Investigation of Polypyrrole-Based Iron Electrodes as Supercapacitors

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Polypyrrole (PPy) was successfully electropolymerized potentiodynamically on prepassivated Fe electrode in an aqueous solution containing monomer and oxalic acid. Electropolymerization of PPy was performed between 0.3 V and 0.8 V vs SCE with a scan rate of 20 mV/s. Electrochemical properties of PPy coated Fe electrode were carried out using cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy. The maximum specific capacitance of PPy coated Fe electrode is 2280 F/g. This indicates the feasibility of the PPy coated Fe electrode for use in electrochemical capacitor. However, the PPy coated Fe system behaved like PAni and not as Ppy, exhibited high capacitance.

1. INTRODUCTION

Electrochemical capacitors (supercapacitors) have been the focus of considerable attention due to their high power and energy density and high cyclability, especially in many advanced power systems. Supercapacitors are generally classified into three types: (i) high surface area materials such as carbon, (ii) metal oxide systems such as RuO_2 and MnO_2 and (iii) conducting polymers-based substrates such as polypyrrole (PPy) and polyaniline [1-3]. Conducting polymer coated electrodes are suitable systems as the active materials in the energy storage devices due to some important properties such as high charge capacity, electrochemical reversibility and stability, good conductivity, low production cost, light weight and stability in air [4-7]. Supercapacitors can be designed in three different types: two electrodes can be p-dopable (type I) or n-dopable (type II) conducting polymers, or one is n- and the other is p-dopable conducting polymer (type III) [4] which is the most favorable type due to energy and power density.

One of the most interesting characteristics of conducting polymers is their electrolpolymerization easily on oxidizable metals in the presence aqueous electrolytes containing monomers [8]. This makes them a good candidate as anti-corrosive coatings for ennoble metals in corrosive environments. Electrochemically deposited conducting polymers on oxidizable metals are promising due to their various advantages such as non-toxic, electrically conducting and good adhesion properties for prospective technical applications [9-13]. The most crucial factors governing the potential applications of PPy coatings are lower oxidation potential of its starting monomer, its high stability and corrosion prevention properties. It is shown that conducting polymer-coated stainless steel can be served for supercapacitor applications. Specific capacitances of about 770-800 F g^{-1} are estimated for PANI-coated stainless steel electrodes [11, 12]. However, Fe is the lightest and cheapest material compared to extensively used mild and stainless steel in industrial applications. Conducting polymer coated on the surfaces of Fe could be possible to examine of this cheap material to supercapacitor application.

Based on the foregoing results, the aim of the present work is to investigate the electrochemical properties of PPy coated Fe electrode for supercapacitors. PPy was successfully deposited via electropolymerization method onto the passivated surface of Fe electrode after the application of electrochemical prepassivation process. Cyclic voltammetry, galvanostatic charge–discharge cycling and impedance measurement are carried out in order to represent its potential use in supercapacitors.

2. EXPERIMENTAL

Pyrrole (Aldrich) monomer was distilled under vacuum and stored under nitrogen atmosphere before use. Oxalic acid dihydrate (Merc) was used as an electrolyte. Electrochemical polymerization studies were performed in an aqueous solution of the pyrrole (0.1 M) and oxalic acid (0.3 M) dissolved in doubly distilled water. Electrochemical measurements were carried out in a single compartment three-electrode system where Fe rod embedded in Teflon holder as a working electrode (0.07 cm^2), a platinum sheet as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode were used. 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 electrochemical studies. Electrosynthesis 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 by repeating cycling between 0.3 V and 0.8V at a scan rate of 20 mV/s. Cyclic voltammetry, galvanostatic charge/discharge cycling experiments and electrochemical impedance spectroscopy (EIS) measurements of the PPy coated Fe electrodes were performed in a monomer free electrolyte solution containing 0.3 M oxalic acid. The charge–discharge curves of the Fe and Fe/PPy 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 amplitude of 7 mV at the open circuit potential of substrates under unstirred conditions.
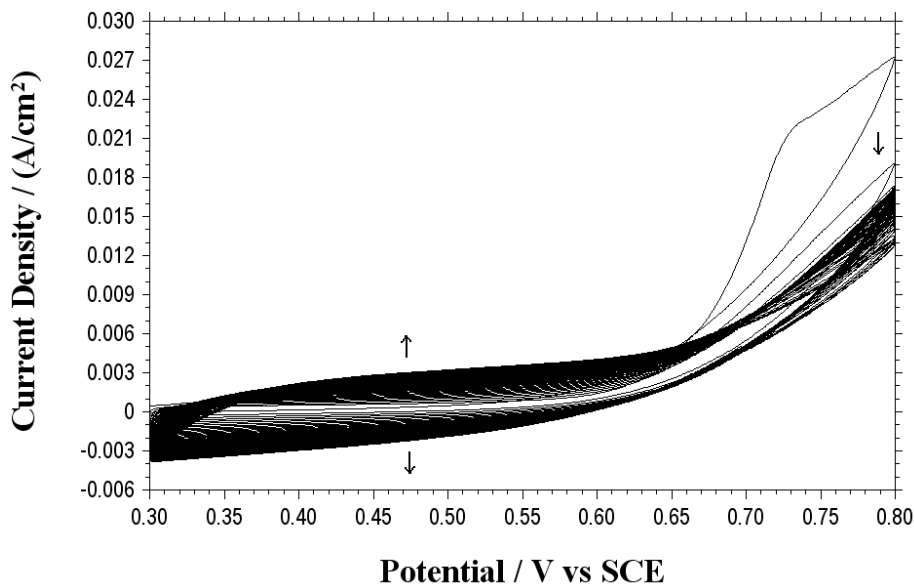
3. RESULTS AND DISCUSSION

