

Electrochemical Impedance Spectroscopic Study of Polyaniline on Platinum, Glassy Carbon and Carbon Fiber Microelectrodes

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In this study, aniline (ANI) was electropolymerized on three different electrodes; platinum (Pt), glassy carbon (GC), and carbon fiber micro electrodes (CFME) in acid aqueous solution (0.5 M H₂SO₄) by cyclic voltammetry (CV). Electrode / PANI / electrolyte system was studied by electrochemical impedance spectroscopy (EIS). The results indicate the choice of electrode has a little effect on anodic (E_a) and cathodic peak potentials (E_c) during electropolymerization process. An equivalent electrical circuit (R(Q(R(C(R(C(RW)))))(CR)) was proposed for PANI on three different electrodes. The highest low frequency capacitance (C_{sp}=120 mF / cm²) was obtained for PANI / Pt electrode compared to PANI / CFME (239.1 μF / cm²) and PANI / GC (38.9 μF / cm²) electrode. However, the highest double layer capacitance was obtained for PANI / CFME (C_{dl} = 190.9 mF / cm²) than Pt electrode (58.2 mF / cm²) and GC (24.3 mF / cm²).

Keywords: Polyaniline, carbon fiber microelectrode, electropolymerization, electrochemical impedance spectroscopy, equivalent circuit.

1. INTRODUCTION

Electrochemical capacitors (ECs) have been vigorously developed due to the increasing need for energy storage systems capable of providing electricity with high power density and/or pulse power [1]. In recent years, porous carbon is the most frequently used electrode material for supercapacitors [2,3,4]. Among the different polymers, PANI films appear to be attractive candidates for electrochemical studies due to the satisfactory stability in different aqueous electrolytes as well as to the reversibility of the first doping-undoping process [5]. The oxidized and reduced states of PANI films, including the effect of the dopants and electrolytes effects have been extensively studied [6,7,8]. Different kinds of monomers and their copolymers (i.e., pyrrole [9,10,11,12,13], carbazole [14,15,16], N-vinylcarbazole [17], thiophene [18], ethylenedioxythiophene [19] were previously electropolymerized

by CV method on Pt, or GC, or CFME electrodes. Among the carbon substrates, carbon fiber has been used for the deposition of conducting polymers[20,21,22,23].

Electrochemical impedance spectroscopy (EIS) seems to be a valuable technique for determining the properties of PANI films and the analysis of data affords information on charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and specific capacitances (C_{sp})[24]. For the oxidized PANI thin film electrodes in acid electrolyte solutions impedance spectra (IS) measurements were performed at frequencies up to 10^4 – 10^6 Hz using conventional three-electrode electrochemical cell[25,26].

Capacitive behavior of PANI film coated carbon fiber microelectrode[27] has been shown before. Electropolymerized ANI on mesophase pitch based carbon foam has been investigated, the effect of scan rate, and concentration were studied on the electrochemical properties of modified carbon foam electrodes. In this work, the polymerization of ANI was achieved electrochemically onto three different electrodes (Pt, GC, and CFME), and electrochemical impedance behaviors of these thin films on different substrates were studied comparatively.

2. EXPERIMENTAL PART

2.1. Materials and Instrumentation

Aniline (ANI) was obtained from Aldrich. Sulphuric acid (H_2SO_4) was obtained from Alfa Aesar. All chemicals were high grade reagents and were used as received.

Cyclo voltammetric coating of ANI was carried out by a Princeton Applied Research (PAR) Parstat 2263 potentiostat, which is a self-contained unit that combines potentiostatic circuitry with phase-sensitive detection. The potentiostat connected to a Faraday cage, BAS cell stand C₃. A three-electrode system was comprised of a Pt, GC, or CFME as the working electrode, a platinum wire electrode as the counter electrode, and a silver wire as the pseudo reference electrode. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene / ferrocenium (Fc/Fc^+) couple in the electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were carried out in an air-conditioned room at 20 ± 1 °C using a conventional three electrode cell configuration. The electrochemical cell was connected to a Potentiostat (PAR 2263) with interfaced to a PC. An electrochemical impedance software Power Sine was used to carry out impedance measurements between 10 mHz and 100 kHz. The AC amplitude voltage used for the experiments was 10 mV and DC potential referenced versus Ag electrode. The impedance spectra were further analyzed using ZSimpWin V3.10.

