

Capacitance of the polypyrrole/polyimide composite by electrochemical impedance spectroscopy

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Abstract

Electrically conducting polymers and their composites attract a lot of attention because of their high charge storage ability. As was shown previously, the composite of polypyrrole (PPy) and polyimide (PI) possesses better charge storage properties than pure PPy. Probably the PI matrix protects PPy from oxidative destruction and serves as a high molecular weight dopant. In this paper, the PPy/PI composite was studied by electrochemical impedance spectroscopy at different applied dc polarization potentials. The properties of the coatings were found to differ significantly between pure PI and the PPy/PI composite, depending on the applied potential and on the amount of the conducting polymer. An additional time constant related to the PPy/PI interface appears when PPy is added to PI. The pseudocapacitance of the PPy/PI composite increased significantly with increased cathodic potential. This was explained by additional doping of PPy by the PI matrix.

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1. Introduction

Conducting polymers (CPs) are a type of polymer that contain conjugated double bonds in the backbone of their macromolecule. This allows free movement of electrons within the conjugation length. To be electrically conducting, CPs should be doped with counter ions of the opposite sign, for example, PF_6^- or BF_4^- . Examples of CPs are: polypyrrole (PPy), polythiophene (PTPh), polyaniline (PANI) and polyacetylene (PAC) (Fig. 1). CPs find practical application in industry, electronics, microelectronics and medicine, for example, in corrosion protection [1], light emitting diodes (LEDs) [2], electro magnetic interference (EMI) shielding [3] and drug delivery [4].

Drawbacks of pure CPs are poor mechanical properties of their films and the instability of electronic properties because of the diffusion of the low molecular weight dopant out of the film. Polyimide (PI) can be used as a matrix for the composite with CPs [5] because it has excellent thermal stability [6] and very good mechanical properties and because it serves as a high molecular weight dopant [7].

CPs are under investigation in polymer-based charge storage devices because of their high charge storage ability [8,9]. Capacitors based on CPs show very high values of the capacitance because of doping–dedoping (pseudocapacitance) behavior.

PPy and PANI were reported in the literature as electrodes for supercapacitors [10,11]. PPy is well known to be anodically electroactive while PIs possess cathodic electroactivity [12]. Under applied anodic potential, PPy film can be positively charged (Scheme 1). This process is followed by the formation of a cation radical in the pyrrole chain with corresponding formation of a salt with dopant ion to maintain the electroneutrality.

Pis are capable of showing cathodic electroactivity. Electrochemical reduction of PI is shown in the Scheme 2. Under applied negative potential in the presence of cations in a solution, a PI film can change its oxidation state reversibly, forming anion radicals and dianions. This suggests the possibility to use PIs as a high molecular weight dopant to PPy. PPy/PI composites have been reported to possess very good charge storage properties [7].

In this paper, the charge and discharge properties of the PPy/PI composite are studied by electrochemical impedance spectroscopy (EIS). From the literature it is known that PPy shows high-frequency impedance behavior [13]. The Nyquist plot for PPy shows a semicircle at high frequencies which is attributed to the charge transfer process at the

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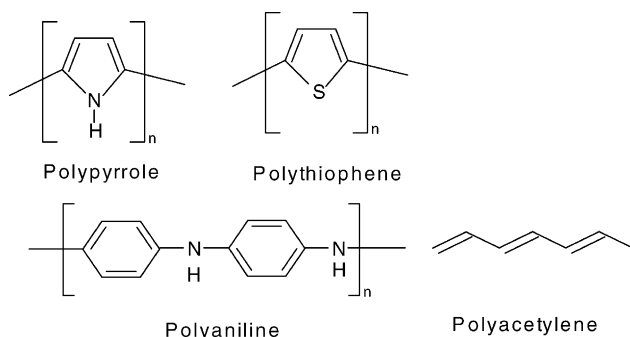
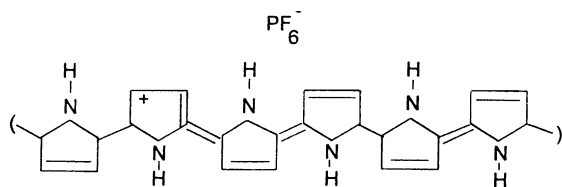


Fig. 1. Examples of conducting polymers.



