

Anticorrosion behavior of deposited nanostructured polythiophene on stainless steel, carbon steel, and aluminum in sea water

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Abstract— In this study adherent films of polythiophene were deposited by electropolymerization of thiophene monomer onto stainless steel 316, carbon steel (C45), and aluminum (6061), the anticorrosion performance in artificial seawater (3.5% NaCl) solution were investigated at four temperatures, namely 20,30,40,50°C using Tafel plots. The FTIR, XRD, TG, AFM, and SEM techniques, were used to evaluate the polythiophene deposited layer, they revealed nanofibers like structures with diameters around 40-50 nm, the thermal stability reach 300°C.

Keywords— polythiophene, electropolymerization, corrosion protection, nanostructure

I. INTRODUCTION

The most interesting property of conducting polymers (CPs) is their high conductivity, which can be changed by simple oxidation or reduction. Conducting polymers usually have good corrosion stability when in contact with solution and in the dry state. In the recent years many papers have reported the use of CPs as materials for anti-corrosion coatings, applied on both ferrous and nonferrous metals, providing a potential cheap alternative to chromium and phosphate treatments and their pollution [1-4]. For long time, polythiophene (PTh) has been widely used in environmentally and thermally stable conjugated polymer materials, Partly because of their good solubility, polythiophenes are among the better characterized conducting polymers have received considerable attention because of their remarkable electronic, magnetic and optical properties and their wide range of potential applications in many areas, such as chemical and optical sensors, light-emitting diodes, displays, photovoltaic devices, molecular devices, DNA detection, polymer electronic interconnects, solar cells, transistors, and corrosion protection [5-7].

PTh can be synthesized using several techniques such as chemical and electrochemical methods [8-11]. The electrochemical method is used more often because it is environmental friendly and presents several advantages, this work focused on the electrochemical methods to apply layers of polythiophene through the electro-polymerization process on some metals and alloys namely carbon steel, stainless steel, and Aluminum to investigate the corrosion protection capability of this coating in saline water at different temperature by measuring corrosion rates and other factors including kinetics and thermodynamics parameters for the bare and coated specimens [12-16].

II. EXPERIMENTAL

2.1 Materials and chemicals;

The metal materials which used in this work are commercially grades of; stainless steel (SS316), carbon steel (C45), and aluminum 6063. All chemicals including; thiophene, acetonitrile, and sodium perchlorate were purchased from Fluka with purity not less than 99%. A sample of Stainless steel, carbon steel and aluminum were cut into a circle shape with a diameter of 2.5 cm using press technique, then a mirror like surfaces were achieved by grinding and polishing using a series of grits of increasing fineness, (120,240,320,600, 800, 1200 and 2000). The samples washed with acetone, distilled water and ethanol finally dried and stored in desiccator.

2.2 Samples coating with Electropolymerized polythiophene

The cleaned polished samples were coated with polythiophene by electropolymerization process using Mlab 200 of Bank Elek.GmbH, Germany via cyclic voltammetry procedure carried out in a three electrode cell using the metal samples as working electrode, platinum as auxiliary electrode and an Ag/AgCl as reference electrode. A suitable solution for electropolymerization of Thiophene were prepared using 0.5M of Thiophene monomer and 0.1M of Sodium Perchlorate as a dopant, acetonitrile used as a solvent, a solution prepared and saved for coating process. The potential was varied between

-100 mV and 2000 mV and scan rate of 40 mVs⁻¹ with 6 to 10 repetitions for depositing PTh, an ideal voltogram and the photograph image of coated samples shown in fig.1 and 2 respectively.

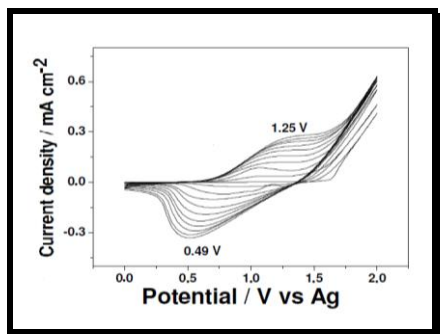


FIG.1 THE CYCLIC VOLTAMGRAM OF THE THIOPHENE SPECIMENS

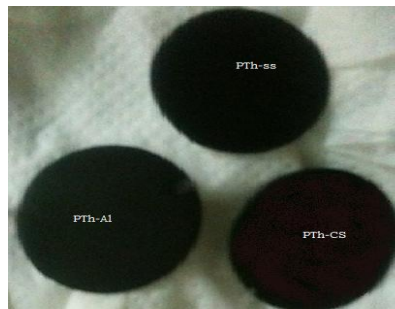


FIG. 2 ELECTROPOLYMERIZED POLYTHIOPHENE COATED

ELECTROPOLYMERIZATION ON CARBON STEEL FOR 10 CYCLES

The deposited PThs layers were characterized using XRD, FTIR, UV-visible, TG, AFM, and SEM.

