (dashed curve) during sequential adsorption of Mefp-1 and ceria nanoparticles. Regions I and II show the water and 1 wt% citric acid baselines, respectively, region III the protein adsorption step (0.01 mg mL\(^{-1}\)), regions IV and VI rinsing steps with water, and region V ceria nanoparticles adsorption using a particle concentration of 0.5 mg mL\(^{-1}\).](image-url)
3.2.2 Effect of Mefp-1 concentration and Mefp-1 aggregate size on nanocomposite formation

Figure 15 shows dissipation and frequency shifts during adsorption and rinsing for Mefp-1 and ceria nanoparticles for six layers, for different concentrations of Mefp-1 and for initially aggregated Mefp-1 with a hydrodynamic radius of 20 nm. It should be noted that filled symbols are for $\Delta f$ and $\Delta D$ (frequency and dissipation difference) during adsorption, and the unfilled symbols after rinsing step in Figure 14. Likewise, dissipation of the layer increases for the third layer after Mefp-1 adsorption and decreases after ceria nanoparticles adsorption, and these sequential changes continue with increasing number of layers (Figure 15-A-C). The dissipation increase is slightly higher at higher Mefp-1 concentrations and even higher for aggregated Mefp-1. The frequency decreases linearly with increasing number of layers. The only significant difference between the first layer of Mefp-1 and the next layers is that after rinsing with water the layer shows a more pronounced change in dissipation and frequency. This indicates more desorption from the silica surface than from the Mefp-1/ceria composite layer and therefore stronger interaction between Mefp-1 and ceria than between Mefp-1 and silica.
Figure 15. Total energy dissipation (A, B, C) and frequency (D, E, F) change as a function of layer number. Filled symbols correspond to data obtained after the adsorption of Mefp-1 and ceria nanoparticles, and open symbols to data obtained after the rinsing step. The Mefp-1 concentration (non-aggregated sample) during adsorption was 0.01 mg mL\(^{-1}\) (A, D) and 0.1 mg mL\(^{-1}\) (B, E). The Mefp-1 concentration from the aggregated sample (C, F) was 0.1 mg mL\(^{-1}\).

3.2.3 Effect of the number of layers of Mefp-1/ceria nanocomposite

The sensed mass during LbL formation of Mefp-1/ceria nanocomposite with aggregated Mefp-1 and concentration of 0.1 mg mL\(^{-1}\) was modeled with both the Sauerbrey and the Voigt equations (Figure 16). Both models give very similar values, which is due to the high rigidity of the composite layer. An almost linear growth is observed for the composite film up to 18 layers, as shown in Figure 16. The dissipation value increases with Mefp-1 addition and decreases with ceria adsorption. After the sixth layer, however, the overall dissipation value starts to increase which can be explained as growth of the composite film beyond complete monolayer coverage after this step.
Figure 16. (A) Sensed mass as a function of layer number, calculated using the Voigt (filled symbols) and the Sauerbrey (open symbols) models. The sensed mass obtained with these two models overlap and therefore only one symbol is seen in most cases, (B) Total energy dissipation change vs. layer number.

3.2.4 Nanomechanical properties of the composite layer

Peak Force QNM was used in order to study physical and mechanical properties of the nanocomposite layer in air. Figure 17 shows height profile as well as elastic modulus, adhesion and deformation properties for 6 layers of Mefp-1/ceria nanocomposite prepared with 0.01 mg mL\(^{-1}\) Mefp-1 on silica QCM crystal (MC10-6Q) and 6 layers of Mefp-1/ceria nanocomposite prepared with 0.1 mg mL\(^{-1}\) Mefp-1 on silica QCM crystal (MC100-6Q).
Increasing protein concentration did not change the topography and mechanical properties profile of the composite layer. The elastic modulus for the composite layer with higher protein concentration (6.5±0.3 GPa) was higher than the elastic modulus of the composite layer with lower protein concentration (4.5±0.3 GPa). The average adhesion value did not change due to increasing protein concentration, which is reasonable because adhesion was measured between tip and the topmost layer which is composed of ceria nanoparticles, and thus not affected by protein concentration.

