Int. J. Electrochem. Sci., 14 **(2019)** 3718 – 3726, doi: 10.20964/2019.04.10

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Capacitor Behavior of Polypyrrole Coated Mild Steel Electrodes

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Received: 26 October 2018 / *Accepted:* 27 December 2018 / *Published:* 10 March 2019

Polypyrrole (PPy) coatings have been deposited potentiodynamically on mild steel surface from 0.3 M aqueous oxalic acid solutions containing 0.1 M pyrrole. Cyclic voltammetry and electrochemical impedance spectroscopy techniques (EIS) were used to investigate the electrochemical properties of coatings in 0.3 M oxalic acid solutions. The performance of the capacitors was tested by using galvanostatic charge-discharge cycling within a potential range from 0.0 to 0.6 V. The maximum specific capacitance of PPy coated mild steel electrode is 8.57 x 10^3 F g^{-1}. The Pyy-coated mild steel system behaved like PAni and not as Ppy, exhibited high capacitance. It can be safely concluded the feasibility of the PPy coated mild steel electrode for use in electrochemical capacitor.

Keywords: Supercapacitor; Polypyrrole; Mild steel electrode; Cyclic voltammetry; Pseudocapacitance

1. INTRODUCTION

Electrochemical capacitors (supercapacitors) have been interesting subjects of much research since they have high power density, high energy density and high cyclability, which make them amenable for use in many advanced power systems. Conducting polymers constitute to take the attraction of many sciences due to their potential supercapacitor applications. Among conducting polymers polypyrrole (PPy) films bearing high charge capacity, low production cost, light weight and electrochemical reversibility and stability are one of the attractive candidates for electrochemical studies [1-5].

Conducting polymers are also very attractive materials to be used as corrosion protective coatings for oxidizable metals such as Fe and its alloys [6-8]. Recently, the electrochemical properties of supercapacitors obtained using conducting polymers on stainless steel electrode have attracted much interest [9-12] especially because of their cost effectiveness and ease of synthesis, which make them amenable in successful commercialization of supercapacitors. Although the applications of polymers coated stainless steels in supercapacitor applications were previously reported [2, 4, 14-16], there is no report on mild steel. Mild steel is a very cheap material extensively used in industrial applications when compared to stainless steel. Moreover, The passive layer obtained via prevasivation process electrochemically on the mild steel surface can provide the appropriate interlayer for electropolymerization [15, 16]. This layer should be tested in supercapacitor applications. The mild steel electrodes in supercapacitor applications can thus be used as a cheap electrode without a corrosion risk.

In this study, the electrochemical properties of PPy electrochemically deposited on prepassivated mild steel, to the best of my knowledge, will be firstly investigated as an electrode material for supercapacitor applications. Some electrochemical techniques like cyclic voltammetry, galvanostatic charge–discharge cycling and impedance measurements were used to support the modified electrode as a supercapacitor.

2. EXPERIMENTAL

Freshly distilled pyrrole (Aldrich) monomer was used and stored under N_2 atmosphere. Oxalic acid dihydrate was purchased from Merck. In all electrosynthesis experiments, doubly distilled water was used to prepare an aqueous solution of the monomer (0.1 M) and oxalic acid (0.3 M). A single compartment three-electrode cell was used for electrochemical measurements. In the cell, a mild steel rod embedded in Teflon holder (0.07 cm^2), a platinum sheet and a saturated calomel electrode (SCE) were used as a working, a counter and a reference electrode, respectively. The working electrode was polished by using a series of wet sandings of different grit sizes (320 to 1200) before each experiment. CHI 660B electrochemical analyzer was used for the electrochemical studies. Electrodeposition was carried out potentiodynamically: first of all, prepassivation process was performed via an anodic scan from -0.5 V to 0.3 V at a scan rate of 4 mV/s and then electrodeposition was done repeating cycling between 0.3 V and 0.8V at a scan rate of 20 mV/s. Cyclic voltammetry, galvanostatic charge/discharge experiments and EIS measurements were carried out in a monomer free electrolyte solution containing 0.3 M oxalic acid. The charge–discharge curves of polymer film coated and uncoated electrodes were obtained at applied current densities of 3, 5 and 7 mA/cm^2 over a potential window between 0.0 V and 0.6 V vs. SCE in 0.3 M oxalic acid solution. EIS measurements were carried out in the frequency range of 10^5 to 10^{-2} Hz with an amplitude of 7 mV at the open circuit potential of substrates under unstirred conditions.