Figure 1. Potentiodynamic synthesis of PPy coated on Fe electrode in 0.3 M oxalic acid solution containing 0.1 M Py at a scan rate of 20 mV/s.
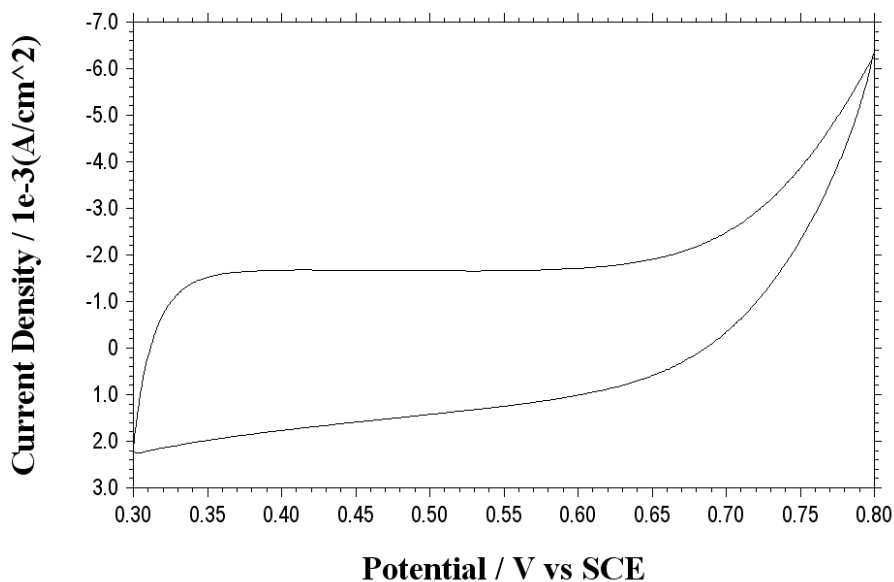

Figure 2. Cyclic voltammogram of of PPy coated Fe electrode in 0.3 M oxalic acid solution at a scan rate of 20 mV/s.

Upon moving from –0.5 V to 0.3 V vs SCE at a scan rate of 4 mV/s, prepassivation process of iron electrode was performed potentiodynamically in 0.3 M oxalic acid solution containing 0.1 M monomer [13,14]. This low scan rate was applied to obtain effectively passive layer on the electrode surface [14]. After that electropolymerization of PPy was carried out successfully between 0.3 V and 0.8 V vs SCE for 50 cycles at a scan rate of 20 mV/s. Figure 1 showed a fingerprint voltammogram for the formation of an electroactive polymer film on Fe electrode surface during repetitive cycling. As expected