The effect of the nature of the last layer, number of layers and structure of the underlying surface were investigated. Table 3 shows six different types of samples that were studied and named as in the following discussion: MCX-YZ, where MC stands for Mefp-1/ceria composite, X is Mefp-1 concentration used during deposition in μg mL⁻¹, and Y is the total number of deposited layers. Z refers to type of underlying substrate where Q means QCM crystal and W silica wafer. Table 4 summarizes the physical and mechanical properties of the samples named in Table 3, and the bare QCM crystal and silica wafer as references.
In general, surface roughness increased with added number of nanocomposite layers. Figure 18 shows the elastic modulus for the nanocomposite films having 17 and 18 layers of adsorbed Mefp-1 and ceria nanoparticles on a QCM silica crystal and on a silica wafer. This figure shows the effect of the underlying substrate and nature of last added layer. Increasing the number of layers leads to a slightly rougher surface, \( R_q = 2.8\pm0.3 \text{ nm (MC100-17Q)} \) and \( R_q = 2.2\pm0.3 \text{ nm (MC100-18Q)} \). This can be compared to layers formed with the same concentration of Mefp-1 but a fewer number of layers (\( R_q = 1.6\pm0.1 \text{ nm for MC100-6Q} \)). The adhesion values are 2-3 times higher for Mefp-1 in the last layer (Table 4). This shows that Mefp-1 contributes more to the sample-tip adhesion than do ceria nanoparticles. The elastic modulus of the layer decreases from 6.5±0.3 GPa to 4.4±0.9 GPa with increasing number of layers, which is related to the increased thickness. A more homogeneous surface with fewer domain structures is obtained when Mefp-1 is added last in comparison to when ceria nanoparticles are added last (Figure 18). Also the silica wafer is smoother, \( R_q = 0.1\pm0.03 \text{ nm, with less domain structure compared to the QCM crystal, \( R_q = 0.4\pm0.1 \text{ nm} \). It is interesting that these initial surface features can affect the layer even after 18 deposition steps, with smaller domains being seen on the QCM crystal substrate than on the flatter silica wafer.

Table 3. Information on the Mefp-1 and ceria nanocomposite layers analyzed with Peak Force QNM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mefp-1 concentration (mg mL(^{-1}))</th>
<th>Ceria concentration (mg mL(^{-1}))</th>
<th>Number of layers</th>
<th>The last layer</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC10-6Q</td>
<td>0.01</td>
<td>0.5</td>
<td>6</td>
<td>Ceria</td>
<td>QCM</td>
</tr>
<tr>
<td>MC100-6Q</td>
<td>0.1</td>
<td>0.5</td>
<td>6</td>
<td>Ceria</td>
<td>QCM</td>
</tr>
<tr>
<td>MC100-17Q</td>
<td>0.1</td>
<td>0.5</td>
<td>17</td>
<td>Mefp-1</td>
<td>QCM</td>
</tr>
<tr>
<td>MC100-18Q</td>
<td>0.1</td>
<td>0.5</td>
<td>18</td>
<td>Ceria</td>
<td>QCM</td>
</tr>
<tr>
<td>MC100-17W</td>
<td>0.1</td>
<td>0.5</td>
<td>17</td>
<td>Mefp-1</td>
<td>Wafer</td>
</tr>
<tr>
<td>MC100-18W</td>
<td>0.1</td>
<td>0.5</td>
<td>18</td>
<td>Ceria</td>
<td>Wafer</td>
</tr>
</tbody>
</table>
Table 4. Summary of surface properties of bare silica surfaces and of Mefp-1/ceria nanocomposite layers determined by means of Peak Force QNM tapping in air.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Roughness (nm)</th>
<th>Elastic Modulus (GPa)</th>
<th>Adhesion (nN)</th>
<th>Deformation (nm)</th>
<th>Peak Force Setpoint (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCM crystal</td>
<td>0.5±0.1</td>
<td>0.4±0.1</td>
<td>78±8</td>
<td>17±2</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>Silica wafer</td>
<td>0.1±0.03</td>
<td>0.1±0.03</td>
<td>113±7</td>
<td>11.6±0.6</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>MC10-6Q</td>
<td>2.0±0.1</td>
<td>1.6±0.1</td>
<td>4.5±0.6</td>
<td>2.8±0.4</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>MC100-6Q</td>
<td>2.1±0.1</td>
<td>1.6±0.1</td>
<td>6.5±0.3</td>
<td>2.6±0.3</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>MC100-17Q</td>
<td>2.2±0.2</td>
<td>2.8±0.3</td>
<td>4.0±0.7</td>
<td>7.2±1.6</td>
<td>1.2±0.21</td>
</tr>
<tr>
<td>MC100-17W</td>
<td>3.2±0.5</td>
<td>2.3±0.2</td>
<td>3.7±0.9</td>
<td>5.7±0.9</td>
<td>1.8±0.26</td>
</tr>
<tr>
<td>MC100-18Q</td>
<td>2.7±0.4</td>
<td>2.2±0.3</td>
<td>4.4±0.9</td>
<td>1.9±0.7</td>
<td>1.5±0.21</td>
</tr>
<tr>
<td>MC100-18W</td>
<td>2.4±0.2</td>
<td>2.3±0.3</td>
<td>4.7±0.8</td>
<td>2.3±0.7</td>
<td>1.6±0.22</td>
</tr>
</tbody>
</table>

Figure 18. Peak Force QNM images of DMT modulus, (A-I) bare QCM crystal, (A-II) 17 Mefp-1/ceria layers on QCM crystal, (A-III) 18 Mefp-1/ceria layers on QCM crystal, (B-I) bare silica wafer, (B-II) 17 Mefp-1/ceria layers on silica wafer and (B-III) 18 Mefp-1/ceria layers on silica wafer.