3. RESULT AND DISCUSSION

In order to prepare an oxidized layer, which provides to study at higher positive potential, for the polymerization of pyrrole, the prepassivation process was carried out in 0.3 M oxalic acid containing 0.1 M monomer upon moving from –0.5 V to 0.3 V at a scan rate of 4 mV s^{-1} during anodic scan [15, 16]. After the prepassivation process, electrolpolymerization of polypyrrole (PPy) was carried out between 0.3 and 0.8 V with a scan rate of 20 mV/s [15]. Therefore, more compact layers were obtained by the generation of the passive layer and successfully electrodeposited polymer film on the electrode surface. It can be safely concluded that the process provides both suitable physical barriers and the formation of a polymer film in an oxidized and conductive state as if it had been deposited on an inert metal like platinum [15-17].

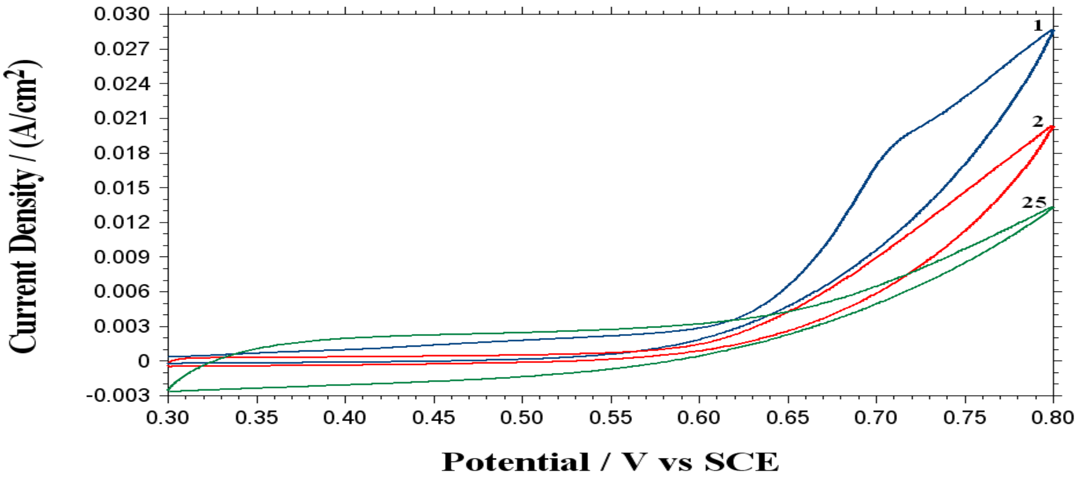

Figure 1. Potentiodynamic polarization curves of a mild steel electrode in 0.1 M pyrrole solution containing 0.3 oxalic acid between 0.3 V and 0.8 V at a scan rate of 20 mV/s. 1st cycle (**1**), 2nd cycle (**2**) and 25th cycle (**25**)

Cyclic voltammograms of the electrolpolymerization of Py on the electrode surface of the mild steel were given in Figure 1. As shown in Figure 1, after initial oxidation of the monomer during first anodic scan, the currents of the oxidation and reduction waves intensified after each successive scan, which can be thought as a fingerprint of the formation of the electroactive PPy film on the mild steel electrode surface.

The current-potential behavior of PPy coated on the electrode surface in 0.3 M oxalic acid is depicted in Figure 2. Voltammetric charge density required for determining the thickness of polymer films was calculated from the area under cathodic peak formed in the second scan in the monomer-free electrolyte solution. Passed charge was found to be 40 mC cm^{-2}, and then, the weight of PPy coating was estimated to be 0.011 mg cm^{-2}. This voltammograms reveal that the electroactivity of PPy film was almost stable in oxalic acidic solution within the applied potential range. The electrochemical stability of materials is of great importance for their possible use in batteries and supercapacitors [18]. As depicted in Figure 2, charge and discharge capabilities of the electrode capacitor carried out at a pseudoconstant rate during the voltammetric cycle [19], which can be proved by the curves showing roughly the rectangular mirror image of each cycle. Deviation from the rectangular form of the curves is a characteristic of an ideal double-layer capacitor [20]. It can be easily seen in Figure 2, both the absence of sharp current peaks and the presence of large magnitudes of current intensities are the characteristic features of the promising materials which can be used in electrochemical capacitors [21-23, 22-28].