A high strength (HS) carbon fibers C 320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320000 single filaments in a roving were used as working electrodes. All of the electrodes were prepared by using CF (diameter ~ 7 μm) attached to a copper wire with a Teflon tape. The electrode area keeps up constant (Pt plate ~ 1.5 cm^2 , GC ~ 0.07 cm^2 , and CFME ~ 0.022 cm^2) by adjusting the dipping length and covering the rest of the fibers with the Teflon tape.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Synthesis of PANI on Pt, GC and CFME.

PANI can be synthesized by electrochemical methods under different aqueous acidic conditions (H_2SO_4 , HNO_3 , HClO_4 , etc.) by applying an appropriate oxidation potential in literature. Zotti, who investigated the mechanism and growth of PANI by CV, found that polyaniline growth depends greatly on the type and concentration of the supporting electrolyte anion[28]. In this work, the polymer growth of aniline was obtained by CV method at a scan rate of 100 mV s^{-1} , applying 10 scans on Pt-plate, glassy carbon disc and carbon fiber microelectrodes from solutions containing 0.1 M aniline concentrations and 0.5 M H_2SO_4 (Fig. 1a, b, c).

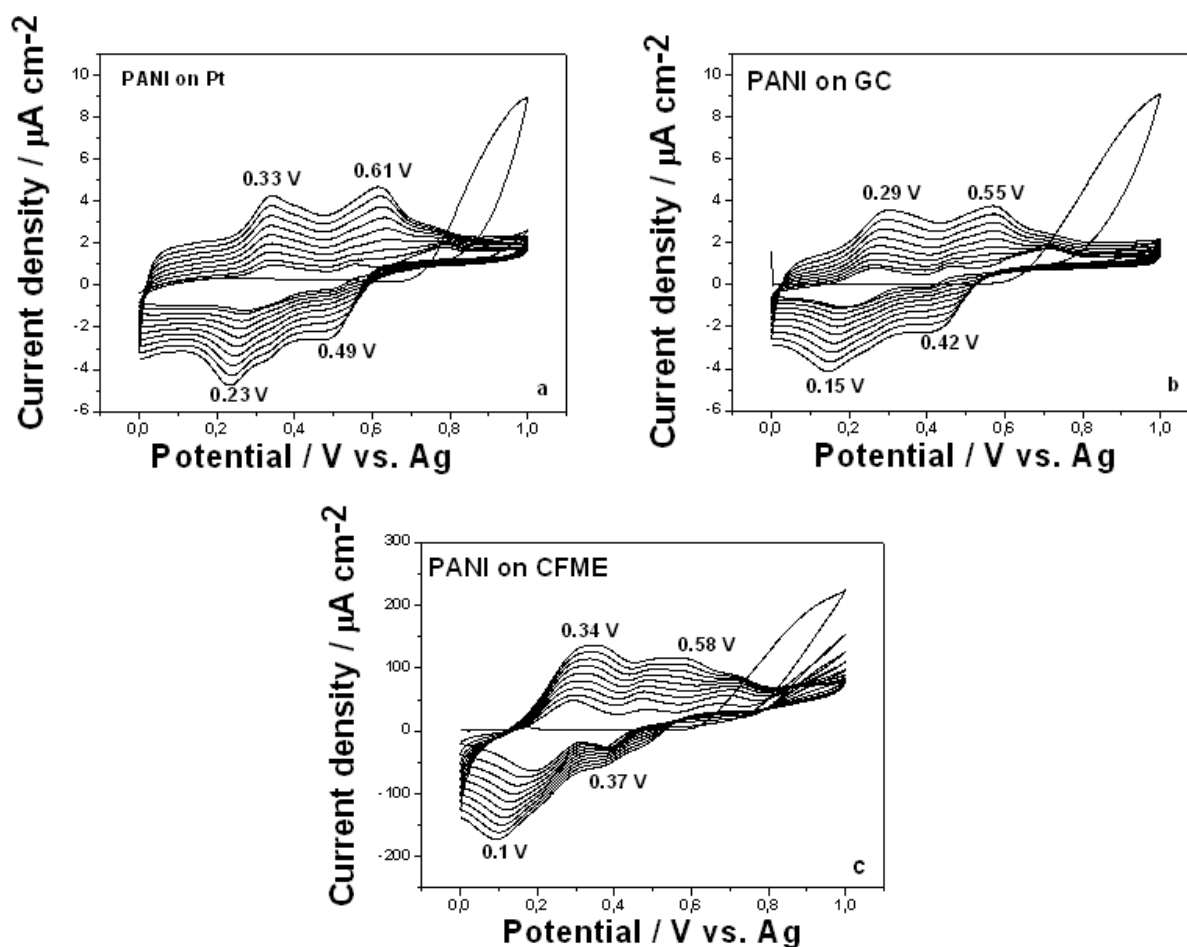


Figure 1. The polymer growth of ANI on Pt plate, GC electrode and CFME in 0.5 M H_2SO_4 at a scan rate of 100 mV s^{-1} , applying 10 scans. $[\text{ANI}] = 0.1 \text{ M}$.