2.3 Corrosion tests

The corrosion tests were performed using the same potentiostat system used in making polythiophene film, the corrosive media was artificial sea water made by dissolving 35 g of NaCl in 1 liter distilled water. Three electrodes cell used to investigate the corrosion rates and ocp from tafel plots, and pitting probabilities by cyclic scans for the bare and coated samples at four different temperatures; 20, 30, 40, and 50°C.

III. RESULTS & DISCUSSION

3.1 Characterization of deposited polythiophene;

The voltgram of the electropolymerization process shown in fig.1 shows a wide anodic peak at 1.25v which refers to anodic oxidation of Thiophene and formation of polythiophene particles this process exhibited transfer of two electrons per molecule of Thiophene monomer, and it proceeds through a radical coupling mechanism. During the formation, an equal amount of anions provided by the supporting electrolyte are inserted into the polymer to neutralize the positive charge of the PTh chains. At the cathodic region of the voltammogram for the first cycle, a reduction cathodic peak appears which is much lower than the anodic peak. After ten cycles, the cyclic voltammogram shape obtained changed in comparison with first cyclic voltammogram, peaks decreases with the increase of the cycles number, the shape of the voltgrams for all samples are almost identical but the oxidation-reduction potential are somehow changed because of the different over potential of the vsamples , proposed mechanisim[17] shown in fig. 3

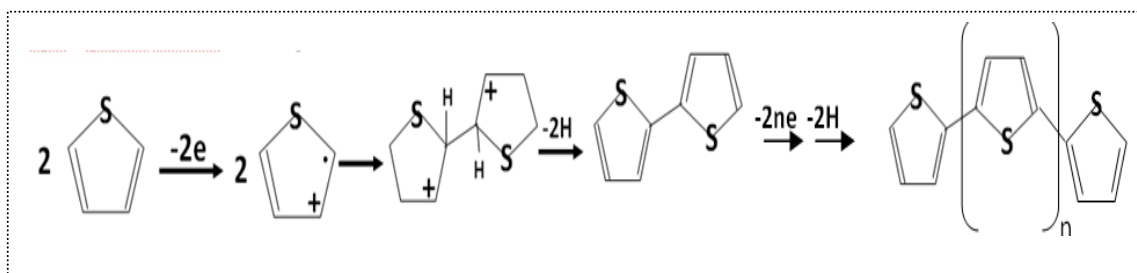


FIG. 3 PROPOSED MECHANISM OF ELECTROPOLYMERIZATION OF THIOPHENE MONOMERS.

Figure 4 show the SEM image of the deposited polythiophene via cyclic electropolymerization it show compact highly ordered homogeneous fiber like nanostructure with particle size around 50nm over a large area of the surfaces

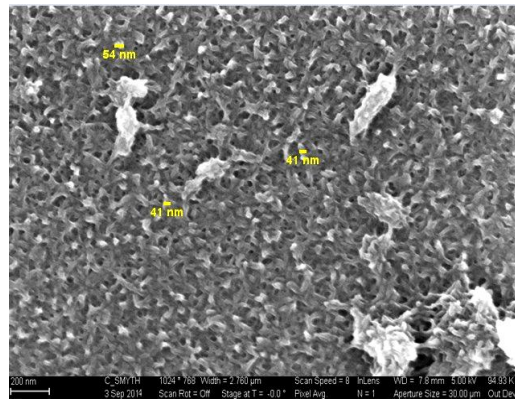


FIG. 4 SEM IMAGE OF ELECTROPOLYMERIZED POLYTHIOPHENE

AFM images for the electrodeposited polythiophene are represented in Figures 5 a, b, c, and d, they show the particle diameter, the surface roughness, the surface waves, and 3D morphology view.