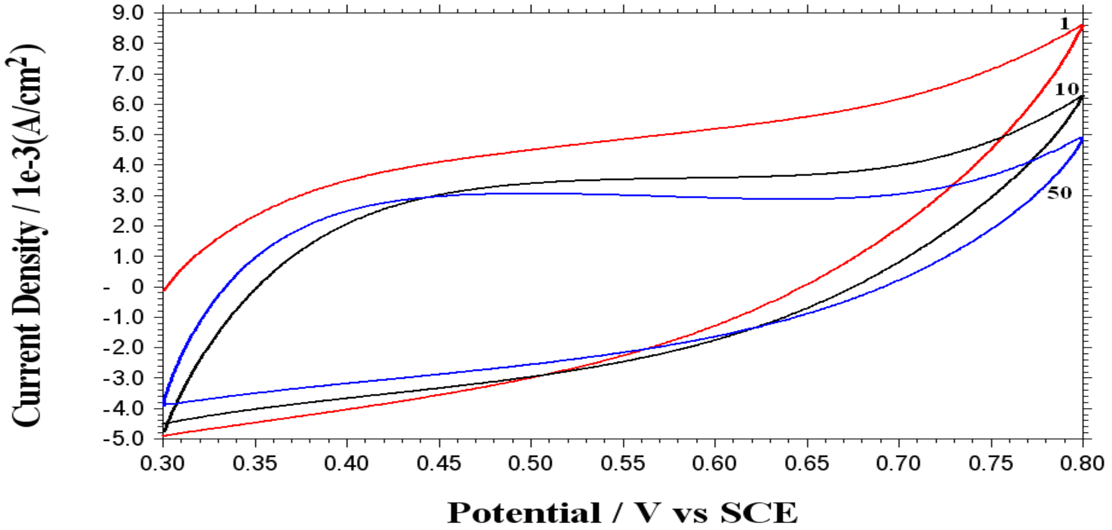

Figure 2. Cyclic voltammograms of PPy film coated on mild steel electrode in the monomer-free electrolyte solution containing 0.3 M oxalic acid between 0.3 V to 0.8 V at a scan rate of 20 mV/s. 1st cycle (1), 10th cycle (10) and 50th cycle (50)

The change in the PPy electroactivity as a function of the area of cathodic peak after each successive cycle proved the electrochemical stability of the film on the electrode surface under ambient conditions (see Figure 3). As shown in Figure 3, after 50 cycles, PPy coated mild steel electrode retains its electroactivity.

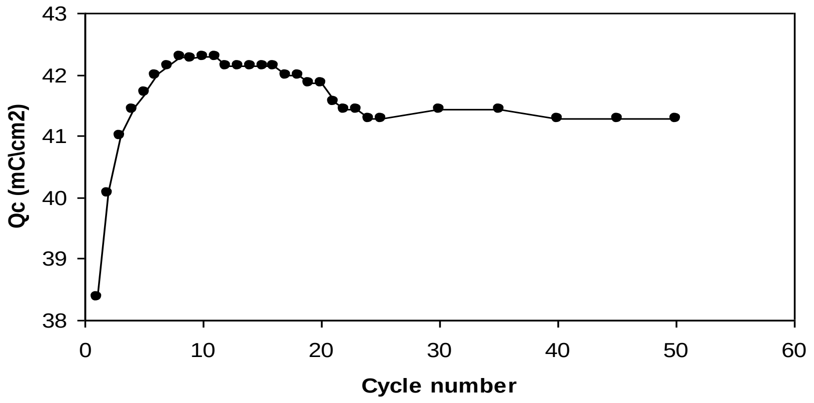

Figure 3. Variation of the cathodic charge density (Q_c) vs. cycle number during polarization of PPy coated mild steel electrode in 0.3 M oxalic acid solution between 0.3 to 0.8 V at a scan rate of 20 mV/s.

Galvanostatic charge-discharge cycling test was carried out in 0.3 M oxalic acid solution for uncoated mild steel electrode before testing the performance of PPy coated mild steel substrate. The galvanostatic charge-discharge curves regarding non-pretreated mild steel electrode were obtained at a current density of 5 mAcm^{-2} between 0.0 V and 0.6 V. As represented in Figure 4, bare electrode undergoes a strong dissolution with an applied current density during about 60 s. During this process, an insoluble and passive iron(II)oxalate film was deposited on the electrode surface due to the interaction between dissolved Fe^{2+} ions and the oxalate ions [8].it may look like potential oscillations, also, the surface protected against dissolution by the protective oxide layer exhibits supercapacitor behavior. As shown in Figure 4, after passivation process, potential value could not be fixed due to very fast charge and discharge process between 0.0 V and 0.6 V and therefore charge–discharge curve exhibited ill-defined curves in very short time intervals.