Firstly, The CV exhibited two pairs of redox current peaks centered roughly at 0.33 V and 0.61 V on Pt-plate electrode, and their peak heights increased with the increase of number of potential scans

(potential range between 0 and 1 V) suggested that the films were electroactive (Fig.1a). Upon repeated scans, new redox processes appeared at lower potentials, indicating the formation of an electroactive polymer film. It was suggested that the polymerization of electroactive monomers are initiated by the monomer radical cation formation and their coupling reactions in a fast step. When polymer is thick, electron transfer would be difficult so doping (H_2SO_4) will be harder that is a resistance will be formed to doping ion migration.

Secondly, Aniline was also electropolymerized on glassy carbon electrode in 0.5 M H_2SO_4 solution (Fig.1b). Two redox peaks was also seen by CV. However, the oxidation peaks shifted to the lower values 0.29 V and 0.55 V that might be an advantage of glassy carbon electrode (Fig.1b) compare to Pt electrode.

Table 1. Redox parameters were obtained by electrodeposition by Pt, GC, and CFMEs.

Electrodes	E_{a1}/V	E_{c1}/V	ΔE_1	i_{a1}/i_{c1}	E_{a2}/V	E_{c2}/V	ΔE_2	i_{a2}/i_{c2}
Pt	0.33	0.23	0.10	0.91	0.61	0.49	0.12	0.73
GC	0.29	0.15	0.14	0.89	0.55	0.42	0.13	1.72
CFME	0.34	0.10	0.24	0.81	0.58	0.37	0.21	2.09

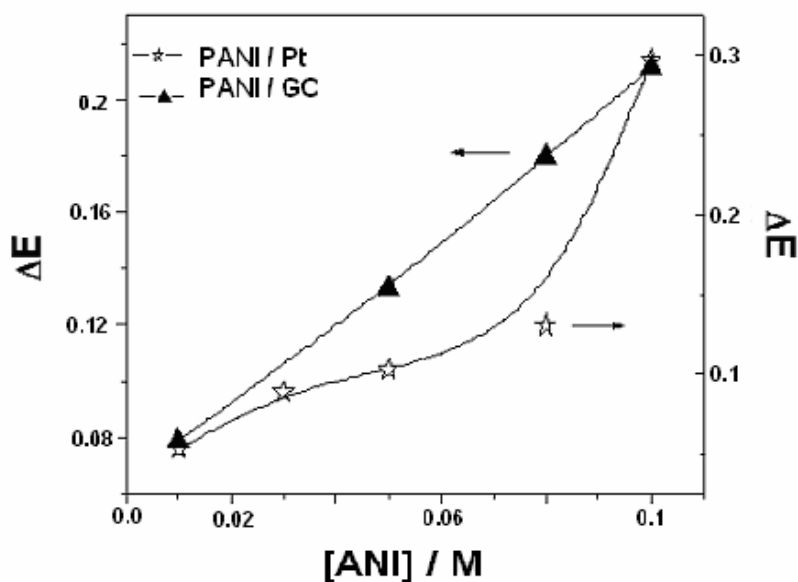


Figure 2. Effect of initial monomer concentration on PANI vs. ΔE for a) Pt, b) GC.