from an electroactive polymer film formation, after each successive cycle the currents of redox couple was intensified and the polymer film thickness was increased as a function of scan number [13-15].
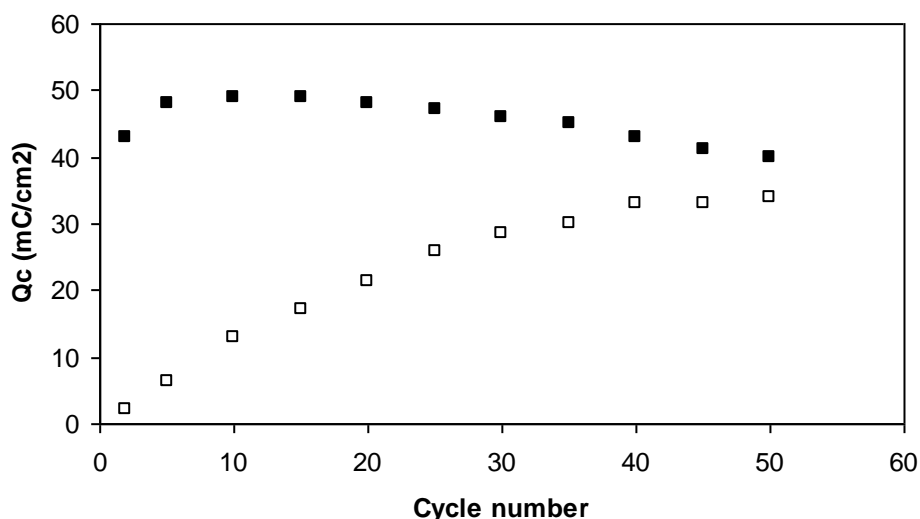

Figure 3. Variation of the cathodic charge density (Q_c) during electrosynthesis of PPy (□) and polarization of PPy coated Fe electrode (■) vs. cycle number.
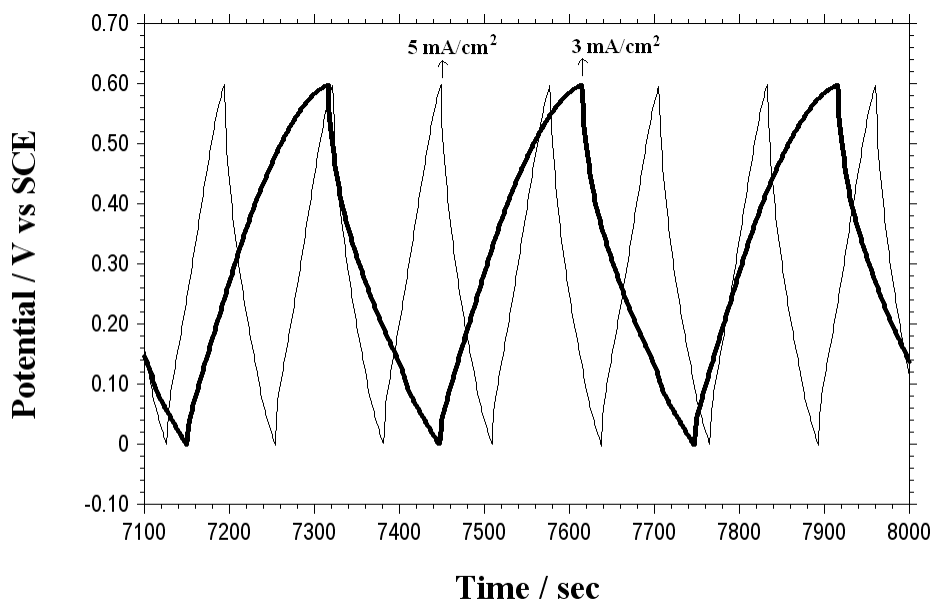

Figure 4. Charge/discharge curves of PPy coated Fe electrodes at different currents (▬) 3 and (—) 5 mA cm^{-2}.

The current-potential behavior of PPy coated Fe surface in electrolyte was shown in the Figure 2. There is no distinct redox peaks and roughly rectangular mirror image of each cycle can be attributed to the capacitive behavior of PPy modified electrode. These two properties indicated the capacitor behavior of the metal/polymer surface [16-18]. Also, the stability of electroactive PPy film on Fe

electrode is protected during successive cycles. Change in the cathodic charge density as a function of cycle number during the electropolymerization was shown in Figure 3. In addition, as shown in Figure 3, the charge (Q_c) passed during the electro-reduction of PPy in a monomer-free electrolyte solution containing 0.3 M oxalic acid was shown that there is no appreciable change in the electrical reduction charge of the electrode and the modified electrode retained its electrochemical stability during each successive cycle. This behavior confirmed the most important sign of the supercapacitor property [6, 19-21].