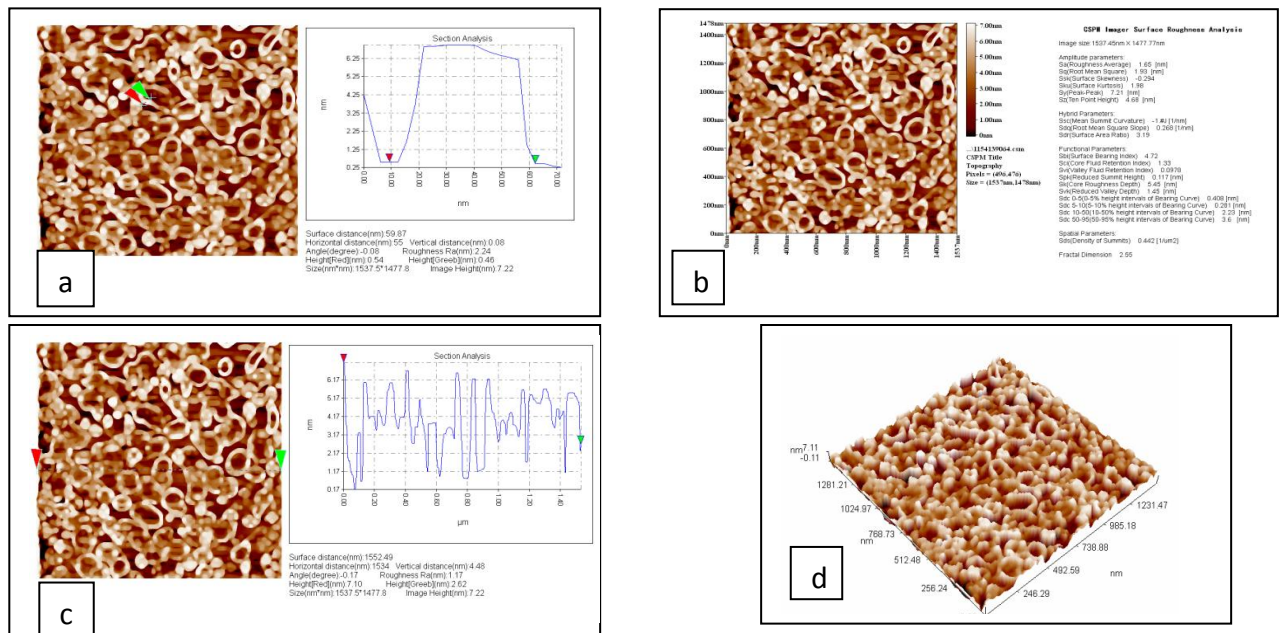


FIG. 5 AFM IMAGES OF ELECTROPOLYMERIZED POLYTHIOPHENE. A-PARTICLE DIAMETER, B-ROUGHNESS REPORT, C-SURFACE WAVE SECTION, AND D-3D MORPHOLOGY .

The crystal structure of deposited Polythiophene was examined by the X-ray diffraction (XRD), figure 5 shows the XRD patterns of PTh, it shows a broad peaks around 2 Theta of 14°, that indicate a weak crystalline structure of the deposited PTh.

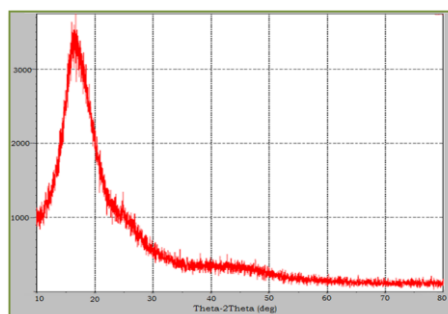


FIG. 6 SHOWS THE XRD OF PTH DEPOSITED ON SS 316.

Figure 7 show the FTIR spectrum in the frequency range ($400\text{-}4000\text{ cm}^{-1}$) of electropolymerized polythiophene, the major peaks at 629 cm^{-1} , 1085 cm^{-1} , 1631 cm^{-1} and 3416 cm^{-1} indicates the presence of C=C, C-S, C-C and C-H bonds in polythiophene, respectively [18]. Which very close to the standard FTIR spectrum of polythiophene and totally different from that of monomer Thiophene, which confirms the successful polymerization of Thiophene monomer and formation of polythiophene. The UV-Vis spectrum of polythiophene was recorded after dissolving it in dimethyl sulphoxide (DMSO), Figure 8. The main charge carriers in polythiophene were polaron and bipolaron. A new broad absorption band related to bipolaron states appeared around $730\text{-}890\text{ nm}$. The absorption bands were obtained approximately at 306 and 377 nm . The band at 306 nm was associated with $\pi\text{-}\pi^*$ inter band transition and band 377 nm was associated with $n\text{-}\pi^*$ transition. Increasing the degree of polymer resulted in a blue shift of λ_{max} , confirmed a shorter conjugation length of the polymer [19].