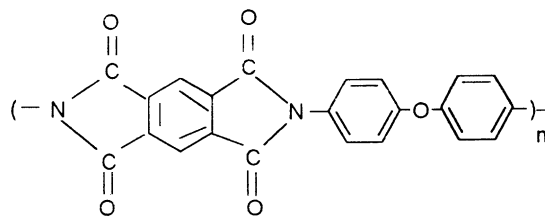
Scheme 1.

metal/electrolyte interface [14–17]. The low frequency behavior of the PPy-coated electrode shows a pseudocapacitive behavior consistent with the charge–discharge behavior of the polymer film through electron injection at the metal/film interface and simultaneous counter ion exchange at the film/electrolyte interface [18]. The advantage of using EIS in the study of the capacitance is the possibility to apply different dc polarization potentials and therefore to study the properties of the composite film at different levels of oxidation and reduction. In this paper, we report the results of the EIS study of a PPy/PI composite, composed of varying amounts of PPy, at different applied potentials.

2. Experimental

2.1. Samples preparation

A solution of poly(amic acid) of pyromellitic dianhydride 4,4'-oxydianiline (Scheme 3) in dimethylacetamide (DMAc) was cast and dried on an ultrasonically cleaned stainless steel (SS) surface. The solid content of the PAAc



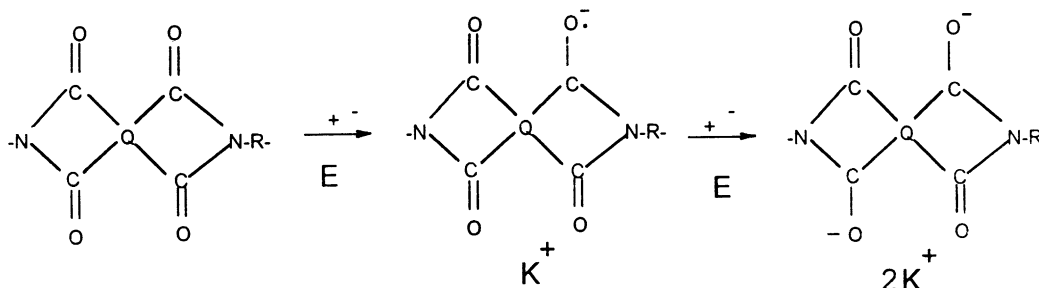
Scheme 3. Pyromellitic dianhydride 4,4'-oxydianiline.

solution was varied in order to obtain the desired film thickness in the range from 10 to 20 μm . Conversion of PAAc to PI (imidization) was performed by immersing the PAAc-coated electrodes into a mixture containing pyridine and acetic anhydride [19]. An electrode coated with a PI film adhered to its surface was subsequently used as the working electrode.

PPy was electrochemically deposited onto a PI-coated SS surface to form the PPy/PI composites as described in [20]. Electrodeposition of PPy was performed in a one-compartment electrochemical cell at a current density of 1 mA/cm^2 . The electrochemical cell consisted of working electrode (PI-coated stainless steel), stainless steel counter electrode and saturated calomel (SCE) reference electrode. Pyrrole concentration was 0.05 M, potassium hexafluorophosphate (KPF_6) in concentration 0.01 M was used as the electrolyte and the dopant, acetonitrile (AN) was used as a solvent. All chemicals except PAAc were purchased from Aldrich and used without further purification. PAAc was obtained from the DuPont chemical company. After electrodeposition of PPy, the PPy/PI composite film was kept on the same electrode. It was rinsed in AN and then transferred to the EIS cell.

2.2. Electrochemical impedance spectroscopy

EIS was performed by using a SR10 DSR electrochemical spectrometer connected to a lock-in amplifier with a frequency range of 0.05 Hz to 100 kHz. A 1 cm^2 SS plate was used as the working electrode, while a graphite cylinder was used as a counter electrode. A saturated calomel electrode was used as a reference electrode. The solution consisted of potassium hexafluorophosphate at a concentration of 0.01 M that served as dopant and electrolyte, dissolved in AN. EIS



Scheme 2. Electroactivity of polyimide.