3.2.5 Robustness of nanocomposite coating

The sample with 18 layers of Mefp-1/ceria on the QCM crystal (MC100-18Q) was selected in order to measure the scratch resistance of the nanocomposite coating. It was scratched with a sharp silica tip (15 nm
tip radius) over an area of 1μm×1μm with different contact forces using contact mode AFM. Figure 19 shows how the topography of the surface changes due to scratching with different applied normal forces. The applied normal force was converted to contact pressure from the force and tip surface area. The calculated contact pressure is shown in Figure 19-B beside the scratched area. The contact pressure was increased from right to left and up to down by increasing the applied normal force. Also the average scratch depth is plotted versus contact pressure in Figure 19-B-I. Figure 19-B-II shows the surface roughness inside the scratched area as a function of contact pressure. The minimum applied pressure, 16 MPa, created grooves 2 nm deep. This can be compared to the unscratched area having the surface height of 0.0±0.5 nm.

There is a decrease in average scratch depth and surface roughness with increasing contact pressure up to around 80 MPa, where the tip pushes down the nanocomposite layer. With contact pressures over 80 MPa, there is sudden increase in scratch depth and surface roughness with some debris particles appearing at the edge of the scratched region, indicating abrasion of the coating with the AFM tip. It can be concluded that the composite films are plastically deformed at pressures below 16 MPa, but are not abraded until the contact pressure exceeds about 80 MPa.
Figure 19. Surface height (A) before scratching, (B) after scratching with different applied contact pressure, which are marked (in MPa) next to the scratched areas. The contact pressure increases from right to left and from top to bottom, (B-I) Average scratch depth vs. contact pressure, (B-II) Roughness in the scratched area vs. contact pressure. The error bars are based on three separate measurements, the surface height and surface roughness for an undisturbed surface are 0.0±0.5 and 2.5±0.2 nm, respectively.

3.2.6 Adsorption of Mefp-1 on iron surface

The aim of making this nanocomposite film on surfaces is to make a corrosion resistant film for metals, especially iron-based alloys. The interaction of Mefp-1 with an iron-coated quartz crystal, and the effects of iron ions (Fe³⁺) were studied. Figure 20-A shows the dissipation change ($\Delta D$) as a function of frequency change ($\Delta f$) during adsorption, and in Figure 20-B during rinsing with 10 μM FeCl₃ solution. In Figure 20-A, dissipation increases with decreasing frequency which shows the adsorption of Mefp-1, but after about 25 Hz (shown with arrow ‘a’) the
rate of dissipation change increases with decreasing frequency which means the adsorbed layer develops a more extended structure. This can be due to increased repulsion between neighboring molecules at higher surface coverage. Figure 20-B shows dissipation change versus frequency change during rinsing with 10 μM FeCl₃ solution. First, dissipation decrease almost linearly with increasing frequency. This may indicate removal of loosely attached Mefp-1 from the surface, or removal of water from the adsorbed protein layer and compaction. Increasing the frequency beyond 26 Hz results in a rapid increase in the dissipation value without any change in frequency, which indicates change in conformation to more extended structure in the adsorbed layer. This can be due to complexation of iron ions (Fe³⁺) with DOPA groups in Mefp-1 and increasing net positive charge of the surface film which causes increasing electrostatic repulsion within the layer.

Figure 20. Dissipation change (ΔD) as a function of frequency change (Δf) during Mefp-1 adsorption (A) and Fe³⁺ induced complexation (B). Arrow ‘a’ is the transition point from fast initial adsorption to slow adsorption, and arrow ‘b’ is the transition point where a transformation of the film structure occurred. The time line on both figures goes from left to right.
3.2.7 Chemical information about Mefp-1 adsorbed on iron surfaces

