Steel Coated with Cationic Poly (Ethylenimine) (PEI) and Anionic Poly (Vinylsulfate) (PVS) Polyelectrolyte Multilayer Nanofilm with Different Benzotriazole Inhibitor Concentrations

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Abstract

Nano-films consisting of an alternating sequence of positively and negatively charged polyelectrolytes have been prepared by means of the electrostatic layer-by-layer sequential assembly technique on mild steels. The mild steels were pretreated electrochemically to modify the mild steel surface. The modification of the mild steel surface resulted in increasing the adhesion of the obtained nano-films and prevented the corrosion attack during the coating processes. Different concentrations of Benzotriazole inhibitor were encapsulated between cationic and anionic polyelectrolytes nano films. The encapsulation of benzotriazole in the deposited nano-films was verified by U.V visible spectroscopy. The work mainly focuses on the effect of these nano-films of polyelectrolytes with inhibitor and without inhibitors on the corrosion protection. Tafel, corrosion potential, potentiostatic and Econ *vs.* time experiments were carried out in 0.7M NaCl solution. Weight loss method was used for measuring the corrosion rate of coated and uncoated mild steel substrate. A significant improvement in the corrosion protection was achieved especially in the case of electrochemically modifying the mild steel surface and encapsulating the inhibitors between the polyelectrolytes nano-films.

Key words: Corrosion, Coating, Inhibitor, Electrolyte, Potentiostat.

Introduction

The major purpose of coating a metal is to protect it from a corrosive environment. Protection can be achieved in five ways, with many coatings functioning in more than one way.

    1) A barrier coating that prevents the corrosive environment from contacting the base metal.

    2) A sacrificial metal coating that corrodes while giving cathodic protection to the underlying metal.

    3) A noble metal coating that ensures the base metal passive.

    4) An inhibitor coating that slows electrode reactions.

    5) An electrically resistive coating that stifles electrochemical corrosion cells.

Numerous corrosion protective coatings are typically utilized in the automotive, steel, pipe, linings and petroleum industry [1,2,3,4,5]. However, the vast majority of these coatings are generally categorized into two major divisions, *viz.* inorganic or organic based coatings.

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Inorganic Coatings

Corrosion resistant inorganic coating materials could be applied using different techniques. Chemical or physical vapor depositions are usually employed when hard protective coatings such as TiC, Si_3N_4 or FeB are required [3]. In a different approach, corrosion protection using cathodic sacrificial metal coatings such as Zn, Al, Mg, Cd, or different combinations of their alloys have also been reported [5]. To be effective in preventing corrosion, a metal should have its reduction potential more negative than those of iron, steel or the metal it is trying to protect. Anodic control protection works in a similar manner, however it uses noble metal coatings such as Ni, Cr, Sn, Cu, Ag or Au when decorative appearance is desired. These coatings are generally characterized by the passivation of their surface prompting inertness to environmental wear and degradation. Inorganic coatings are expensive and cracks tend to develop after relatively short periods of time [1,3,5,6].

Organic Coatings

On the other hand, organic coatings are very effective in corrosion prevention and consist of paints or polymeric coatings. Paint coatings are composed of a mixture of resin, oil, solvents, pigments, metal powders, inorganic salts (TiO_2) and additives such as dryers, hardeners or plasticizers. Paint coatings break down when overexposed to light, heat or humidity. They are also susceptible to blistering and mechanical failure such as rupturing, wrinkling, cracking and peeling. Blisters are formed when water molecules and moisture permeate into the paint/substrate interface. A blister starts with the micro entrapment of water that causes the formation of corrosion cells and causes rust to form at the solid paint interface. Typical corrosion resistant paints are oils, phenolic, phthalic, melamine, vinyl, epoxy, polyurethane and acrylic resins [2,5,6].

Polyelectrolytes

A polyelectrolyte, by definition, is a macromolecular species that upon being placed in water or any other ionizing solvent dissociates into a highly charged polymeric molecule. Such dissociation is typically accompanied by smaller oppositely charged counter ions that tend to neutralize the charge on the repeating units of the macromolecule preserving electro-neutrality [5,7].