Thirdly, Electrogrowth of ANI was obtained on CFME as shown in Figure 1c. Effect of substrate on electropolymerization of aniline was exhibited in Table 1. Pt electrodes showed more

reversible behavior ($i_a / i_c = 0.91$) than CFME ($i_a / i_c = 0.89$) and glassy carbon ($i_a / i_c = 0.81$) electrodes. The first oxidation potential of CFME ($E_{a1} = 0.34$ V) was higher than Pt ($E_{a1} = 0.33$ V) and GC ($E_{a1} = 0.29$ V). So, electrodepositions charge of ANI was higher on Pt electrode ($\Delta Q = 3.75$ C) compared to GC ($\Delta Q = 31.79 \mu\text{C}$) and CFME ($\Delta Q = 207.20 \mu\text{C}$).

Effect of initial monomer concentration of aniline on Pt and GC electrodes versus anodic and cathodic peak potential separation (ΔE) was given in Figure 2. Both electrodes show that ΔE increases by increasing initial monomer concentration of aniline. ΔE value was obtained at the highest initial aniline concentration (0.1 M). The highest anodic and cathodic peak potential separation ($\Delta E = 0.3$ V) indicates highest ion penetration resistance.

3.2. Electrochemical Impedance Spectroscopy of PANI on Pt, GC and CFME.

The electrical conductivity is the most important property of PANI and impedance measurements were used for conductivity studies as well as to elucidate mechanism and kinetics of chemical and electrochemical reactions on PANI films [29,30,31]. EIS measurements were performed in monomer-free electrolyte solution with three different electrodes (Pt, GC, and CFME). The low frequency capacitance (C_{sp}) values of PANI film (at 0.01 Hz) were calculated by the following equation, where C_{sp} is the specific capacitance; (Z_{im}) is the slope of a plot of the imaginary component of impedance versus the inverse of the frequency (f) [32].

$$C_{sp} = (2\pi f \cdot Z_{im})^{-1} \quad (1)$$

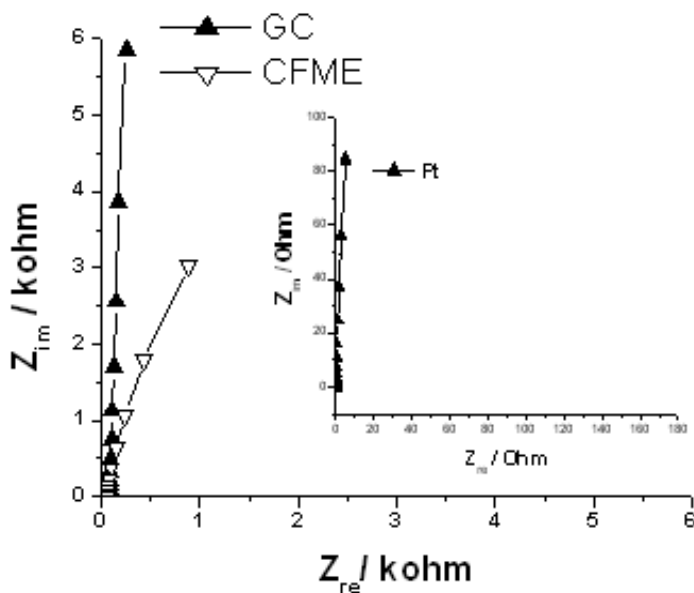


Figure 3. Nyquist plot obtained from EIS measurements on PANI for Pt, GC, and CFME

The low frequency capacitive behavior was obtained generally as a vertical line for Pt, GC and CFMEs from Nyquist plot. Higher low frequency (C_{sp}) capacitances were obtained for the case of PANI film on Pt electrode, which might be due the thicker PANI / Pt film formation ($120 \text{ mF} / \text{cm}^2$) than the PANI / CFME ($239.1 \mu\text{F} / \text{cm}^2$) and PANI / GC ($38.9 \mu\text{F} / \text{cm}^2$) formations (Fig.3).

