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Multilayer Nano Films for Corrosion Control

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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 (LBL) sequential assembly technique on treated and untreated mild steel wires. Inhibitor was encapsulated between cationic and anionic polyelectrolyte nano films. This paper mainly focuses on the effect of these nano-films of polyelectrolytes with different functional groups on corrosion protection. Weight loss method was used for measuring the corrosion rate of coated and uncoated mild steel substrate. Scanning Tunneling Microscope (STM) and Scanning Electron Microscope (SEM) were used for monitoring the surface morphology of the obtained nano films. Finally, the best efficiency was realized with 40 layers deposited on treated mild steel in the presence of 1mM benzotriazole inhibitor.
Keywords: *Corrosion, Nano films, Nanotechnology*

1. INTRODUCTION

Corrosion can be defined as degradation or destruction of metals resulting from their chemical interaction with the environment [1]. Polyelectrolyte multilayers have been used by CibaVision as hydrophilic coatings on their contact lenses. Another application was the Yasa-Sheet food wrapper, which prevents bacterial and mold build up on fruits and vegetables [2-4]. Layer assembly on surface is not as "new" as the multilayer thin films field. Previous methods of deposition include the Langmuir-Blodgett (LB) technique. LB films have low stability toward external stimuli, such as solvent and temperature changes [4-7]. Other deposition methods include solvent casting and spin coating. LBL 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 [8-12]. Polyelectrolyte multilayers built through LBL assembly can be deposited on several materials. Multilayers can also be assembled on several substrates such as gold, quartz, silicon, germanium, platinum, plastic and etc. [13]. Multilayer systems can be prepared using the layer-by-layer self assembly method. At high salt concentration or at low polymer charge density, the electrostatic repulsion between different electrolyte segments is reduced, thereby favoring adsorption [14-15]. The LBL assembly technique involves alternating rinse of a substrate or a solid support in two oppositely charged polyelectrolytes to remove any extra material that is loosely bound to the surface. It must be noted that multilayers reported in the literature are extending from 10 nm to 10 μm [10, 12, 13-15]. Farhat et. al., deposited thin films of polyelectrolyte complex were on stainless steel wire using (Poly diallyl dimethyl ammonium chloride) (PDADMAC), as cationic

polyelectrolyte, and poly (styrene sulfonate) (PSS), as anionic polyelectrolyte [10].

Several PEMU combinations were assembled and tested by Schlenoff et. al., the used polyelectrolytes were PSS (anionic, water insoluble) and PNO2EPB (cationic, water soluble). There was an observed general trend that the polyelectrolytes were dissolved in organic solvents (hydrophobic) performed better than the water soluble ones. The water insoluble polymer chains created a far less water permeable environment [11].

When the stainless steel wires immersed in salt water the classical behavior of steel in a corroding medium was compared to the behavior of the PEMU film coated wires. All wires were oxidized up to 1.2V. The polyelectrolyte coated wires remained in a metastable phase for much longer than the bare wires; depending on the polyelectrolyte combination used [16]. It is investigated that increasing the ionic character of a highly hydrophobic PE (SPEEK) and also increasing hydrophobicity result in improving corrosion protection. Increasing the hydrophobe contents and sizes beyond a certain limit results in slight, increases in corrosion protection [17,18].

2. EXPERIMENTAL

Mild steel wires with 1.6 mm diameter were polished with emery paper of 800, 1000 and 1200 grit successively, were rinsed with acetone and then were washed with deionizer water prior to the coating and electrochemical experiments. The nano films of polyelectrolytes, starting with the cationic, were deposited on wires using the alternating LBL deposition method with 1 mM polyelectrolyte solution. Aqueous solution of PDADMAC was the cationic polyelectrolyte, and the anionic polyelectrolyte was PSS. PDADMA and PSS with 1mM Benzotriazole inhibitor were used. In the first system three minute immersions in the cationic PDADMA solution followed by 90 second rinsing in deionizer water. Then, three minute immersion in the anionic poly electrolyte (PSS) followed by 90 second rinsing in deionizer water and so on. In the second system the mild steel wires were treated electrochemically after polishing and rinsing with deionizer water to form a base coat. Then three minutes immersion in the PDADMA followed by three minutes immersion in 1mM Benzotriazole inhibitor and after three minutes immersion in the anionic PSS they were immersed by three minutes in the previous inhibitor. Each immersion was followed by 30 second rising in deionizer water.