A polyelectrolyte, in low ionic strength solutions, tends to be in its most extended and uncoiled form due to the intermolecular repulsion of the unscreened charges on each monomeric unit of the macromolecule. On the other hand, when the ionic strength of the solution is increased, a polyelectrolyte tends to become more coiled due to the screening effects of polymer charges by the excessive presence of smaller salt counter ions in solution, as shown in Figure 1 [5].
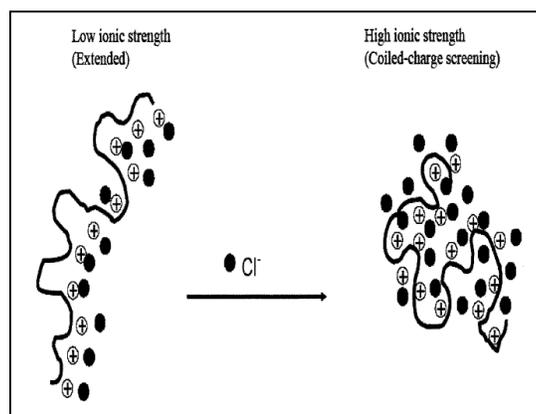

Fig. 1. Effect of ionic strength on the conformation of a polyelectrolyte in solution [5].

Polyelectrolyte Multilayers: Layer-by-Layer Sequential Assembly

Polyelectrolyte multilayer thin films (PEMUs) evolved from polyelectrolyte complexes. PEMUs were first mentioned by Her in 1966. However, the method only gained widespread scientific attention and industrial consideration after Decher developed the process of multilayer formation as it is known today. Since then, around 2000 scientific publications about multilayer thin films have been reported. The knowledge and science of material deposition on surfaces has increased tremendously since then, and industry caught notice of this inexpensive yet very effective technique. Polyelectrolyte multilayers have been used by CibaVision as hydrophilic coatings on their contact lenses. Another application was the Yasa-Sheet food wrapper, which was developed by Semei Shiratori, and which prevents bacterial and mold buildup on fruits and vegetables [8]. Layer assembly on surfaces is not as new as the multilayer thin films field. Previous methods of deposition include the Langmuir-Blodgett technique (LB), which makes use of expensive and specialized equipment to produce highly ordered and uniform films from materials placed at the air-liquid interface. The LB technique, however, is limited by the choice of solvent and the requirement of very smooth and homogenous surfaces for deposition. Moreover, LB films have low stability towards external stimuli, such as solvent and temperature changes. Other deposition methods include solvent casting and spin coating. The question that arises is why polyelectrolyte layer-by-layer assembly is so much more favorable than these other methods. The answer to this question is simple. Layer-by-layer assembly provides an inexpensive, cost effective, highly reproducible, environmentally friendly, and robust method to build ultra thin polymer films that are water resistant and stable, even at high ionic strength, and in acidic and basic media over a wide range of temperature, pH, and solvent changes. Polyelectrolyte multilayers built through layer-by-layer assembly can be deposited on several materials. A few examples are polymers, clay, proteins, dyes, colloids, carbon nanotubes, ion exchange resins, and nanoparticles [8]. Multilayers can also be assembled on several substrates such as gold, quartz, silicon, glass, germanium, platinum, plastic, stainless steel, etc... Polyelectrolyte multilayers can be constructed from proteins, DNA, dyes, inorganic platelets, latex particles, dendrimers, and even viruses. This method has very few limitations if any, and it can also be automated to provide excellent control over the film build up reproducibility and thickness down to few angstroms [8,9].

Multilayer Formation

Multilayer systems can be prepared using the method of layer-by-layer self assembly. This technique involves alternating exposure of a charged substrate to solutions of positive and negative polyelectrolytes, respectively, with rinse step in between to remove any extra material that is loosely bound to the surface. Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilized by strong electrostatic forces. Such self-assembled polyelectrolyte multilayers (PEMUs) have proven to be versatile materials with respect to the incorporation of different charged compounds or nano-objects [10,11]. In this research, polyelectrolytes that used in multilayer formation were poly(ethyleneimine) (PEI) and poly(vinyl sulfate) potassium salt (PVS) that are shown in Figure 2.
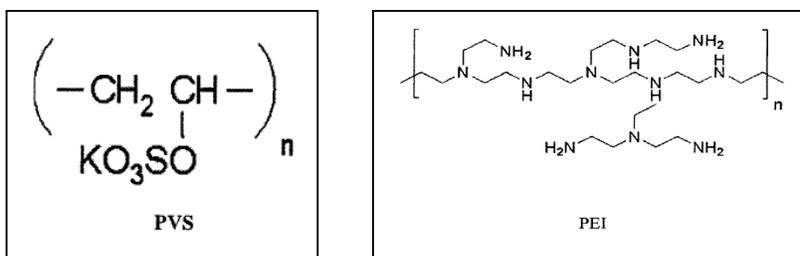
Fig. 2. Chemical scheme of the polyelectrolytes used in the multilayer formation [10].