The total capacitance value of PANI / Pt electrode has the highest value as shown in Figure 4.

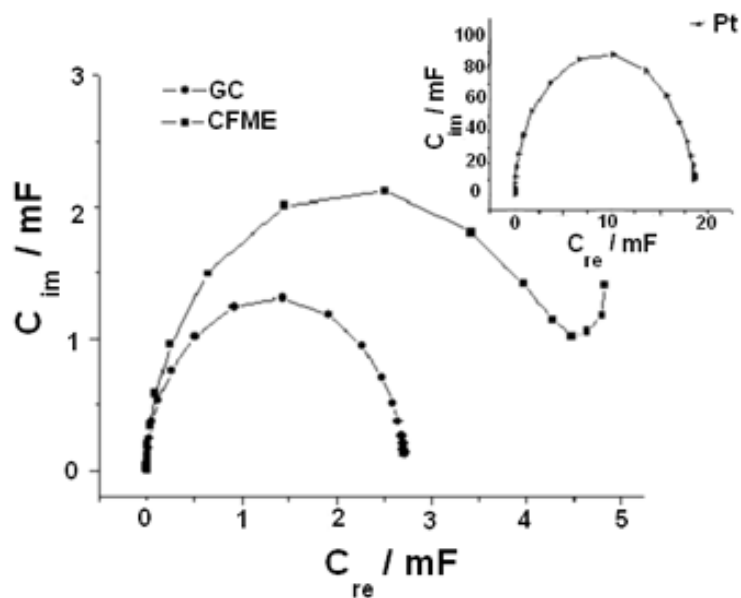


Figure 4. Capacitance plot obtained from EIS measurements on PANI for Pt, GC, and CFME

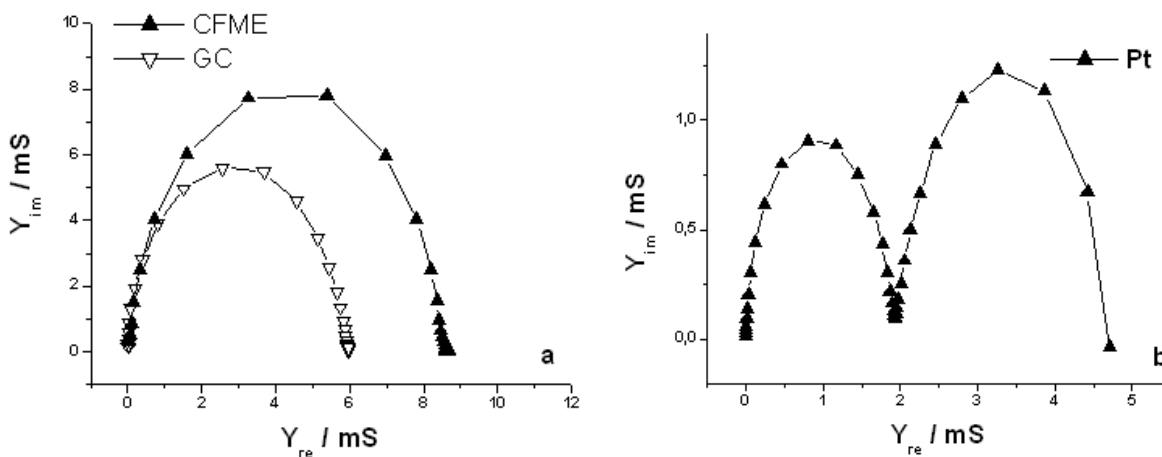


Figure 5. Admittance plot obtained from EIS measurements on PANI for Pt, GC, and CFME

On the other hand, PANI / GC modified electrodes has the lowest conductivity according to the Admittance plot as shown in Figure 5, but it has the highest resistance since Z' axis could be named as pure resistor while the Z'' is pure capacitor.