In order to understand chemical aspects of adsorption of Mefp-1 onto a carbon steel surface, the chemical absorbance bands of Mefp-1 have been studied on an iron coated ZnSe crystal and on an uncoated ZnSe crystal. Figure 21 shows the in situ ATR-FTIR spectra of Mefp-1 adsorption on a pre-oxidized iron surface and on an uncoated ZnSe crystal as a reference. The broad peaks in the region of 3050-3650 cm⁻¹, belonging to the O-H stretching band of water, become negative with time which means a lowering of water content in the adsorbed layer on the iron surface. Also the bands in the region 1200 cm⁻¹ to 1700 cm⁻¹ belonging to O-H and N-H stretching bands of Mefp-1 become positive, and increase with exposure time. In Figure 21-B, the strong band around 1640 cm⁻¹ is associated with C=O stretching in amide groups along the backbone. The peak around 1550 cm⁻¹ can have been influenced by two different type of bands, i.e. N-H bending and aromatic C-C stretching of the catechol aromatic ring of the DOPA residue. Comparing absorbance spectra for Mefp-1 on the two type surface shows a clear difference with a strong peak at 1485 cm⁻¹ on the iron surface, which does not exist for Mefp-1 on the ZnSe surface (Figure 21-C). Further, a stronger peak around 1285 cm⁻¹ is observed for Mefp-1 on iron which is replaced with a much weaker peak at 1243 cm⁻¹ for Mefp-1 on the ZnSe surface. This peak is suggested to be related to the catechol ring which complexes with Fe³⁺ ions.
Figure 21. ATR-FTIR spectra for substrates in 0.1 mg mL\(^{-1}\) \textit{Mefp-1} solution. (A) on the iron surface, (B) the same data on the iron surface in the wavenumber region from 1200 cm\(^{-1}\) to 1700 cm\(^{-1}\), and (C) on the ZnSe crystal surface.

3.2.8 Nanomechanical properties of adsorbed \textit{Mefp-1} on iron surfaces

The nanomechanical properties of \textit{Mefp-1} adsorbed onto the iron surface in a 1 wt\% citric acid buffer and iron chloride solution was studied with Peak Force QNM. Figure 22 shows the height, modulus and adhesion results for \textit{Mefp-1} under these two conditions. Also the mean values for surface roughness and other mechanical properties of the films are reported in Table 5. Comparing height profiles and roughness values does not show very clear difference between the \textit{Mefp-1} film in citric acid buffer solution and after complexation in the iron chloride solution. Nevertheless, other mechanical properties give a better indication for complexation. After complexation, the layer showed lower deformation at
the constant peak force setpoint, and a higher modulus which indicates a stiffer layer on the surface.

Figure 22. Peak Force QNM images of adsorbed Mefp-1 on an iron surface in 1 wt% citric acid solution, (A-I) height, (A-II) modulus, (A-III) adhesion, and in 10 μM FeCl₃ solution, (B-I) height, (B-II) modulus, (B-III) Adhesion.

Table 5. Mean value of surface roughness and mechanical properties of Mefp-1 films on an iron surface.

<table>
<thead>
<tr>
<th>State of Mefp-1 film</th>
<th>Rₛ (nm)</th>
<th>Deformation (nm)</th>
<th>Adhesion (nN)</th>
<th>Dissipation (eV)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before complexation</td>
<td>3.6±0.4</td>
<td>6.96±2.1</td>
<td>1.02±0.34</td>
<td>170±38.1</td>
<td>38.2±21.9</td>
</tr>
<tr>
<td>After complexation</td>
<td>3.2±0.1</td>
<td>5.62±0.7</td>
<td>0.68±0.13</td>
<td>160±20.6</td>
<td>185±51.3</td>
</tr>
</tbody>
</table>

3.2.9 Mefp-1/ceria nanocomposite formation on a stainless steel surface

In order to understand the formation mechanism for Mefp-1/ceria nanocomposite on metal surfaces via the LbL technique, a stainless steel-like coated quartz crystal has been used, which is a more stable substrate than an iron surface. Figure 23 shows sensed mass and dissipation change during adsorption and rinsing with pure water. Mefp-1 is adsorbed from a 0.1 mg mL⁻¹ solution and ceria adsorbed from a 0.5 mg mL⁻¹ solution.
Figure 23-A shows an almost linear growth for sequential adsorption of \textit{Mefp-1} and ceria nanoparticles, and rinsing with pure water caused a decrease in sensed mass for \textit{Mefp-1} which can indicate removal of loosely attached proteins, but there is almost no change in sensed mass for ceria nanoparticles. Figure 23-B shows the energy dissipation change during adsorption of \textit{Mefp-1} with a higher dissipation which decreases significantly after rinsing with pure water but still with higher dissipation than after adsorption of ceria nanoparticles. The change in dissipation for \textit{Mefp-1} after rinsing with water can come from a bulk effect, and it is better to compare the data after rinsing for both protein and ceria. In general, formation of composite layer shows similar trends on stainless steel and silica surfaces but the sensed mass is slightly higher on stainless steel than on the silica surface.

![Graph A](image1.png) ![Graph B](image2.png)

Figure 23. (A) Changes in sensed mass of \textit{Mefp-1} (filled and open squares represent adsorption and rinsing steps, respectively) and ceria nanoparticles (filled and open circles represent adsorption and rinsing steps, respectively) analyzed using the Voigt model and, (B) total energy dissipation during adsorption vs. layer number.