Materals and Procedures
Preparation of Steel Samples

At first, mild steel wires with 1.6 mm diameter prepared. Each wire was 100 cm in length and it was cut into small rods with 7 cm in length. These rods were polished with emery paper of 800, 1000 and 1200 grit successively, rinsed with acetone for 2 minutes and then washed with deionized water prior to the coating and electrochemical experiments.

Preparation of Polyelectrolytes and Inhibitor Solutions

The cationic and anionic polyelectrolytes that used were Polyethyleneimine (PEI) average M_w ~ 750,000 and Poly (vinyl sulfate) potassium salt (PVS), average M_w ~ 170,000 respectively. The concentrations of the polyelectrolytes solutions were 1 mM calculated based on the repeat unit of the polyelectrolytes. Different concentrations of Benzotriazole inhibitor was prepared using deionized water. The structure of this inhibitor is shown in Figure 3.
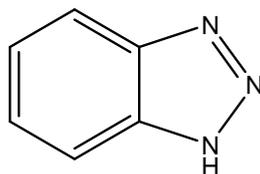
1*H*-benzo[*d*][1,2,3]triazole

Fig. 3. The chemical scheme of the inhibitor that used in encapsulating with polyelectrolytes [10].

Coating Process

The wires were deposited firstly in the cationic polyelectrolyte solution for three minutes while spinning at a rate of 300 rpm. The wires were subsequently rinsed for 90 seconds using deionized water in three different beakers, 30 seconds in each. Then another deposition for three minutes in the anionic polyelectrolyte solution was done. So we have two layers, and the process is repeated until reaching the required number of layers. In the case of encapsulating inhibitor in between cationic and anionic polyelectrolytes, the wires deposited in the inhibitor solution immediately after 30 seconds rinsing in deionized water, which follow the immersion in cationic polyelectrolyte solution. This in turn followed by 30 seconds rinsing in deionized water and three minutes immersion in anionic polyelectrolyte solution. This process repeated until reaching the required number of layers. Figure 4 is a diagram detailing the layer-by-layer assembly process.
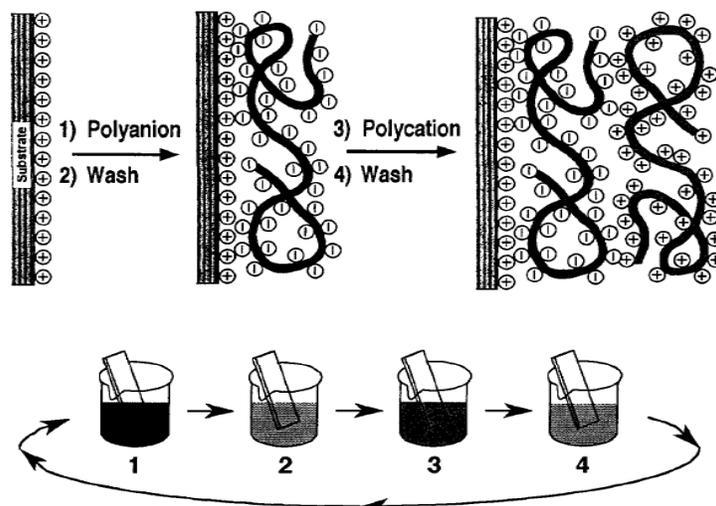
Fig. 4. Schematic of the layer-by-layer deposition process.

Tafel Test

The Tafel technique is used to obtain an accurate estimate of the corrosion rate of a metal in a solution. Cell current is measured during a slow sweep of the potential. The sweep typically is from - 250 to + 250 mV relative to E_{oc}. A fit of the data to a standard model (Butler-Volmer model) yields an estimate of Icon- which is used to calculate a corrosion rate. A graphical output of the experiment is a plot of log current versus potential. Analysis of the curve can yield the following types of information: Corrosion potential, corrosion current, and corrosion rate and kinetic information (Beta coefficients; β_a and β_c) for the anodic and cathodic reactions.

Potentiostatic

The Potentiostatic technique does not have a single purpose. It can be used to study the formation or breakdown of passive films, measure pitting by means of electrochemical noise measurements, or just electrochemically pretreat a sample. The Potentiostatic experiment in the DC 105 consists of a series of current measurements made with a metal sample held at a constant voltage. A graphical output of the experiment is a plot of current versus time. Analysis of the curve can yield the following types of information: Rate of film formation, Mechanistic information and Noise spectra.