3. RESULTS AND DISCUSSION

Tafel experiments were carried out in 0.7M NaCl solution with Ag/AgCl reference electrode and scanning rate of 0.166 mV/s for uncoated mild steel wires and for wires coated with 10, 20 and 40 multilayer. Mild Steel wires are treated electrochemically to modify the mild steel surface. This modification prevented the corrosion process which took place during the coating process with polyelectrolytes and increased the adhesion of the formed thin nano film. Corrosion parameters are shown in Tables (1,2,3) and the corrosion efficiency for wires coated with 10, 20 and 40 layers were shown in Tables (4,5,6).

Figures (1,2,3) indicate that the corrosion potential increased as the number of layers increased. Figure (1) shows that the highest value was obtained at 10 layers at which it reached -504 mV. An increase of 88 mV in the corrosion potential for 10 layers was realized compared to the uncoated mild steel. This indicates an improvement in the corrosion protection of the coated mild steel wires. Figure (2) presents that the corrosion potential decreased from -592 mV for uncoated mild steel to -632mV for treated mild steel and then, the corrosion potential increased to reach -581, -534 and -510 mV for wires coated with 10, 20, 40 layers, respectively. Also, Figure (3) shows no significant differences in the Ecorr for treated mild steel coated with 10, 20 and 40 multilayers. The Ecorr shows an increase from -632 mV for treated mild steel to -596 mV for wire coated with 10 multilayers.

Figures (4,5,6) show the variation of corrosion rates with increasing the number of multilayers. Figure (4) shows the effect of the thin nano film on the corrosion rates. It was observed that the corrosion rate for 10 and 20 layers were approximately the same; however, the corrosion rate of 40 layers reached its lower value (5.11 mpy). Although, the corrosion potential and the corrosion rate improve, the obtained thin film has a brown color and can be removed easily from the mild

Table 1: *Electrochemical corrosion Parameters of the system PDADMA/PSS on mild steel.*

Number of Layers	βa V/decade	βc V/decade	E_{corr} (mV)	I_{corr} (μ A)/cm^2	corrosion rate (mpy)
uncoated	0.0999	0.3194	-592	24.9	17
10	0.0527	0.052	-504	19	12.4
20	0.0849	0.61	-549	20.6	13.4
40	0.062	0.208	-535	7.83	5.11

Table 2: *Electrochemical corrosion parameters of the system PDADMA/PSS on treated mild steel.*

Number of Layers	βa V/decade	βc V/decade	E_{corrr} (mV)	I_{corr} (μ A)/cm^2	Corrosion Rate(mpy)
Uncoated	0.0999	0.3194	-592	24.9	17.00
Treated mild Steel	0.0689	0.629	-632	24.4	17.2
10	0.0717	0.524	-581	16.2	10.6
20	0.0673	0.429	-534	13.5	8.8
40	0.0492	0.196	-510	5.5	3.6

Table 3: *Electrochemical corrosion parameters of the systems PDADMA/PSS and 1mM Benzotriazole on treated mild steel.*

Number of Layers	Ba V/decade	Bc V/decade	Ecorr (mV)	I_{corr} (μ A)/cm^2	Corrosion Rate(mpy)
Uncoated	0.0999	0.3194	-592	23.3	17.0
Treated Mild Steel	0.689	0.629	-632	24.4	17.2
10	0.084	0.565	-596	20.2	13.2
20	0.080	0.348	-569	14.1	9.2
40	0.0767	0.261	-565	8.9	5.8

Table 4: *Corrosion efficiency of species coated with multilayers of PDADMA/PSS on mild steel.*

Number of layers	Inhibition efficiency
10	27.1
20	21.2
40	69.9

Table 5: *Corrosion efficiency of species coated with multilayers of PDADMA/PSS on treated mild steel.*