3.2.10 \textit{Structure of the nanocomposite film on mild carbon steel}

Nanocomposite films were also formed on mild carbon steel via the LbL technique. The microstructure of the film was studied with BSE-SEM and an electron probe micro analyzer (EPMA). As shown in Figure 24, the composite film has micro domains which are enriched in carbon, cerium and oxygen indicating that \textit{Mefp-1} and ceria nanoparticles aggregate and
stick together. It is important to determine if there is a coverage of the composite film in non-agglomerated areas because lack of coverage can cause corrosion problems for carbon steel.

Figure 24. BSE-SEM image of the Mefp-1/ceria composite film on carbon steel and corresponding WDS/EDS elemental maps of C, Ce and O.

AFM imaging in tapping mode was performed in non-agglomerated areas (compact part) of a composite film. The topographic image and phase image are shown in Figure 25. It is clear from the height image that there are some particles in this area with average size of 100 nm. Moreover, phase imaging revealed that these areas have a duplex structure which can cause different phase shifts. This can be related to soft and hard nature of Mefp-1 and ceria nanoparticles. Chemical analysis of the area would be helpful in order to verify this interpretation.
Figure 25. (A) Tapping mode AFM topographic image of the compact part of the composite film on carbon steel. (B) Corresponding phase image showing two distinct phases.

Confocal Raman Microscopy (CRM) was performed to gain an understanding of chemical composition of the composite film. Figure 26 shows the optical and Raman images of a composite film on carbon steel and Raman spectra for different areas. The reference spectrum of ceria shows one strong peak at 465 cm\(^{-1}\), characteristic for Ce-O vibration in the fluorite-type structure of CeO\(_2\) [84-86]. The reference spectrum of Mefp-1 shows the major characteristic peaks of the functional group DOPA. The small peak at 1700 cm\(^{-1}\) (amid I) is almost entirely due to C=O stretching. The peak at 1595 cm\(^{-1}\) (amid II) is assigned to in plane N-H bending and C-N stretching of DOPA [87]. The peak at 1330 cm\(^{-1}\) (amid III) is related to the vibrational mode of DOPA, C–C bond connecting the two oxygen-bearing carbon atoms [88-90]. The peak centered at 1490 cm\(^{-1}\) is also attributed to a predominant bending of DOPA, which is greatly enhanced and slightly downshifted with a shoulder peak appearing at 1440 cm\(^{-1}\) upon complexation with iron [91]. It is clear that the spectrum from the non-aggregated part (area 1) is similar to the spectrum from the agglomerated area (area 2). However, the intensity is lower for the non-agglomerated area and the assigned peak is related to iron-DOPA complex confirming the presence of Mefp-1 in this area.
Figure 26. Raman spectra and optical and Raman images of the Mefp-1/ceria film on carbon steel deposited in 4 alternating immersions. The graph shows four spectra with arbitrary units on the ordinate: ref. ceria is a reference spectrum for a thick layer of ceria deposited on carbon steel; ref. Mefp-1 is a reference spectrum for a thick layer of Mefp-1 deposited on carbon steel; (area 1) is an average spectrum over the transparent film; (area 2) is an average spectrum over the aggregates on the surface (marked with an arrow). (A) Optical image of the film deposited on carbon steel and (B) Raman image of the same area interpolated over the 1490 cm⁻¹ characteristic peak of Mefp-1 (DOPA-Fe complex).

3.2.11 Corrosion resistance of Mefp-1/ceria nanocomposite film for carbon steel

Corrosion resistance of the composite coating was evaluated with electrochemical techniques, EIS and polarization measurements. The results for the composite film are compared to those for bare carbon steel, and for carbon steel in in 0.1 mg mL⁻¹ Mefp-1 solution as an inhibitor. EIS measurements were performed after 1 hour, and 1, 3 and 7 days of exposure to 0.1 M NaCl solution at pH 4.6. Figure 27 shows representative Bode and phase plots for at least three different measurements having good reproducibility. The EIS results were analyzed by spectral fitting and using a simple equivalent circuit describing the
metal-electrolyte interface, which consists of the polarization resistance ($R_p$), the interfacial capacitance ($C$) in parallel, and the solution resistance ($R_s$) connected in series. The fitting results are reported in Table 6, and inhibition efficiency is calculated based on the increase in polarization resistance in comparison to the control sample. The inhibition efficiency at the onset of exposure is low for Mefp-1 as an inhibitor or as composite film with ceria. However, the inhibition effect increases after just one day of exposure and reaches a high value after one week. This increment in inhibition is much lower when Mefp-1 acts as an inhibitor in solution.