Corrosion Potential

The Corrosion Potential technique is the simplest of the DC 105 techniques. It is the only technique in which there is no current flow through the sample. The DC 105 just measures the open circuit potential, Eoc of the sample as it changes over time. The graphical output of the experiment is potential (Eoc) versus time (ks). Corrosion Potential experiments are usually used to obtain quantitative information. The primary use of the analysis packages is for graphing and curve comparison.

Result and Discussion
Coating With Cationic PEI and Anionic PVS

Potentio-dynamic experiments were performed in 0.7 M NaCl solution for the uncoated mild steel and specimen coated with 10, 20, 40 and 60 multilayers of PEI/PVS. Tafel plots for these experiments are shown in Figure 5.
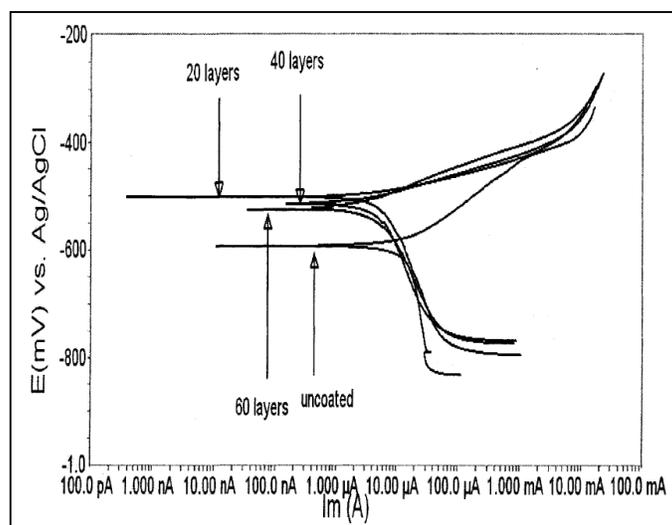
Fig. 5. Tafel plots of uncoated mild steel and coated with 20, 40 and 60 multilayers of PEI/PVS in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Tafel plots were analyzed to obtain the corrosion potential, corrosion current, beta coefficient and the corrosion rate values. These values are shown in Table 1. The graphical representation of the data in Table 1 is given in Figures 6 and 7It is noted from Figure 6 that the corrosion potential increases from -592 mV for the uncoated sample to -502, -512 and -527 mV for 20, 40 and 60 layers, respectively. Increasing in corrosion potential indicates the improvements of corrosion protection performance. There is a significant change in E_{corr} value between the uncoated and the 20 layers (approximately 90 mV). It is noted that a slight decrease in corrosion potential for 40 and 60 layers compared to 20 layers.

Table 1. Electrochemical corrosion parameters (E_{corr}, I_{corr}, β_a, β_c and Corrosion Rate) deduced from Tafel plots of the systems PEI/PVS in 0.7 M NaCl and scan rate 0.166 mV/s

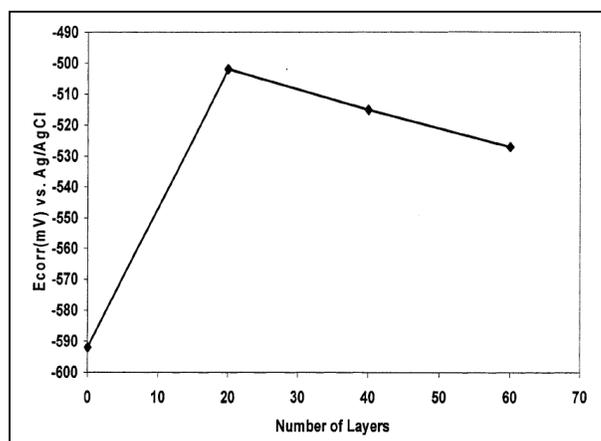| Number of Layer	β_a V/decade	β_c V/decade	E_{corr} (mV)/cm^2	I_{corr} (μA)/cm^2	Corrosion Rate (MPY)
0	0.0999	0.3194	-592	24.9	17.00
20	0.036	0.278	-502	7.6	4.98
40	0.041	0.226	-515	4.9	3.35
60	0.050	0.167	-527	4.9	1.98