Number of layers	Inhibition efficiency
10	37.6
20	48.2
40	78.8

Table 6: *Corrosion efficiency of species coated with multilayers of PDADMA/PSS and 1mM Benzotriazole on treated mild steel*

Number of layers	Inhibition efficiency
10	22.4
20	45.9
40	65.9

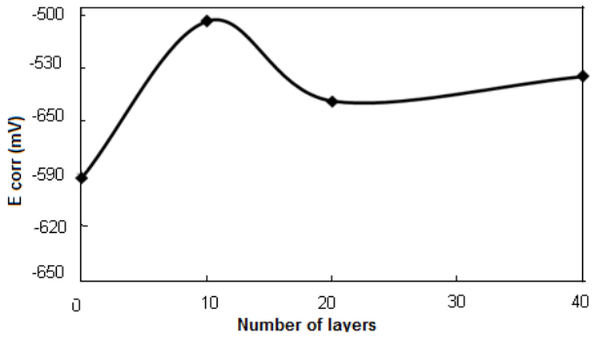

Figure 1: *Corrosion potential for uncoated mild steel and coated with multilayer of PDADMA/PSS.*

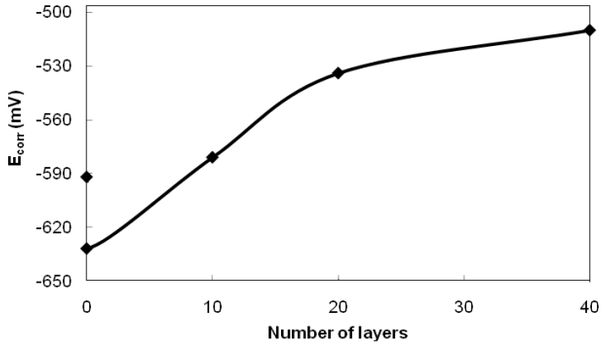

Figure 2: *Corrosion potential for treated mild steel and coated with multilayer of PDADMA/PSS.*

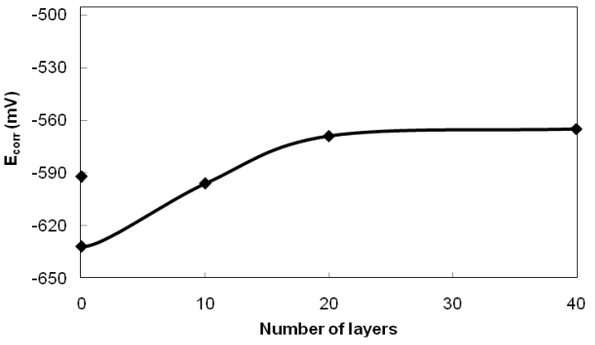

Figure 3: *Corrosion potential for treated mild steel and coated with multilayer of PDADMA/PSS and 1mM Benzotriazole inhibitor*

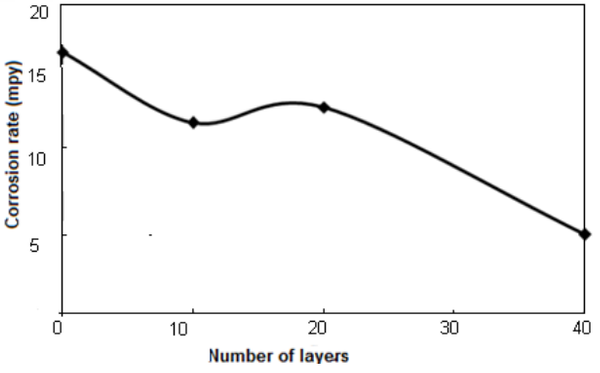

Figure 4: *Corrosion rates in mpy for uncoated mild steel and coated with multilayer of PDADMA/PSS*