One of the most important parameters is the performance of the electrode for supercapacitors under ambient conditions. In order to test the performance of the Fe/PPy electrode, galvanostatic charge–discharge cycling experiments were performed. Figure 4 showed cross section of typical constant current charge–discharge curves of the Fe/PPy electrode in 0.3 M oxalic acid solution at applied current densities of 3 and 5 mA/cm^2 over a potential window between 0.0 V and 0.6 V vs. SCE. The shape of curves indicated an ideal capacitor behavior for supercapacitors [6]. Moreover, the charge curves are symetric to discharge curves between potential intervals indicating feasibility of Fe/PPy surface for supercapacitor [7,11] The mass of deposited PPy on Fe electrode was calculated as 0.031 mg cm^{-2}. The specific discharge capacitance (C) of electrodes from discharge segments of the curves was calculated according to Eq. (1);

$$C = (I\Delta t)/(m\Delta V) \tag{1}$$

Where *I* is used for the discharge current, *Δt* is used for the discharge time, m is used for the PPy mass and ΔV is used the voltage difference in discharge segment and the section of IR drop was neglected.

The maximum specific capacitances of the Fe/PPy electrode system are found to be 2280, 1950 and 572 F g^{-1} at current densities of 3, 5 and 7 mA cm^{-2}, respectively (Figure 5).

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

Polymer	Substrate	Electrolyte	Specific capacitance (F/g)	Reference
PPy	GC	NaNO$_3$	261	[14]
PPy	SS	H$_3$PO$_4$	345	[17]
PPy	Ni	Na$_2$SO$_4$	420	[18]
PPy/RuO$_2$	Ti	H$_3$PO$_4$ buffer	302	[19]
PAni	SS	PTSA	805	[11]
PAni	SS	H$_2$SO$_4$	2000	[20]

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

As shown in Figure 5, there is an appreciable decrease in specific capacitance with an increase in current density except for the currrent densitiy of 7 mA cm^{-2}. As can be shown in Table 1, when

compared to the literature, PPy coated Fe electrodes are promising supercapacitor systems. Possible changes in capacitance and durability by placing metal oxides on the PPy-coated Fe 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. PAni is usually obtained with high values, while PPy films is exhibited of lower capacitance values [11, 14, 17-19]. As can be also seen in Table 1, the Pyy-coated Fe system behaved like PAni and not as Ppy, exhibited high capacitance.

The coulombic efficiency, η, was evaluated from the linear part of the charging and the discharging curves using Eq. (2):

$$\eta = t_D / t_C \times 100\% \tag{2}$$

where t_D and t_C denote the times for discharging and charging, respectively. According to the results of estimated coulombic efficiency per cycle shown in Figure 6, it can be safely concluded that the coulombic efficiency retained unchanged even after 1000 cycles.
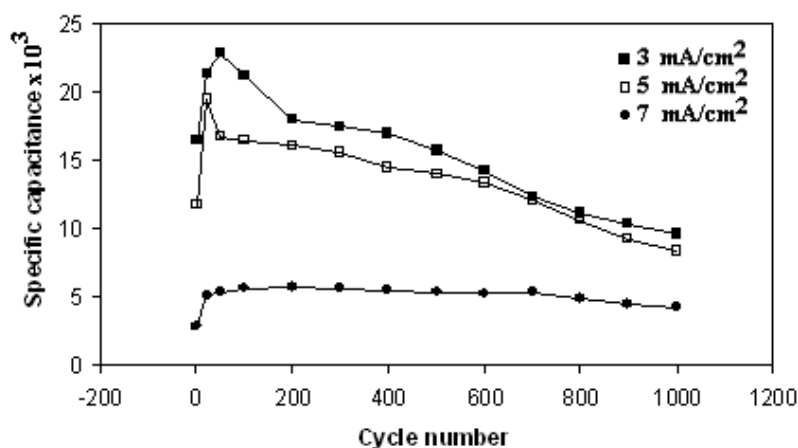

Figure 5. Variation of specific capacitance of PPy coated Fe electrodes as a function of cycle number at applied constant current densities of (■) 3, (□) 5 and (●) 7 mA/cm².
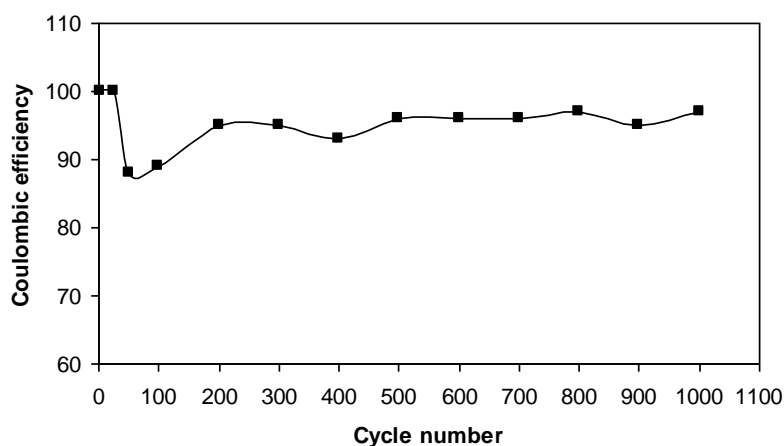