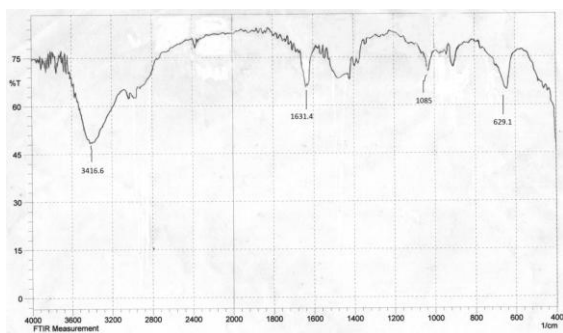


FIG. 7 FTIR SPECTRUM OF ELECTRO DEPOSITED

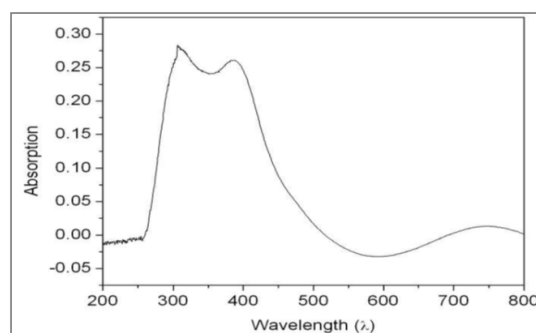


FIG. 8 THE UV-VIS SPECTRUM OF ELECTROPOLYMERIZED POLYTHIOPHENE

The TGA behavior of Polythiophene start with the loss of weight below 100°C , due to the evaporation of solvent and water inside the sample, then dissociation of the oligomers noticed at elevated temperature between 150°C to 400°C , At higher temperature 450°C to 900°C , decomposition of the oxidized polythiophene occurs, figure 9.

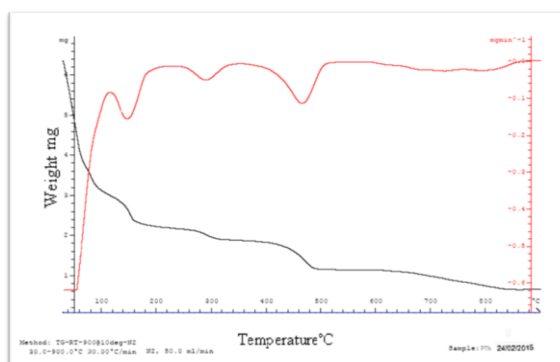


FIG. 9 THERMOGRAVIMETRIC ANALYSIS(TGA)OF ELECTROPOLYMERIZED POLYTHIOPHENE

3.2 Corrosion rates measurements

Electrochemical corrosion kinetics characterized by determining three polarization parameters, corrosion current density (i_{corr}), corrosion potential (E_{corr}) and Tafel slopes, anodic region (β_a) and cathodic region (β_c), by a polarization curve (E vs. i) and the corrosion rate as which is often converted into Faradaic corrosion rate having units of (mm/y). Evaluation of these parameters leads to the determination of the polarization resistance (R_p) as in the following eq (1). [20] ;

$$R_p = \left(\frac{B}{i_{\text{corr}}} \right) \quad \text{Where} \quad B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (1)$$

The corrosion protection abilities in saline water (3.5% NaCl), of all PTh-coated samples were estimated from Tafel extrapolation plots and compared with the uncounted ones. The relation determining the inhibition efficiency (PE%) is shown in eq.2 [21] :

$$PE\% = \left[1 - \frac{i_{corr}}{i_{corr}^0} \right] \tag{2}$$

Where ; i_{corr}^0 and i_{corr} are the corrosion current densities of uncoated and coated specimens respectively

Figures 10 ,11, and 12 show the tafel plots of the coated and uncoated stainless steel, carbon steel, and aluminum in 3.5% NaCl solution respectively ,at different temperatures (20, 30, 40, and 50°C).