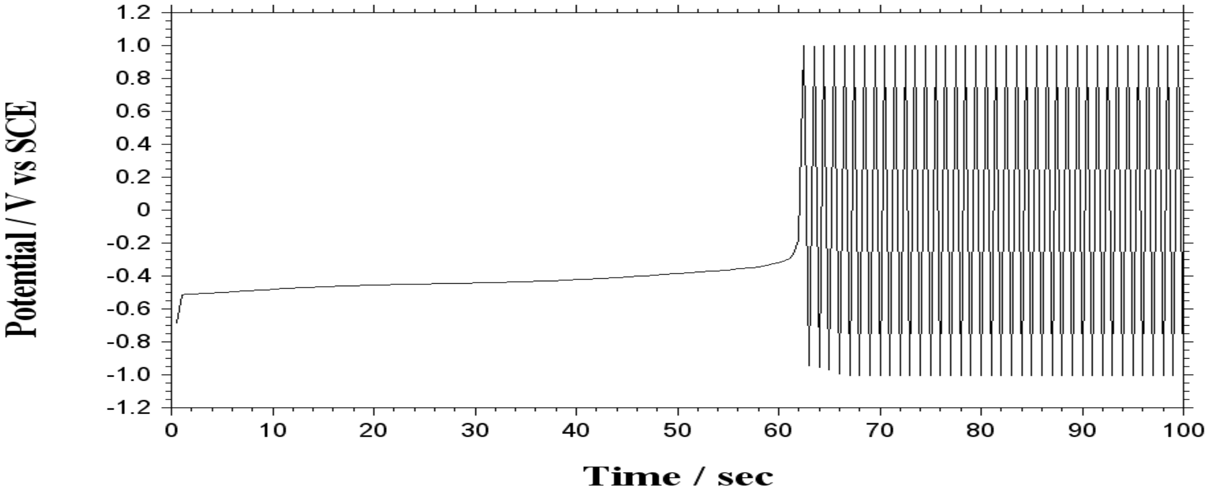

Figure 4. Galvanostatic charge–discharge curves of uncoated mild steel electrode in 0.3 M oxalic acid solution at a current density of 5 mAcm^{-2}.

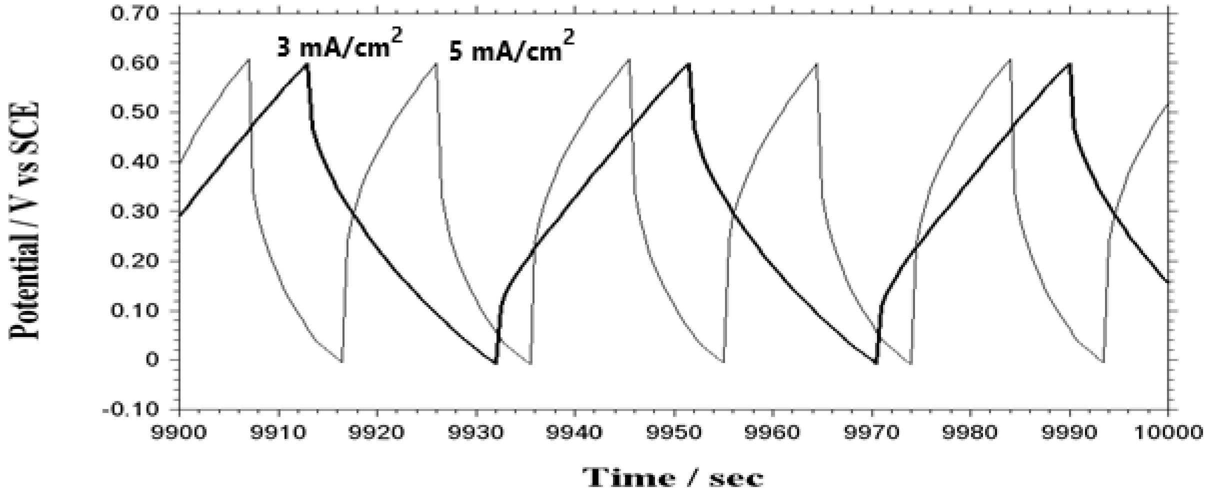

Figure 5. Galvanostatic charge–discharge curves of PPy coated mild steel electrodes at current densities of ━ 3 and —5 mAcm^{-2} in 0.3 M oxalic acid solution.