Figure 6. Variation of coulombic efficiency of PPy coated Fe electrodes as a function of cycle number at an applied constant current density of 5 mA/cm².
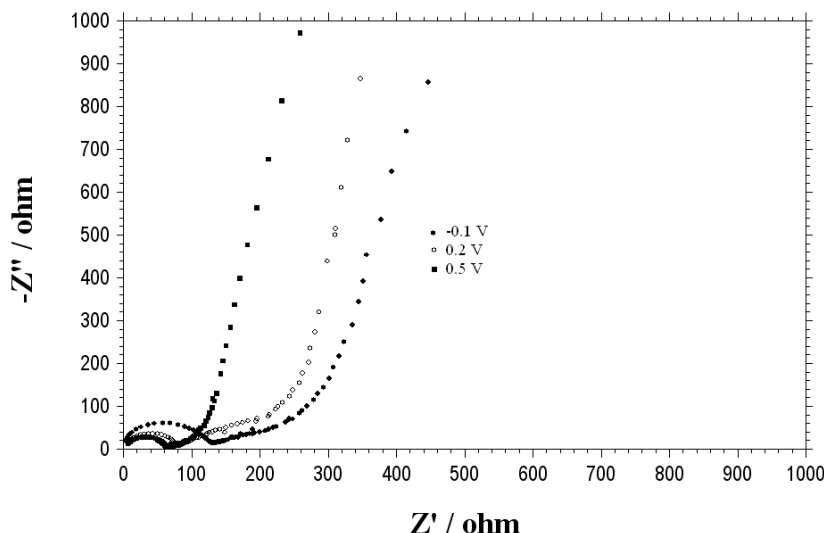
Figure 7. Impedance spectra of PPy coated Fe electrode at various potentials of (♦) -0.10 V, (◇) 0.20 V, (■) 0.50 V vs. SCE in a solution of 0.3 M oxalic acid.

Figure 7 showed the impedance spectra obtained after applied external potentials of (♦) -0.10 V, (◇) 0.20 V, and (■) 0.50 V vs. SCE for 300 s to Fe/PPy electrodes in 0.3 M oxalic acid solution. It is well-known that low time constants are preferred for electrochemical supercapacitors in order to ensure fast charge–discharge characteristics [11]. In order to find the time constant (τ) for the modified electrodes the following Eq. (3) was used:

$$\tau = 1/2\pi f^*$$ (3)

where the frequency (f^*) denotes the maximum of the imaginary component ($-Z$) of the semi-circle. From the Eq. (3), the τ values were calculated in the range of $0.03–9.05 \times 10^{-6}$ s, which are suitable for electrochemical supercapacitors.

As expected from a supercapacitor, the impedance spectra consist of a depressed semicircle at high frequency region and a straight line at low frequency region. The ionic charge-transfer resistance (R_{ct}), which is related with the exchange of ions at the polymer-electrolyte interface for charge compensation, decreased with applied potentials. Under this finding it can be suggested that the entrance of the pores becomes wider as a function of potential, which makes the exchange of ions easier [13]. Also, this is supported by a shift from 45 to 90° of plot of the straight line in low frequency region upon shifting the applied potentials from -0.10 to 0.50 V vs. SCE [20-22]. This behavior indicated an increase in the capacitive behavior of metal/conducting polymer coated surface [23-25].

4. CONCLUSION

The feasibility of PPy coated Fe electrode material for supercapacitors is demonstrated. PPy coated Fe electrode is a promising novel material according to the electrochemical properties obtained

by electrochemical techniques such as cyclic voltammetry, galvanostatic charge-discharge cycling test and EIS. The maximum specific capacitance of PPy coated Fe electrode is 2280 F/g. This indicates the feasibility of the PPy coated Fe electrode for use in electrochemical capacitor. However, the PPy coated Fe system behaved like PAni and not as Ppy, exhibited high capacitance.The PPy coated Fe electrode has several crucial advantageous as a 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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