Fig. 6. Corrosion potentials E_{corr} in (mV) for uncoated mild steel and coated with 20, 40 and 60 multilayers of PEI/PVS in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s
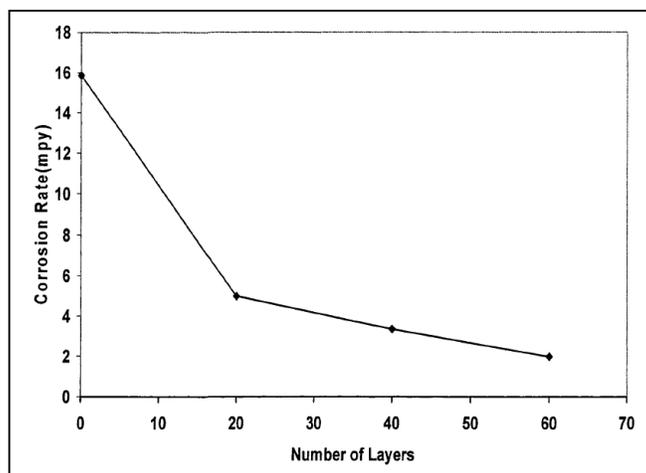

Fig. 7. Corrosion rates in (mpy) for uncoated mild steel and for species coated with 20, 40 and 60 multilayers of PEI/PVS in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Figure 7 shows that the corrosion rate decreases with increasing the number of layers which reflects good corrosion protection. The corrosion rate decreases from 17.0 millimeter per year (mpy) for the uncoated mild steel to 4.98, 3.35 and 1.98 mpy for the mild steel species coated with 20, 40 and 60 layers of PEI/PVS, respectively. As for E_{corr} the difference in corrosion rates between 20 and 40 layers is low, while there is a high drop at 60 layers. The 60 layers coating show a decrease of 88.4% from the corrosion rate of the uncoated mild steel (Table 2). Although the decrease in the corrosion rate and the increase in the corrosion potential, it is noted that the formed film has low adhesion force and can be removed easily from the mild steel surface. It is noted also that the corrosion process takes place during the coating steps due to the effect of anionic poly(vinyl sulfate) (PVS).

It is well to note that the using of Tafel plot for measuring the corrosion rate has the following limitations [12]: (i) The branch of the polarization curve is under activation control, (ii) Corrosion is uniform (general), (iii) There is a well-defined Tafel region and (iv) Changes in electrode potential do not induce additional electrode.

Table 2. Corrosion Efficiency of the 20, 40, and 60 layers for the systems PEI/PVS in 0.7 M NaCl and scan rate of 0.166 mV/s

Number of Layers	Inhibition Efficiency %
20	70.7
40	80.3
60	88.4

Coating with Cationic PEI and Anionic PVS with a Base Coat

Tafel experiments were carried out in 0.7 M NaCl solution for the treated mild steel and specimen (treated mild steel) coated with 10, 20 and 40 multilayers of PEI/PVS. Tafel plots for these experiments are shown in Figure 8. Tafel plots were analyzed to obtain the corrosion potential, the current and the corrosion rate values. These values are shown in Table 3. The graphical representation of the data of Table 3 is given in Figures 9 and 10. It is noted from Figure 9 that the corrosion potential increases from -632 mV for the treated wire to -578, -536 and -573 mV for 10, 20 and 40 layers, respectively. An increase of 96 mV in E_{corr} value was observed as a result of coating the wire with 20 layers. The E_{corr} reached to its highest value at 20 layers with an increment of 96 mV above its value for the treated mild steel wire. A slight decrease in E_{corr} was observed for the wires coated with 40 layers. This result also indicates that deposition of layers beyond 20 does no lead to improvement in corrosion resistance.

The corrosion rate of the treated mild steel wire was 17.2 mpy. Figure 10 shows that upon coating with 10 multilayers of PEI/PVS the corrosion rate dropped to 13.4 and 3.9 mpy for wires coated with 10 and 20 layers, respectively. The corrosion rate increased again at 40 layers to reach 9.3 mpy. These results also indicate that the deposition of layers beyond 20 does not result in improvement of the corrosion resistance. The swilling of water may be resulted in the weakness of the formed thin film. A total decrease of 77.3% in corrosion rate was realized upon coating with 20 layers of the PE. Table 4 shows that the corrosion efficiency reached to 77.3% at 20 multilayers. Considering the very low thickness of the layers, which is in the nano scale, this protection efficiency is significant. The slight increase in corrosion rate observed between the 20 and 40 layers is consistent with the E_{corr} measurement results that displayed no improvement in the corrosion protection beyond 20 layered.
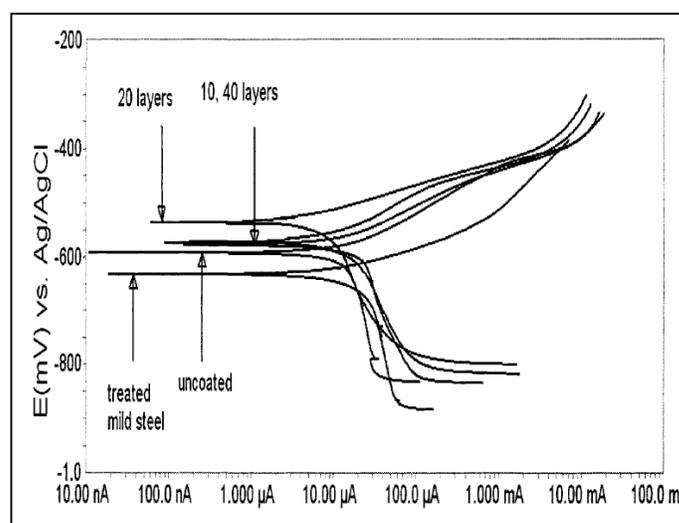