Figure 27. Bode and phase plots for carbon steel with a Mefp-1/ceria film coating (4 alternating depositions) after different periods of exposure to the 0.1 M NaCl solution at pH 4.6, as compared to bare carbon steel and with 0.1 mg mL$^{-1}$ Mefp-1 added in solution.
Table 6. Data obtained from EIS spectra fitting.

<table>
<thead>
<tr>
<th>Time</th>
<th>( \gamma_0, \text{F cm}^{-2} )</th>
<th>( n )</th>
<th>( R_{sp}, \Omega \text{cm}^2 )</th>
<th>( \eta, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>((1.1\pm0.05)\times10^{-4})</td>
<td>0.8</td>
<td>((7.1\pm0.39)\times10^{2})</td>
<td>-</td>
</tr>
<tr>
<td>1d</td>
<td>((1.4\pm0.07)\times10^{-4})</td>
<td>0.8</td>
<td>((8.3\pm0.25)\times10^{2})</td>
<td>-</td>
</tr>
<tr>
<td>3d</td>
<td>((1.8\pm0.21)\times10^{-4})</td>
<td>0.9</td>
<td>((8.2\pm0.32)\times10^{2})</td>
<td>-</td>
</tr>
<tr>
<td>7d</td>
<td>((2.2\pm0.24)\times10^{-4})</td>
<td>0.9</td>
<td>((7.4\pm0.22)\times10^{2})</td>
<td>-</td>
</tr>
<tr>
<td><em>Mefp-1 inhibitor</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>((1.6\pm0.41)\times10^{-4})</td>
<td>0.8</td>
<td>((6.2\pm0.25)\times10^{2})</td>
<td>-15</td>
</tr>
<tr>
<td>1d</td>
<td>((2.0\pm0.47)\times10^{-4})</td>
<td>0.8</td>
<td>((1.0\pm0.16)\times10^{3})</td>
<td>17</td>
</tr>
<tr>
<td>3d</td>
<td>((2.1\pm0.08)\times10^{-4})</td>
<td>0.7</td>
<td>((1.4\pm0.16)\times10^{3})</td>
<td>41</td>
</tr>
<tr>
<td>7d</td>
<td>((1.5\pm0.30)\times10^{-4})</td>
<td>0.7</td>
<td>((3.1\pm0.17)\times10^{3})</td>
<td>76</td>
</tr>
<tr>
<td><em>Mefp-1/ceria composite film</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>((1.7\pm0.12)\times10^{-4})</td>
<td>0.8</td>
<td>((7.4\pm3.9)\times10^{2})</td>
<td>4</td>
</tr>
<tr>
<td>1d</td>
<td>((1.3\pm0.21)\times10^{-4})</td>
<td>0.8</td>
<td>((4.6\pm2.2)\times10^{3})</td>
<td>82</td>
</tr>
<tr>
<td>3d</td>
<td>((1.1\pm0.07)\times10^{-4})</td>
<td>0.7</td>
<td>((3.4\pm1.7)\times10^{4})</td>
<td>97</td>
</tr>
<tr>
<td>7d</td>
<td>((1.0\pm0.05)\times10^{-4})</td>
<td>0.7</td>
<td>((4.0\pm2.0)\times10^{5})</td>
<td>98</td>
</tr>
</tbody>
</table>

Polarization measurements were performed for the samples after one week of exposure in 0.1 M NaCl solution at pH 4.6 (Figure 28). There is an active dissolution in the anodic curve for carbon steel which is increasing with increasing applied potential. Adding *Mefp-1* as an inhibitor decreased both anodic and cathodic current density which indicates decreasing reaction rates on carbon steel and some inhibiting effect from *Mefp-1*. The nanocomposite film on carbon steel not only decreases the rate of anodic reactions but also shifts the corrosion protection to a more noble potential for carbon steel. In Figure 28 the *Mefp-1/ceria* composite film is compared to 316L stainless steel with passive behavior in the same solution indicating that it has semi-passive behavior.
Figure 28. Polarization curves obtained after one week of exposure in 0.1 M NaCl solution at pH 4.6, for carbon steel without protection, with 0.1 mg mL\(^{-1}\) Mefp-1 added as inhibitor, with the Mefp-1/ceria composite film. The curve for stainless steel 316L obtained immediately after immersion is included for comparison.

### 3.3 UV-cure composite coating for corrosion protection

In this part of the thesis, UV-cure polyester acrylate coatings have been studied for the effect on the corrosion protection of mild carbon steel. Coatings were used with different additives like conducting polyaniline doped with phosphoric acid (PAni-PA), and ceria nanoparticles (ceria). The chemical composition study of the composite coating showed the characteristic peak for ceria nanoparticles and polyaniline in the conductive state doped with phosphoric acid. The structural study showed a homogenous and uniform distribution of the additives in the coating matrix.