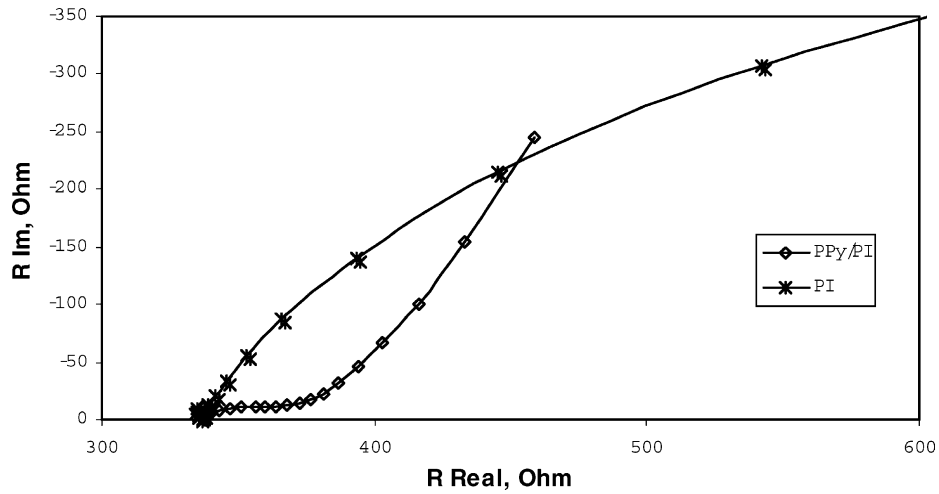


Fig. 2. Potentiostatic EIS of PI film and PPy/PI composite film, Nyquist plot (0.5 mA/cm², 100 s).

was carried out at different dc polarization potentials using 100 mV ac.

$$R_{re} = \frac{1}{\omega C}$$

2.3. Calculation of the capacitance

The capacitance (*C*) of the films was estimated from the following expression:

where ω is the frequency and R_{re} the film resistance.

Graphically, capacitance can be obtained from the Bode plot from the intersection of log modulus *R* versus log *F* curve, with 1/2 π Hz line.

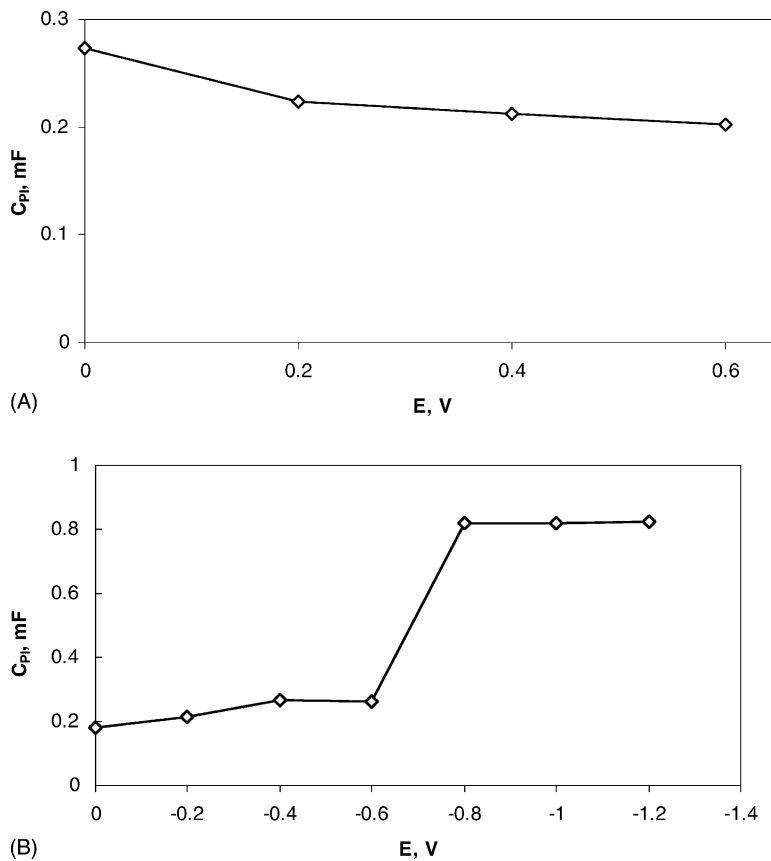


Fig. 3. Capacitance of PI film as a function of potential vs. SCE reference electrode: (A) positive potentials; (B) negative potentials.