3.3. Electrical equivalent circuit of Electrodes / PANI / Electrolyte configuration

The validity of the results obtained by EIS was verified using electrical equivalent circuit which is given in Figure 6b. The electrochemical parameters of this circuit representing Electrode / PANI / electrolyte configuration were evaluated by employing the ZSimpWin (Version 3.10) software from PAR. We observed very good agreement between experimental and the calculated results obtained from the best fitting electrical equivalent circuit model, where the chi-squared (χ^2) minimized below 10^{-4} . χ^2 is the function defined as the sum of the squares of the residuals.

The electrical equivalent circuit model which is used in simulation of the impedance behavior of the film from the experimentally obtained impedance data was investigated by an equivalent circuit with a serial association composed of two components (inset of Fig.6b).

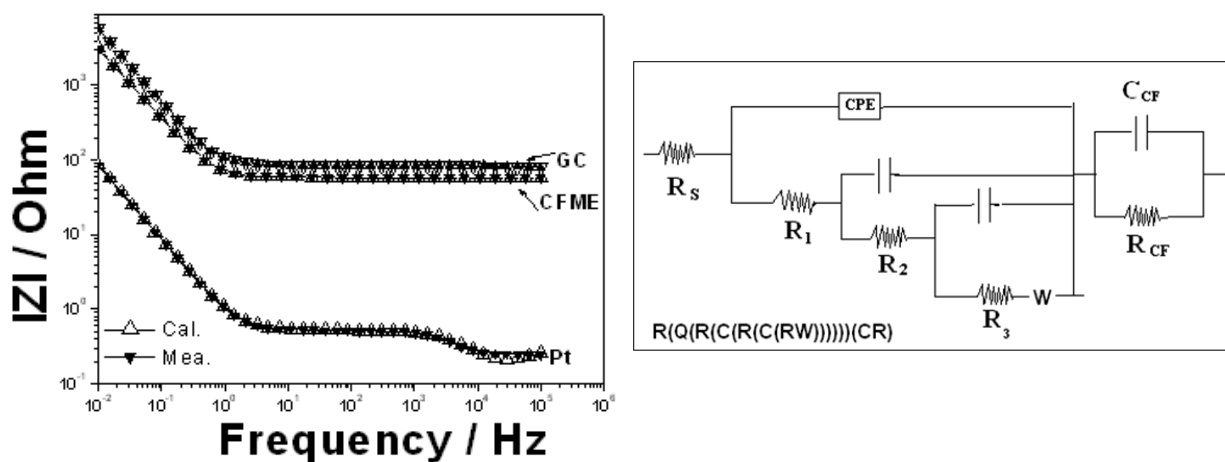


Figure 6. Theoretical and experimental comparison of Bode-Magnitude plot obtaining from Equivalent electrical circuit model, $[ANI]_0=0.1$ M. Inset: Equivalent electrical circuit Model, $(R(Q(R(C(R(C(RW))))))(CR))$ used in simulation.

An examination of the data obtained for Electrode / PANI / electrolyte systems indicate that the proposed equivalent circuit can be used to describe the experimental results (Fig. 6 and 7).