steel surface due to their low adhesion. In Figure (5), it must be noted that the difference in the corrosion rates between uncoated and treated mild steel was within 0.2 mpy which indicates that the treatment of the surface has no effect on the corrosion rate. The corrosion rate decreased from 17(mpy) for uncoated mild steel to 10, 8.6 and 3.6 (mpy) for wires coated with 10, 20, and 40 layers, respectively. The thin nano film was obtained by this method has high adhesion and it was difficult to be removed easily from the treated mild steel surface. Figure (6) shows that the corrosion rate decreases with increasing the number of layers which reflects a good corrosion protection. The corrosion rate decreases from 17.2 mpy for the treated mild steel to 13.2, 9.2 and 5.8 mpy for wires coated with 10, 20 and 40 layers of PDADMA/PSS, respectively. The 40 layer of PDADMA/PSS diminish the corrosion rate of the uncoated mild steel by 65.9 %. It is noted that the presence of Benzotriazole inhibitor results in decreasing the effect of anionic PSS, corrosive material, on the mild steel surface; however, it is observed that the pretreatment of the surface significantly increased the adhesion of the multilayers thin nano film and prevents the corrosion process during the coating steps.

Finally, it must be considered that with scanning tunneling microscopy (STM) technique we can monitor the surface morphology for coated and uncoated mild steel samples. The very high vertical resolution of STM is obtained because the tunnel current varies exponentially with the distance between the two electrodes, that is, the metal tip and the scanned surface. The tungsten tips are used for this work. These are etched from tungsten wire with an electrochemical process, for example by using 1 molar KOH solution with a platinum electrode in a electrochemical cell at about 30 V [19]. Figures (7,8) show the surface morphology for uncoated and coated sample using STM, respectively. Now we have a two dimensional view of our sample surface. So, we can

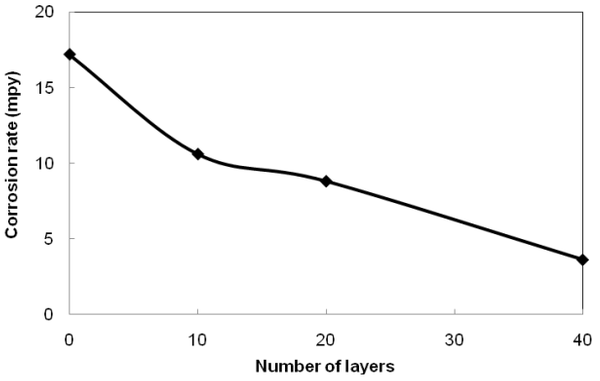

Figure 5: *Corrosion rates in mpy for treated mild steel and coated with multilayer of PDADMA/PSS.*

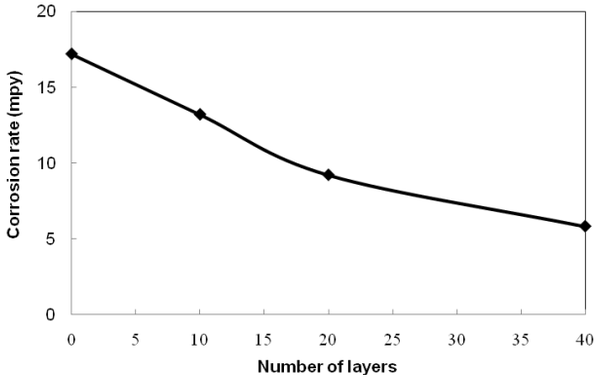

Figure 6: *Corrosion rates in mpy for treated mild steel and coated with multilayer of PDADMA/PSS and 1mM Benzotriazole inhibitor.*