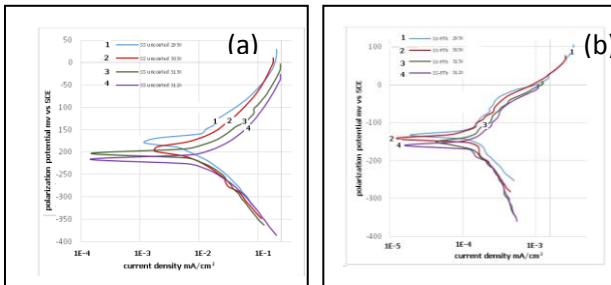


FIG. 10 TAFEL PLOTS OF; A- UNCOATED SS 316, AND B- POLYTHIOPHENE COATED SS 316 IN SEAWATER WATER AT DIFFERENT TEMPERATURES.

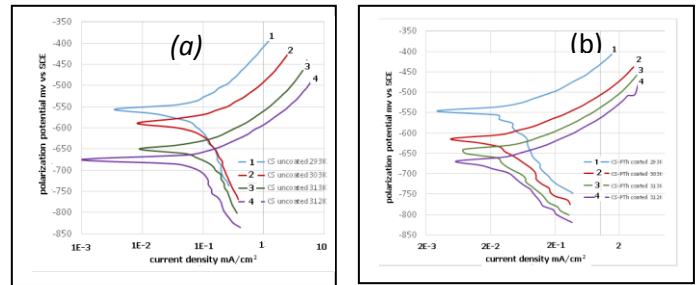


FIG. 11 TAFEL PLOTS OF; A- UNCOATED CARBON STEEL, AND B- POLYTHIOPHENE COATED CARBON STEEL IN SEAWATER WATER AT DIFFERENT TEMPERATURES.

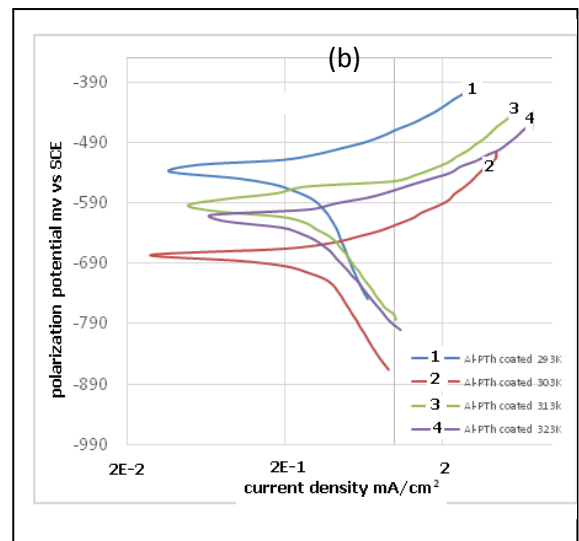
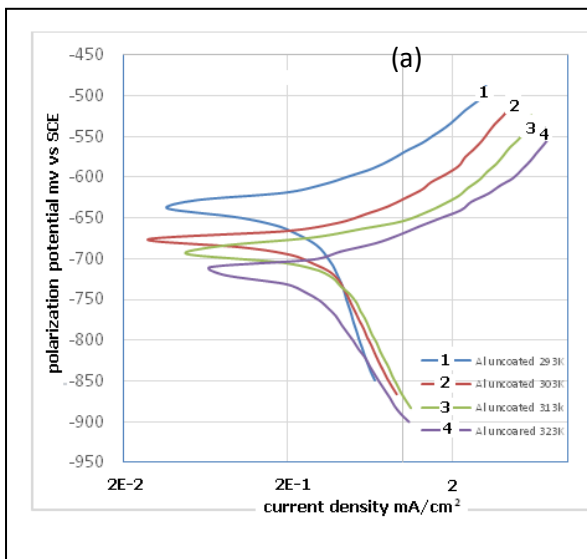


FIG. 12 TAFEL PLOTS OF; A- UNCOATED CARBON STEEL, AND B- POLYTHIOPHENE COATED CARBON STEEL IN SEAWATER WATER AT DIFFERENT TEMPERATURES.

Tables 1 lists all corrosion parameters deduced from above tafel plots for all types of samples.

In general speaking there are small shift in E_{corr} toward less negative values for all PTh- coated samples in comparison with the uncoated ones at various temperature , while the absolute values of tafel slopes b_c and b_a revealed that that the anodic and cathodic reactions affected by different extant.

TABLE 1
CORROSION PARAMETERS FROM TAFEL PLOTS OF SS316, CS, AND AL AT 20,30,40,AND 50°C.