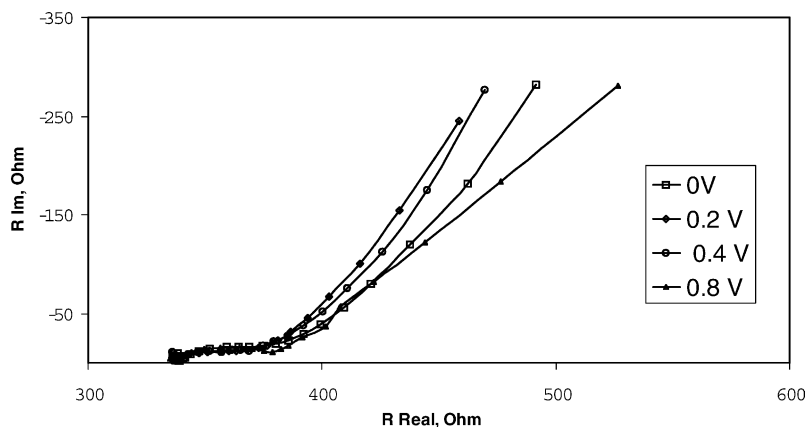


Fig. 4. Potentiostatic EIS of PPy/PI composite ($E_{dc} = 0-1.0$ V vs. SCE).

3. Results and discussion

3.1. Structure of the interface

Fig. 2, top curve, shows the Nyquist plot for a freestanding PI film. The curve consists of a one half of a semicircle, which is typical for polymer-coated electrodes with high ion permeability. The bottom curve in Fig. 2 shows the Nyquist plot for the PPy/PI composite. The PPy/PI composite shows a part of a high frequency semicircle which is due to the interface and a part of the semicircle that is due to PI film.

The equivalent circuit model for pure PI film includes the capacitance of PI film C_{PI} and the resistance of PI film R_{PI} connected in parallel. The resistance of the solution R_S (of the order of 30Ω) is much less than R_{PI} (of the order of 1000Ω).

The interface formed between PPy and PI layer has low resistance to ions at high frequencies because of its capacitive properties, but high resistance at low frequencies. Its equivalent circuit includes the PI part that is same as previous case connected in series with the equivalent circuit for the PPy/PI composite. The PPy/PI composite has the capacitance $C_{PPy/PI}$ and the resistance $R_{PPy/PI}$ that is the polarization resistance.

3.2. Behavior of pure PI film

The Nyquist plot of the PI film shows uncompleted semicircles at both positive and negative potentials. An uncompleted semicircle is typical of a non-coated metal electrode and may be due to the double electric layer (DEL) [21]. The shape of the Nyquist plot for PI changes with changing polarization potential of the PI. Increased diffusion of ions at low frequencies occurs at $+0.6$ V versus SCE. In general, the shape of Nyquist curves at cathodic potentials resembles those for anodic potentials.

3.3. Effect of the potential

Fig. 3(A) shows that the capacitance (C) of a pure PI film, as a function of increased positive dc electrode potential,

lightly decreases. The capacitance of pure PI film-coated electrode in a solution at positive electrode potentials is due to the DEL (ultracapacitance). The behavior of the capacitance with changed positive potential is possibly influenced by the broadening of the double electric layer at the PI/solution interface. The reasons for this phenomenon are not clearly understood.

A step increase in the capacitance has been observed with the increased absolute value of the negative potential. This process is shown in Fig. 3(B). It is known, that at -0.6 to -0.7 V versus SCE, reduction of PI occurs [12]. Probably, a