Fig. 8. Tafel plots of uncoated, treated mild steel and for species (treated) coated with 10, 20 and 40 multilayers of PEI/PVS in 0.7M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Table 3 - Electrochemical corrosion parameters (E_{corr}, I_{corr}, β_a, β_c and corrosion rate) deduced from Tafel plots of the systems PEI/PVS on treated mild steel in 0.7M NaCl and scan rate 0.166 mV/s

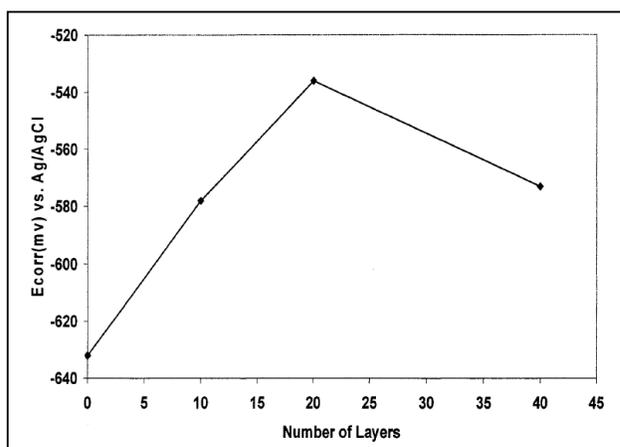| Number of Layers	β_a V/decade	β_c V/decade	E_{corr} (mV)/cm^2	I_{corr} (μA)/cm^2	Corrosion Rate (MPY)
Uncoated	0.0999	0.3194	-592	24.9	17.0
Treated Mild Steel	0.0689	0.629	-632	24.4	17.2
10	0.0879	0.391	-578	20.6	13.4
20	0.0534	0.235	-536	6.0	3.9
40	0.0947	0.264	-573	14.2	9.2

Fig. 9 . Corrosion potentials E_{corr} in (mV) for treated mild steel and for species (treated) coated with 10, 20 and 40 multilayers of PEI/PVS in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s
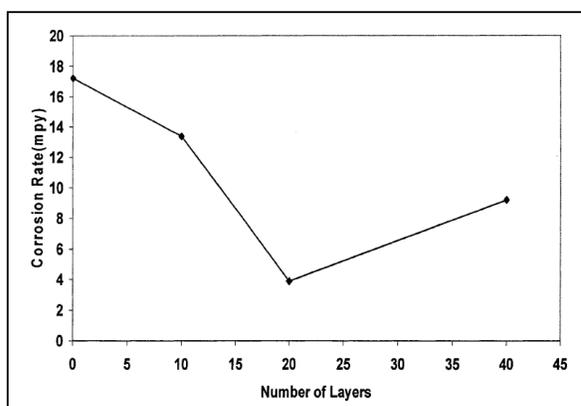

Fig. 10. Corrosion rates in (mpy) for treated mild steel and for species (treated) coated with 10, 20 and 40 multilayers of PEI/PVS in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Table 4. Corrosion Efficiency of the treated, 10, 20 and 40, layers for the systems
PEI/PVS on treated mild steel in 0.7 M NaCl and scan rate of 0.166mV/s

Number of Layers	Inhibition Efficiency %
Treated Mild Steel	-1.2
10	21.2
20	77.1
40	45.9

Coating with Cationic PEI and Anionic PVS with a Base Coat and 1 mM Benzotriazole Inhibitor

As for the previous systems, Fig. 11, shows the Tafel plots of the treated mild steel and the wire, treated, coated with 10, 20 and 40 multilayers of PEI/PVS polyelectrolytes in the presence of 1 mM of benzotriazole inhibitor. Corrosion parameters that obtained by analyzing these plots are shown in Table 3. Figure 12 shows that the corrosion potential was distinctive for different number of layers. The E_{corr} shows an increase from -632 mV for treated mild steel to -540 mV for wire coated with 10 multilayers. Figure 12 shows also no significant differences in the E_{corr} for treated mild steel coated with 20 and 40 multilayers.