In order to calculate specific capacitance and to reveal the stability over a number of cycles *and* to decide on the practical feasibility of PPy coated mild steel substrates as a supercapacitance, they were subjected to galvanostatic charge-discharge cycling test in 0.3 M oxalic acid solution. The typical galvanostatic charge-discharge curves were obtained at current densities of 3 and 5 mAcm^{-2} between 0.0 and 0.6 V for PPy coated mild steel electrode. The presence of PPy film on mild steel electrode changed completely the behaviour of mild steel as shown in Figure 5. When compared to other supercapacitor electrode materials such as conducting polymers coated on activated carbon [7], stainless steel [12], indium tin oxide [26] and Ta [27] substrates, PPy coated mild steel electrode represented similar charging/discharging pattern. On the other hand, charging–discharging responses obtained via chronopotentiometry can be used to evaluate the pseudocapacitance value represented as [11];

$$Ccp = i\,[\Delta t/\Delta E]\,m \qquad (1)$$

where *i* for current density, Δ*t* for discharge time, Δ*E* for potential range and *m* for the active weight of the electrode material.

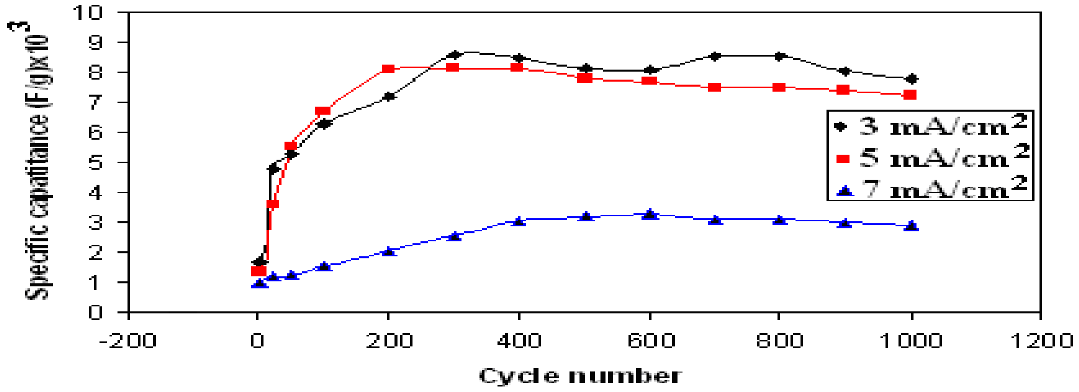

Figure 6. Variation of specific capacitance as a function of cycle number at various current density values of PPy coated mild steel electrodes.

Figure 6 showed the estimated specific capacitance values for 1000 cycles. The maximum specific capacitances of 8500, 8120 and 3210 F/g were calculated for the current densities of 3.0, 5.0 and 7.0 mA cm^{-2}, respectively. The specific capacitances for a current density of 3 and 5 mA/cm^2 are two or three times higher than that for current density of 7 mA/cm^2. The inverse relationship between current density and specific capaciatance can be explained by the enhancement of ohmic drop (related to the electronic and ionic resistance) due to an increase in current density [11]. Also, the specific capacitance values obtained for low current densities can be a result of the whole porosity in the electrode depth [10] which leads to a potential distribution arising across the interelectrode spacing by increasing the current density. According to the data given in Table 1, PPy coated MS electrodes are promising supercapacitor systems. Possible changes in capacitance and durability by placing metal oxides on the PPy-coated MS surface may be the subject of subsequent work.

As can be shown in Table 1, when compared to the literature, PPy coated mild steel electrodes are promising supercapacitor systems. Possible changes in capacitance and durability by placing metal oxides on the PPy-coated mild steel surface may be the subject of subsequent works. As can be seen from Table 1, the specific capacitance values of PAn and PPy films are different. According to the literature, higher capacitance values are obtained from PAni, with compare to PPy [11, 29-33]. As can be also seen in Table 1, the Pyy-coated mild steel system behaved like PAni and not as Ppy, exhibited high capacitance.

Table 1. Various conducting polymers, dopant ions, substrate and their specific capacitances in the literature..