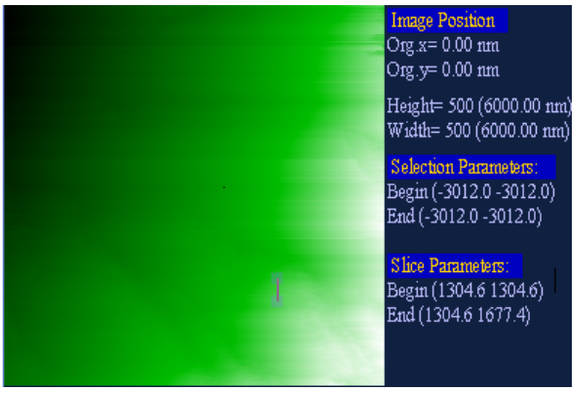

Figure 7: *Morphology of uncoated mild steel samples using STM.*

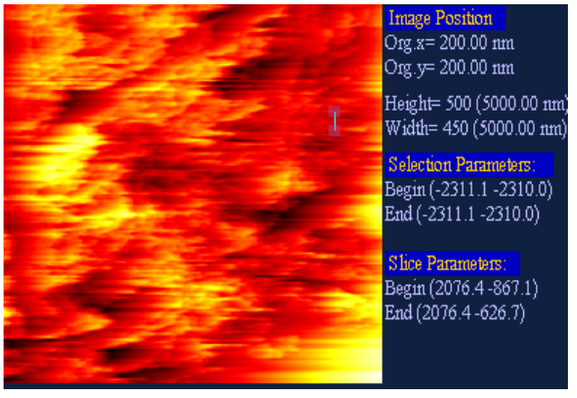

Figure 8: *Morphology of coated mild steel samples using STM.*

analyze surface with additional information. Figures (9,10) show two dimensional view of uncoated and coated mild steel sample. Figure (11) show the microstructures of species coated with multilayers of PDADMA/PSS and 1mM Benzotriazole on treated mild steel by SEM. As shown in this figure, the species that coated with multilayers of PDADMA/PSS and 1mM Benzotriazole on treated mild steel coating has a very good uniformity.

4. CONCLUSIONS

The obtained results show an improvement in the corrosion of wires being coated with different number of layers compared with uncoated samples. The corrosion potential of each coated samples increased significantly with increasing the number layers. That was proved when steel wires were examined. Despite the improvements in the corrosion potential of the coated samples, the proportionalities of increasing the Ecorr with increasing the number of layers were not observed for some systems.

In this work, we demonstrated nanofilm of PEM coating provide substantial corrosion protection of steel in which 87.6% efficiency was obtained with 40 layers of PDADMA/PSS deposited on treated mild steel in the presence of 1mM benzotriazole inhibitor. The immobilized inhibitor sandwiches between Cationic and Anionic polyelectrolytes multilayers prevented the corrosion processes that took place during the coating process. Finally, we obtained that the first and few subsequent layers resulted in sharp reduction in corrosion rate.

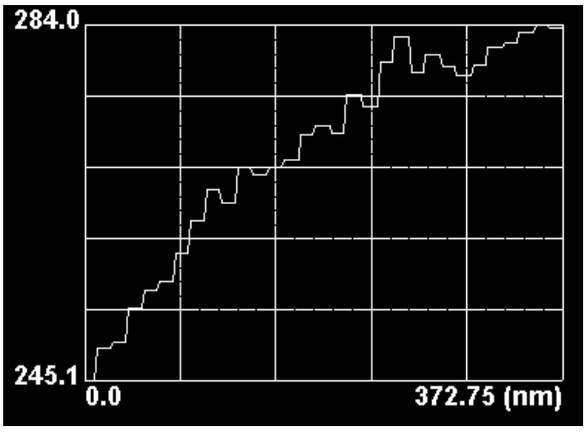

Figure 9: *Two dimensional view of uncoated mild steel sample.*

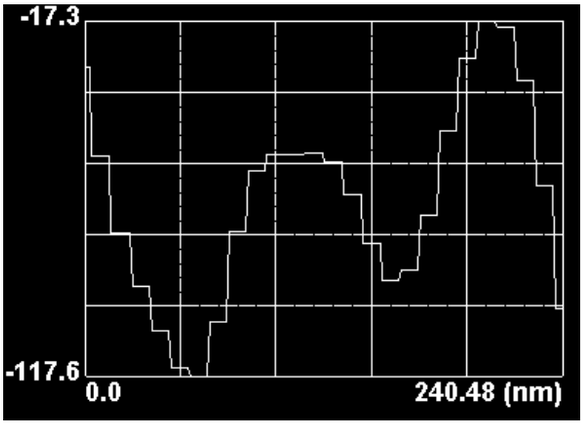

Figure 10: *Two dimensional view of coated mild steel sample.*

Figure 11: *Microstructures (SEM) of species coated with multilayers of PDADMA/PSS and 1mM Benzotriazole on treated mild steel.*

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