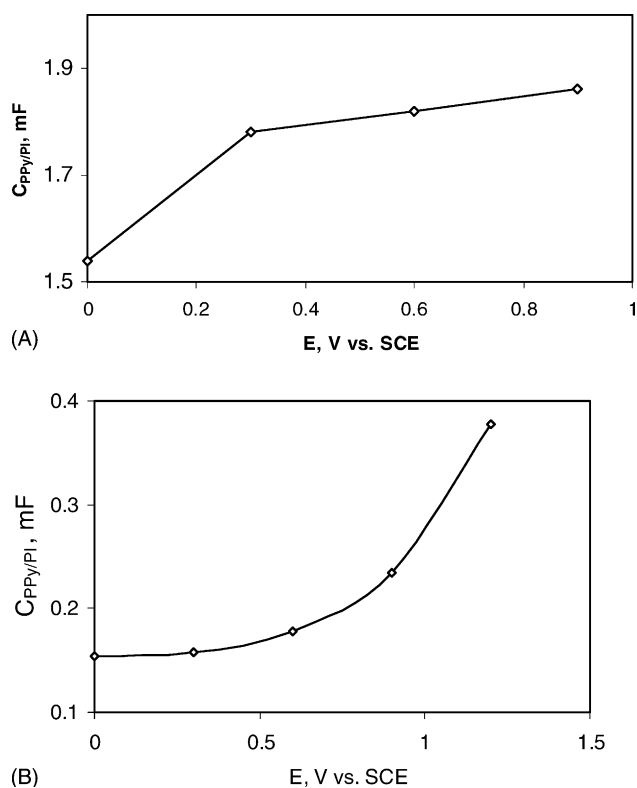


Fig. 5. Capacitance of PPy/PI composite at anode potentials: (A) cathode potential; (B) 0.01 M KPF_6 in AN.

component of a capacitance arising from doping (pseudo-capacitance) becomes dominant over the component that is arising from double layer.

3.4. The polypyrrole/polyimide composite

Fig. 4 shows the EIS data for the PPy/PI composite as a function of applied positive potential in the potential range of 0.0–1.0 V versus SCE. The curves indicate the presence of an additional interface caused by the appearance of PPy. The capacitance $C_{PPy/PI}$ increases with the increase of positive potential Fig. 5(A), possibly because of increased pseudocapacitance.

Fig. 5(B) shows the behavior of the capacitance $C_{PPy/PI}$ of the PPy/PI composite films at negative working electrode potentials. The capacitance increases exponentially with the increase of the absolute value of the potential. This process is stopped by delamination of the composite film from the electrode surface that occurs at high potentials.

As shown in the experimental data, the capacitance of the PPy/PI composite at negative electrode potentials behaves differently from positive potentials. At negative potentials, the PI matrix is much more electroactive than at positive potentials and the activation energy for the formation of the PPy/PI complexes is less. It is assumed that the value of pseudocapacitance is proportional to the amount of dopant. Dopant concentration (N) depends on the activation

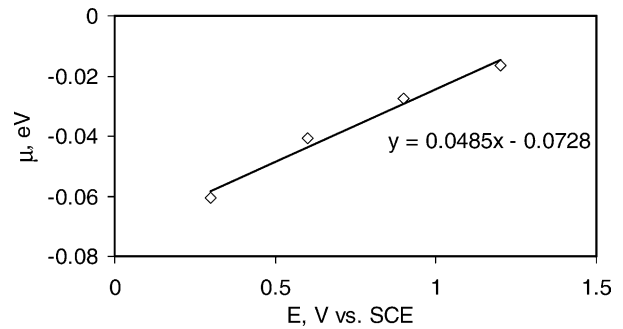


Fig. 6. Activation energy for ion movement as a function of applied potential.

energy of formation (μ) and applied potential (E) as $N \sim \exp[E - \mu]/kT$, where k is the Boltzman constant and T is the absolute temperature.

By plotting $\log(C/C_0) kT$ versus E (Fig. 6), the activation energy for formation of PI^- complexes μ can be determined from the intersection of the line with the $E = 0$ V axes. Value of μ was found to be equal to 0.0728 eV.

3.5. Effect of polypyrrole

Fig. 7 shows the Nyquist plots for the composite as a function of amount of PPy. The capacitance of PPy/PI coating depends on the time of deposition of the conducting polymer (Fig. 8). The capacitance for pure PI was

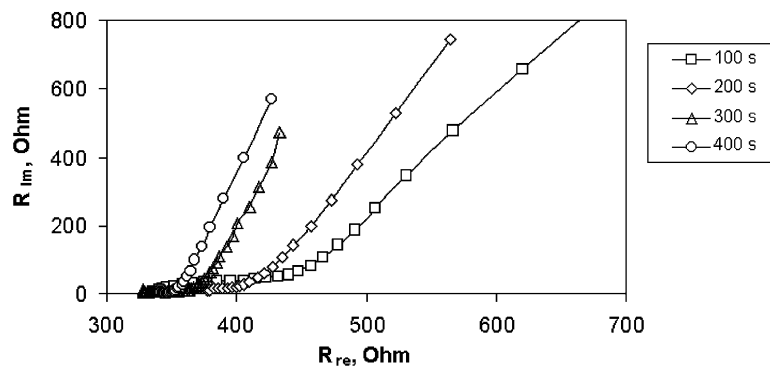


Fig. 7. Potentiostatic EIS of PPy/PI composite at different times of deposition of PPy ($E_{dc} = 0$ V versus SCE (0.01 M KPF_6 in AN)).