#### 3.3.1 Open circuit potential measurements versus time

Open circuit potential (\(E_{OCP}\)) measurements were performed in order to understand the corrosion protection of composite coatings with different compositions. Figure 29-A shows the overall variation of OCP with time for a UV-cured coating with 3 wt% PAni-PA, 3 wt% ceria, 1.5 wt% PAni-PA+1.5 wt% ceria, respectively, and without any additives as a
reference coating, over 50 days immersion in 0.1 M NaCl. Moreover, Figure 29-B shows the $E_{OCP}$ change at initial immersion. $E_{OCP}$ is going down much faster for the coating without any additive compared with the 3 wt% ceria coating. On the other hand, the coating with 3 wt% PANi-PA and 1.5 wt% PANi-PA+1.5 wt% ceria kept the $E_{OCP}$ at a high and stable level over the 50 days of immersion. It is notable for the coatings containing conducting polymer that the $E_{OCP}$ initially drops but then returns to its original high value after a while. This can be related to formation a stable protective layer after initiation of corrosion at coating pinholes.

![Figure 29](image)

Figure 29. Evolution of the open circuit potentials ($E_{OCP}$) with immersion time for the samples with and without additives, (A) general overview of $E_{OCP}$ vs. time, for carbon steel coated with UV-cure resin without additives, with 3 wt% ceria, 3 wt% PANi-PA and 1.5 wt% PANi-PA+1.5 wt% ceria exposed to aerated 0.1 M NaCl solution for 50 days, (B) Initial $E_{OCP}$ vs. time on an enlarged scale.

### 3.3.2 EIS study of polymeric composite coatings

Electrochemical impedance spectroscopy (EIS) was used to understand the protection mechanism of polymeric coatings under corrosive conditions. Figure 30 and Figure 31 show EIS spectra including Nyquist, Bode and phase plots for coatings without additives and with 3 wt% ceria, respectively, as a function of exposure time. The Nyquist diagrams for both coatings show a single capacitive loop over the whole frequency range indicating a capacitive response for these types of coatings. The
diameter of Nyquist semi-circles and impedance magnitude at low frequency, $|Z|_{0.01 \text{Hz}}$, in Bode plots decreased with increasing immersion time which shows that the total impedance of both systems was reduced. Also, the coating with added ceria nanoparticles showed higher impedances at lower frequencies by comparison to the reference sample. Moreover, the rate of decrease of the impedance at low frequency with time is lower than that for the coating without additives. All of these results indicate better barrier properties for the coating containing ceria nanoparticles which is in agreement with OCP results.

Figure 30. EIS spectra for the PEA coating without any additives (reference sample) after 1, 3, 10, 20, and 50 days of exposure in 0.1 M NaCl solution (A) Nyquist plot, (B) Bode and phase plots.
Figure 31. EIS spectra plots for the PEA coating with 3 wt% ceria after 1, 3, 10, 20, and 50 days of exposure in a 0.1 M NaCl solution. (A) Nyquist plot, (B) Bode and phase plots.

Figure 32 and Figure 33 show the EIS spectra for the coatings with 3 wt% PAni-PA and 1.5 wt% PAni-PA+1.5 wt% ceria, respectively. The spectra for the coatings containing conducting polymer (PAni-PA) are notably different from the other coatings. This difference is more obvious in the Nyquist plot showing a linear part in the middle to low frequency range. This type of response is certainly related to the presence of conducting polymer in the coating structure. Many efforts in the literature tried to model the coating containing conductive polymer with a Warburg element and mass diffusion controlling reaction [92-94], or with more complicated equivalent electrical circuits [35, 41]. The physical meaning and interpretation of these models are questionable. Impedance at low frequency, $|Z|_{0.01 \text{Hz}}$, in Bode plots for these type of composite coatings is lower in comparison to coatings without conducting polymer, which also can be related to the conductivity of the conducting polymer. Further, the coating with 3 wt% PAni-PA has a lower impedance compared with coatings having just 1.5 wt% PAni-PA which confirms the quantitative effect of conductive polymer on the PEA composite. Moreover, the EIS spectra for these coatings have a semi-circular shape for the initial immersion in the electrolyte. This can be due to the coatings not being
completely wet during the first day of immersion. The impedance in the low frequency range increases slightly with the exposure time, which is opposite to the situation for the barrier-type coatings. The increasing total impedance may indicate an increasing corrosion resistance of the coating caused by formation of a passive layer on the carbon steel surface. Despite a lower amount of PAni-PA in the composite coating with ceria nanoparticles, the increase in the total impedance is more pronounced than for the coating with only PAni-PA at a higher percent addition. These results may suggest a synergistic effect between PAni-PA and ceria nanoparticles on corrosion protection. This deserves further study.