Sample type	Temp	E_{corr} [mV]	I_{corr} ($\mu\text{A}/\text{cm}^2$)	bc [mV/Dec]	ba [mV/Dec]	R_p $\Omega.\text{cm}^2$	CR ($\text{gm}/\text{m}^2.\text{d}$)	CP (mm/y)	Protection efficiency %
SS 316 Uncoate d	20 ⁰ C	-176.6	18.38	-87	77.0	964.9	4.61	0.194	-
	30 ⁰ C	-198.4	25.65	-97.7	96.9	823.5	6.43	0.286	-
	40 ⁰ C	-198.8	35.44	-121.8	72.4	556.3	8.88	0.395	-
	50 ⁰ C	-217.2	50.52	-137.1	109.5	523.2	12.68	0.653	-
SS316 PTh Coated	20 ⁰ C	-131.3	2.98	-98.8	119.2	7871.6	0.74	0.0558	83.78%
	30 ⁰ C	-135.9	5.14	-129.9	96.6	4680.1	1.29	0.0568	79.96%
	40 ⁰ C	-151.8	7.44	-97.4	94.6	2800.7	1.86	0.0633	79.00%
	50 ⁰ C	-157.8	11.5	-120.5	111.9	2190.7	2.88	0.0844	77.23%
CS Uncoate d	20 ⁰ C	-558.4	66.33	-247.4	71.1	361.53	16.6	0.77	-
	30 ⁰ C	-591.0	75.22	-266.8	77.4	346.32	18.8	0.873	-
	40 ⁰ C	-648.7	89.31	-250.0	90.0	321.74	22.3	1.04	-
	50 ⁰ C	-674.8	107.2	-356.1	100.5	263.82	26.6	1.50	-
CS PTh Coated	20 ⁰ C	-545.9	14.23	-142.2	50.2	1529.3	3.54	0.256	78.54%
	30 ⁰ C	-572.8	22.06	-162.6	63.2	1493.3	5.49	0.349	70.67%
	40 ⁰ C	-644.5	30.25	-183.0	67.2	1386.8	7.53	0.386	66.12%
	50 ⁰ C	-671.5	37.36	-253.1	66.6	1142.1	9.30	0.399	65.14%
Al Uncoate d	20 ⁰ C	-687.8	228.77	-338.6	105.7	152.8	18.4	2.49	-
	30 ⁰ C	-676.8	315.54	-419.5	103.7	114.4	25.4	3.43	-
	40 ⁰ C	-693.8	373.53	-411.2	99.8	93.3	30.1	4.96	-
	50 ⁰ C	-715.6	265.6	-312.0	86.1	110.3	21.0	2.89	-
Al PTh Coated	20 ⁰ C	-666.8	47.16	-224.0	41.6	323.0	3.8	0.513	79.44%
	30 ⁰ C	-679.2	54.18	-220.8	43.2	289.5	4.36	0.589	82.82%
	40 ⁰ C	-650.1	76.05	-216.0	61.3	272.6	6.12	0.827	79.46%
	50 ⁰ C	-668.8	77.71	-173.2	53.0	226.7	6.25	0.845	70.74%

The corrosion rates of all coated specimens were decreased and the corrosion protection efficiencies (PE) ranged between 65 to 84 % , the best PE is achieved at SS316 coated samples at 20°C, as shown in the following order;

$$\text{SS316} > \text{Al} > \text{CS}$$

The more confidence explanation of this positive enhancing of the PE may due to the catalytic action of the conducting polythiophene on the metal oxide layer which prevents penetration of the aggressive anions (Cl^-) to the substrate, the PTh serves as a mediator between the anodic current passive layer and the reduction of oxygen in the polymer film[22].

The R_p increased due to the PTh coating which suggest a complete coverage of the metal surface because the PTh is less conductive than the bare metals [23].

The raising of electrolyte temperature from 20 C to 50 C always led to increasing the corrosion rates for all types of tested samples but the PTh coated ones got less increasing values due to the stability of the polymer layer at this range of temperature, another reflected facts are the good stabilities of the PE values with increasing the temperature ,except that of the CS which show less stable values [24].

IV. CONCLUSIONS

Specimens of SS316, AL, and CS were successfully coated with electrolymerized polythiophene by potentiocyclic procedure using thiophene /acetonitrile /sodium perchlorate as electrolyte , the deposited layer have been well characterized using SEM, AFM, XRD, UV, FTIR, and TGA .They revealed compact highly ordered homogeneous fiber like nanostructure with particle size around 50nm over a large area of the surfaces. All coated samples showed good protection against corrosion in artificial seawater, the best was on SS316 and le lowest on CS.

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