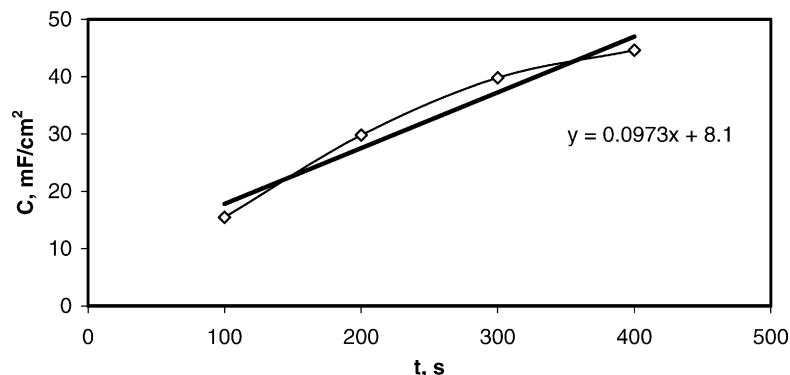


Fig. 8. Capacitance of the PPy/PI composite as a function of time of PPy deposition (0.01 M KPF_6 in AN).

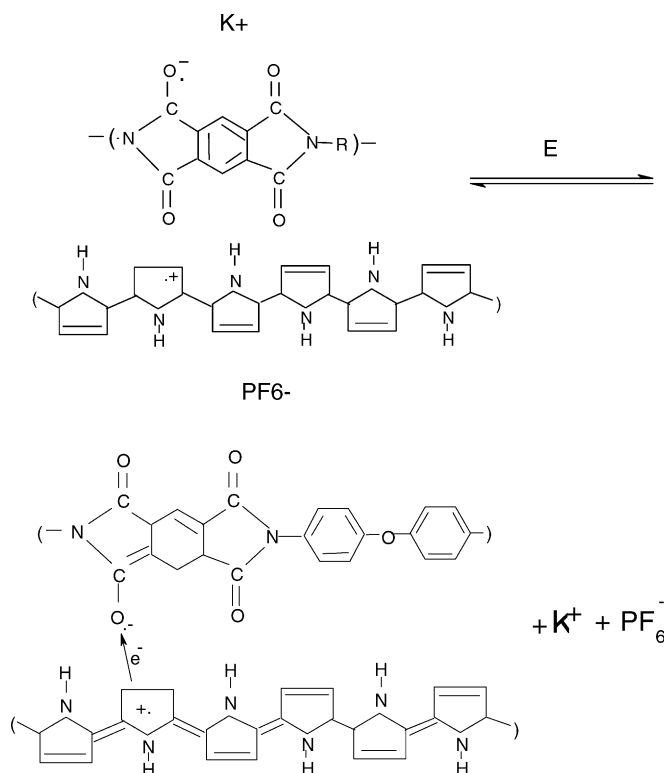
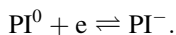


Fig. 9. Formation of complexes with charge transfer in PPy/PI composite.

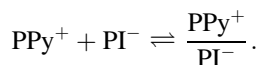
determined to be 8.1 mF/cm^2 from the intercept of the C versus t curve with the $C = 0$ axes. When the amount of PPy increases, the capacitance increases because of the contributing PPy/PI interface. Probably the concentration of PPy^+/PI^- dipoles increases with the increased PPy concentration, which result in the increased pseudocapacitance.

Electroactivity of the PPy/PI composite that contributes to the pseudocapacitance occurs in several steps (Fig. 9). When a negative potential is applied, PI becomes negatively charged with electrons that it receives from the working electrode:



An excessive electron on change PI is possibly compensated by positively charged PPy.

Then, electrostatic coupling occurs in the composite:



This electrochemical reaction is followed by the release of low molecular weight dopant into the solution.

4. Conclusion

The capacitive behavior of a PPy/PI composite was studied by the EIS technique. The results show a high pseudocapacitance per unit area for the composite. Behavior

of the PPy/PI composite at cathodic and anodic potentials essentially differs. At cathodic potentials, where PI is electroactive, an exponential dependence of the capacitance on the applied potential was observed, while a small increase of the capacitance was observed at anodic potentials. The doping of PPy is believed to be responsible for the increase of the pseudocapacitance of the composite at negative potentials.

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