Figure 32. EIS spectra for the coating with 3 wt% PAni-PA after 1, 3, 5, 10, 15 and 50 days of exposure in 0.1 M NaCl solution. (A) Nyquist plots; (B) Bode and phase plots.
Figure 33. EIS spectra for the coating with 1.5 wt% PAni-PA+1.5 wt% ceria after 1, 3, 5, 10, 15 and 50 days of exposure in 0.1 M NaCl solution. (A) Nyquist plots; (B) Bode and phase plots.

3.3.3 Appearance of the composite coatings after immersion

Figure 34 shows the coated samples before and after 50 days immersion in 0.1 M NaCl solution. As can be seen, corrosion has started and is uniformly disturbed over the exposed area for the sample without additives (Figure 34-A), this indicates that electrolyte penetrates through the coating pinholes and caused corrosion. The coating with 3 wt% ceria (Figure 34-B) shows that corrosion starts more locally and is limited. This confirms the better barrier properties of the coating with ceria nanoparticles. The coatings with 3 wt% PAni-PA and with 1.5 wt% PAni-PA+1.5 wt% ceria show almost no corrosion after 50 days of exposure, which indicates that the conducting polymer is providing good corrosion protection for the carbon steel substrate.
Figure 34. Coating surface before (upper part) and after 50 days of exposure (lower part) in 0.1 M NaCl solution. (A) the reference PEA coating, (B) with 3 wt% ceria, (C) with 3 wt% PAni-PA, and (D) with 1.5 wt% PAni-PA+1.5 wt% ceria.
4 Conclusions

The corrosion behavior of new N-based Fe-Cr-V-N tool alloy has been studied. It is shown this alloy has composite structure which consists of different phases with different composition. The Volta potential mapping showed the nitrides have higher nobility than the alloy matrix, and the nitrides with higher amount of V and N have the highest Volta potential. In accelerated corrosion test, when passivity break down happens, local dissolution of the alloy matrix take places, which was in agreement with Volta potential results. On the other hand, the dissolution starts from grain boundary regions and mostly adjacent to the Cr- and Mo-rich nitrides which may suggest chromium depletion can have more impact on corrosion initiation from grain boundaries than potential difference.

The film formation process showed layer-by-layer (LbL) deposition was the practical way to fabricate Mefp-1/ceria nanocomposite on the surface. The film grows linearly with increasing number of layers up to eighteen layers. Increasing Mefp-1 concentration or using Mefp-1 with larger size lead to higher adsorbed mass of Mefp-1 on the surface, whereas size of Mefp-1 increases the adsorbed mass more notably. Peak Force QNM showed to be suitable technique to measure physical and mechanical properties of composite coatings. Elastic modulus of the film increased for the film prepared with higher Mefp-1 concentration during the film deposition and the nature of the outermost layer can affect morphology and surface mechanical properties. The composite film deformed plastically under contact pressure of higher than 16 MPa and starts to abrade at a pressure of around 80 MPa. The QCM-D study of Mefp-1 on oxidized iron substrate showed Mefp-1 adsorbs with high rate on the surface and changes its conformation following with increasing adsorption time. Investigation effect of Fe³⁺ ions on physical and mechanical properties of single layer Mefp-1 layer with QCM-D and in situ-Peak Force QNM showed Fe³⁺ leads to a transition from an extended and soft layer to
a denser and stiffer layer. *In situ* ATR-FTIR and Confocal Raman Microscopy (CRM) showed complex formation between Fe$^{3+}$ and catechol functional group of *Mefp*-1. The film growth on stainless steel-like substrate showed similar linear growth with increasing number of layers. Lastly, *Mefp*-1/ceria nanocomposite film was prepared with LbL technique on industrial mild carbon steel. Electrochemical impedance microscopy (EIS) and potentiodynamic polarization techniques showed corrosion protection of composite film on carbon steel. The measurements indicate that the composite film provides higher protection for carbon steel in comparison with *Mefp*-1 as inhibitor, and the polarization resistance ($R_p$) increases with exposure time.

The other composite coatings can be made from UV-cure polyester acrylate resin with conducting polymer (PAni-PA) and ceria nanoparticles as additives. The 3 wt% addition of ceria nanoparticles significantly slows down electrolyte uptake in 0.1 M NaCl solution and enhances the barrier protection of the coating. In contrast, addition of 3 wt% PAni-PA in the coating provides active protection for carbon steel in 0.1 NaCl solution. Further, the combination of the PAni-PA and the ceria nanoparticles appears to offer a synergistic effect that greatly improves the corrosion protection properties of UV-cured composite coatings in contact with NaCl solution.
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