Figure 13 shows that the corrosion rate decreases with increasing the number of layers which reflects good corrosion protection. The corrosion rate decreases from 17.2 mpy for the treated mild steel to 9.4, 3.9 and 2.1 mpy for the treated mild steel coated with 10, 20 and 40 layers of PEI/PVS, respectively. The 40 layers of PEI/PVS diminish the corrosion rate of the uncoated mild steel by 86.8% (Table 6). It was shown that the pretreatment of the surface increased significantly the adhesion force of the multilayers thin film and prevented the corrosion process during the coating steps as well as increased the ability of multilayers thin film in corrosion protection.
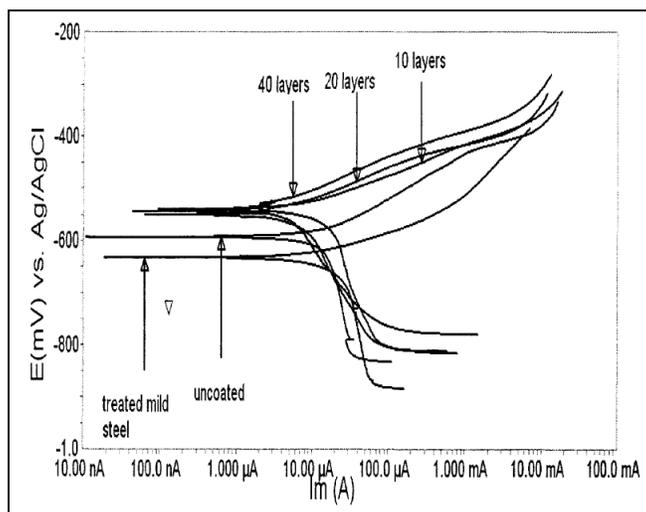

Fig. 11. Tafel plots of uncoated, treated mild steel and of species (treated) coated with 10, 20 and 40 multilayers of PEI/PVS with 0.001 M of benzotriazole inhibitor in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Table 5. Electrochemical corrosion parameters (E_{corr}, I_{Corr}, β_a, β_c and corrosion rate) deduced from Tafel plots of the systems PEI/PVS and 0.001M of benzotriazole on treated mild steel in 0.7 M NaCl and scan rate of 0.166 mV/s

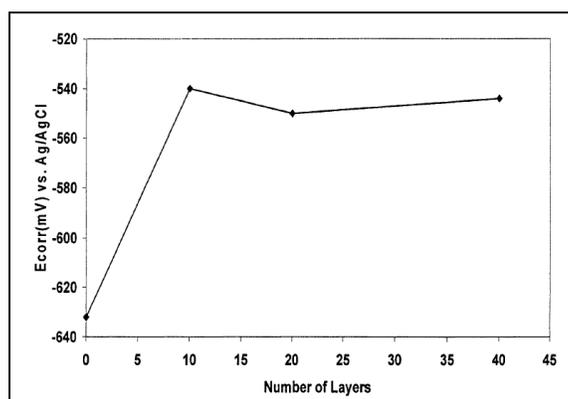| Number of Layers	β_a V/decade	β_c V/decade	E_{corr} (mV)/cm^2	I_{corr} (μA)/cm^2	Corrosion Rate (MPY)
Uncoated	0.0999	0.3194	-592	24.9	17.0
Base Coat	0.0689	0.629	-632	24.4	17.2
10	0.070	0.375	-540	14.4	9.4
20	0.070	0.234	-550	5.9	3.9
40	0.067	0.159	-544	3.3	2.1

Fig. 12. Corrosion potentials E_{corr} (mV) for treated mild steel and for species (treated) coated with 10, 20 and 40 multilayers of PEI/PVS with 0.001 M benzotriazole inhibitor in 0.7 M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s
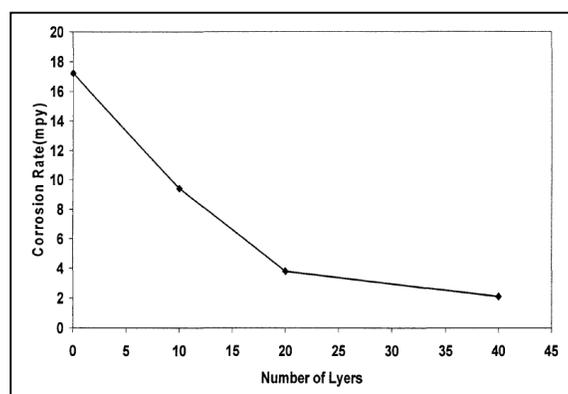