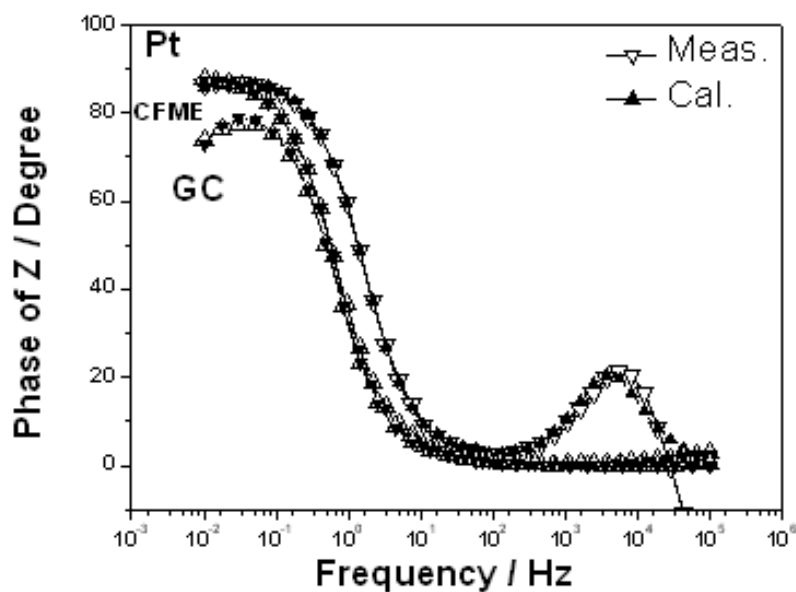


Figure 7. Theoretical and experimental comparison of Bode-Phase plot obtained from Equivalent electrical circuit model, [ANI]₀=0.1 M.

Table 2. R(C(R(Q(RW))))(CR) Circuit modeling results of electrochemically modified CFMEs with ZSimpWin simulating programme.

Polyaniline <small>(R(Q(R(C(R(C(R,W)))))))(CR)</small>	Pt Electrode	GC Electrode	CFME
R_s / Ohm	44.6	76.6	57.9
C_{dl} / mF / cm²	58.2	24.3	190.9
R₁ / Ohm	96	29.2	137.6
Q / Y₀ / mS s⁻ⁿ	0.96	0.94	0.68
n	0.98	0.97	0.83
R₂ / kOhm	1752	406	12.6
W / Y₀ / mS s⁻ⁿ	110000	39.6	123
R₃ / Ohm	1760	56.8	5803
C_{CF} / μF	210	30.1	360
R_{CF} / Ohm	0.26	7.24	1.89
Chi Squared (χ²)	2.04x10 ⁻⁴	4.35x10 ⁻⁵	1.59x10 ⁻⁴

The first component of the model is very similar to the model which was proposed by Fletcher[33] for a porous electrode, where the total impedance of the polymer and the interfacial impedance between the solution and the pore wall. First component of composed of two parts. The first part is the solution resistance of the polymer and the electrolyte, R_s , second part is the parallel combination of the double layer capacitance, C_{dl} , and R_1 is the resistance of the polymer film deposited onto three different electrodes (Pt, GC and CFME). A series connection to R_1 constructed using a constant phase element Q_p (Y_0 , CPE), in parallel to the redox process taking place at the polymer / solution interface and is described by the charge transfer resistance R_2 , a series connection to R_2 made up using C_1 in parallel with R_3 and W . The low frequency behavior is determined by the adsorption of cations and can be described by adsorption resistance parallel R_3 to an adsorption capacitance C_1 ³². Diffusion processes arising in systems were explained by W is the Warburg diffusion impedance element. The second component is (C_{CF}) in parallel to resistance of the carbon fiber electrode R_{CF} . In this circuit, Q_p is one constant phase element that take into account the interfacial irregularities such as porosity, roughness, and geometry. The highest value of double layer capacitance (C_{dl}) was obtained for PANI / CFME (190.9 mF / cm²) than Pt electrode ($C_{dl} = 58.2$ mF / cm²) and GC (24.3 mF / cm²) from equivalent circuit model (Table 2). In previous studies $C_{dl} = 28 \pm 5$ μFcm^{-2} was reported for PANI[34].

4. CONCLUSIONS

Simulation results confirmed that proposed electrical equivalent circuits were successfully matched to explain the polymer film and the electrolyte interface onto Pt, GC, and CFME. Overall CV results support the high quality thin PANI film formation on three different electrodes. Electrocoated thin film on Pt electrode shows the highest low frequency capacitance ($C_{sp}=120$ mF / cm²) than PANI / CFME (239.1 $\mu\text{F} / \text{cm}^2$) and PANI / GC (38.9 $\mu\text{F} / \text{cm}^2$) electrode. The highest value of double layer capacitance (C_{dl}) was obtained for PANI / CFME (190.9 mF / cm²) than Pt electrode ($C_{dl} = 58.2$ mF / cm²) and GC (24.3 mF / cm²).

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