Polymer	**Substrate**	**Electrolyte**	**Specific capacitance (F/g)**	**Reference**
PPy	SS	H_3PO_4	345	[29]
PPy	GC	$NaNO_3$	261	[30]
PPy/RuO_2	Ti	H_3PO_4 buffer	302	[31]
PPy	Ni	Na_2SO_4	420	[32]
PAni	SS	H_2SO_4	2000	[33]
PAni	SS	PTSA	805	[11]

GC: Glassy carbon electrode, PTSA: p-Toluene sulfonic acid

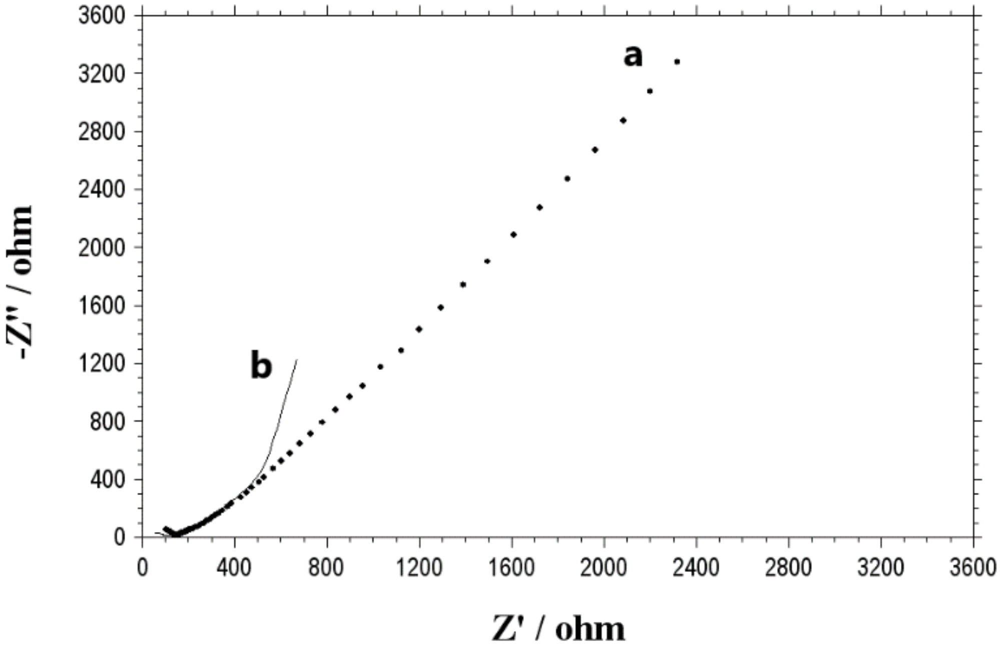

Figure 7. Impedance plots of PPy coated mild steel electrode recorded a) before and b) after galvanostatic charge-discharge test of 500 cycles at a current density of 7 mA cm^{-2} in 0.3 M oxalic acid solution.

The effect of galvanostatic charge-discharge cycling test on PPy coated mild steel substrate was preliminary investigated by EIS. Impedance measurements of PPy coated mild steel electrode were carried out before (Fig. 7a) and after (Fig. 7b) galvanostatic charge-discharge test of 500 cycles at a current density of 7 mA cm^{-2} in 0.3 M oxalic acid solution. As demonstrated in Figure 7, the supercapacitors have a blocking behaviour represented as a straight line in a high frequency region and a capacitive behaviour as represented a semicircle in a low frequency region [5, 9, 11]. Also, the semicircle was related to the charge transfer resistance of the PPy/electrolyte interface and the diameter of this semicircle continue to decrease even after 500 cycles. Therefore, it can be proposed that this behavior is due to a decrease in the electronic and ionic resistance of PPy film. This change can be attributed to an increase in the capaciatnce [5]. The angle observed in the low frequency region on the real axis increases towards ~90° after 500 cycles because of the increase of capacitive properties of

PPy coated mild steel electrodes. These findings can be attributed to the performance of an ideal capacitive behavior.

4. CONCLUSIONS

The feasibility of PPy coated mild steel as an electrode material for supercapacitor was demonstrated. While there was low capacitance behaviour during the initial stage of cycling, substrates were found to be fairly stable over a long cycle-life. The maximum specific capacitance of PPy coated Fe electrode is 8500 F/g. The PPy coated mild steel system has several crucial advantageous as supercapacitor such as inexpensive, easy synthesis, stability, light weight, long cycle life, high specific capacitance values and no corrosion risk in application.

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