Fig. 13. Corrosion rates in (mpy) for treated mild steel and for species (treated) coated with 10, 20and 40 multilayers of PEI/PVS with 0.001M Benzotriazole inhibitor in 0.7M NaCl solution with Ag/AgCl reference electrode and scan rate of 0.166 mV/s

Table 6. Corrosion Efficiency of the treated, 10, 20, and 40 layers for the systems PEI/PVS and 0.001 M benzotriazole inhibitor in 0.7 M NaCl solution and scan rate 0.166 mV/s

Number of Layers	Inhibition Efficiency %
Treated	-1.2
10	44.7
20	77.1
40	86.8

Corrosion Potential vs. Time Test

Figure 14 shows the variation of corrosion potential E_{corr} with an immersion time 8:20 hours in 0.7 M NaCl solution for uncoated and 40 layers PEI/PVS on treated mild steel. It is observed that the corrosion potentials were strongly modified during immersion.

For increasing immersion time, E_{corr} for the uncoated mild steel was lower than that for 40 layers PEI/PVS coated sample. These results show that the polyelectrolyte multilayers of PEI/PVS on treated mild steel significantly increased E_{corr} towards more positive values and hence ensure long term protection.
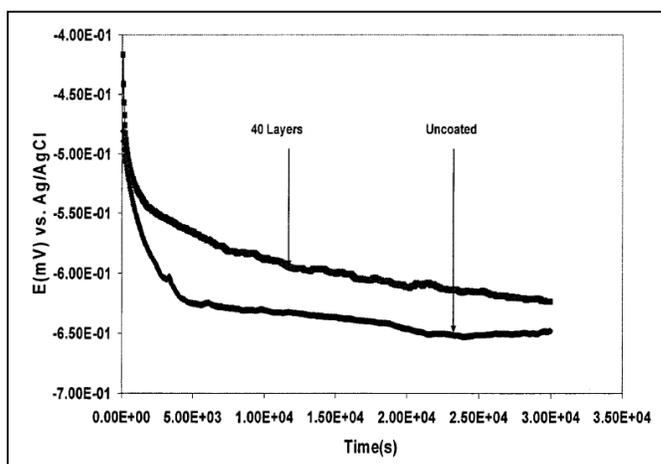

Fig. 14. Corrosion potential for uncoated and 40 layers of PEI/PVS on treated mild steel in 0.7M NaCl and Ag/AgCl reference electrode

Potentiostatic Test

Polyelectrolyte thin films were deposited on the treated mild steel wires. Then the potentiostatic tests were carried out in 0.7 M NaCl solution. The coated and uncoated mild steel samples are exposed to -450 mV for 4500 seconds and the experiment was

recorded as current versus time. It is noted from Figure 15 that the 10 and 40 layers coated wires were significantly protected against corrosion compared to uncoated wire. It is observed that the performance of sample coated with 40 layers was greater than that of sample coated with 10 layers.
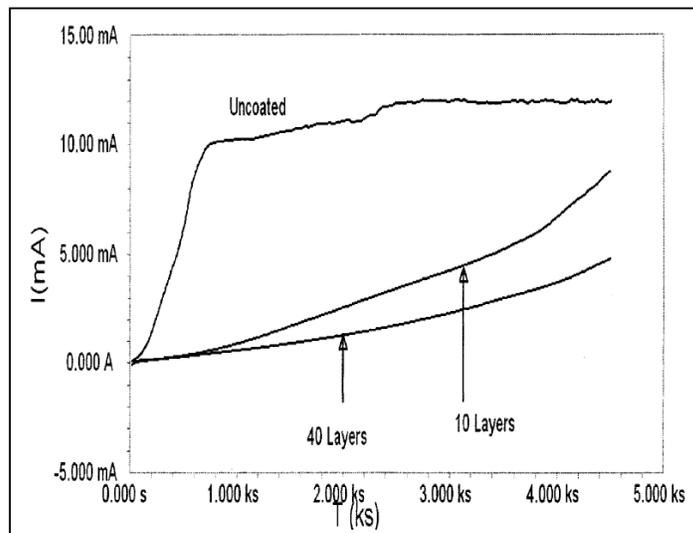
Fig. 15. Potentiostatic scan of uncoated , 10 and 40 layers of PEI/PVS on treated mild steel at -450 mV in 0.7 M NaCl and Ag/AgCl reference electrode.

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