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Development of Conducting Poly(o-Aminophenol) Film and its Capacitance Behavior

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Electroactive and conducting poly(o-Aminophenol) POAP film is prepared firstly via chemical oxidation of o-aminophenol using ammonium persulfate in neutral medium followed by an electrochemical activation in H_2SO_4 solution. The redox processes and super capacitive behavior of the electroactive POAP polymer film were studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical characterization of the activated polymer film shows the presence of distinctive redox sites which is active and stable up to overpotential of 0.8 V vs SCE. The EIS analysis displays the specific capacity of the activated POAP polymer film reaches up to 280 Fg^{-1}.

Keywords: Poly (o-Aminophenol), chemical oxidation, electrochemical impedance spectroscopy

1. INTRODUCTION

Poly(acetylene), poly(pyrrole), poly(aniline) and poly(thiophene) conducting polymers and their derivatives have been heavily studied during the last two decades due to their prospective applications in in energy storage devices, batteries, smart windows, biosensors, electrocatalysis, and surface coatings [1-7]. Conducting polymers have unique chemical structures and are easy to be assembled or deposited into many of electronic devices [8, 9]. Aminophenols are derivatives of anilines in which the hydroxyl group of the aromatic ring can readily oxidize to form quinine redox center [10]. When the aminophenols electropolymerization process takes place in acidic media, the formed poly(o-aminophenol) (POAP) film shows an interesting electrochemical characteristics [11]. POAP has been synthesized chemically and electrochemically by using ortho-amino (o-NH_2) and ortho-hydroxy (o-OH) aniline derivatives. The presence of both –OH and –NH_2 functional groups in o-aminophenol monomer are likely to be oxidized to form polymeric POAP which likely undergoes hydrolysis to reactive and soluble intermediates [10]. During the chemical polymerization, various oxidizing compounds like ammonium persulfate, barium manganate, and sodium dichromate were used in acidic medium to form POAP which showed ladder structures [10]. Though, in the literature it is not clear what type of dimeric structures of POAP are formed by either chemical or electro-oxidation of o-aminophenol (o-AP) in aqueous solution. This because an electrophilic attachment could be occurs at either *meta or para-* position of the -NH_2 group in O-AP which produces two types of heteroaromatic structures. Although the chemical oxidation of o-AP yields 2-aminophenoxazin-3-one (APZ) [10], the redox reactions involving phenoxazine structure have been suggested for POAP prepared by the electrochemical deposition [12]. The POAP formed in neutral solution is non-conducting and have the advantage of very thin and more uniform than the conducting polymer formed in acidic solution. The thickness of the polymer film is self-controlled and significantly affects the electroactive species diffusion process from the electrolyte solution [13]. Moreover, a strong electropolymerization inhibition effect was observed when the o-AP concentration in the solution was increased [14].

The redox mechanism and charge-transport process of electroactive POAP film was studied by different electrochemical methods and shown to be involving a proton addition/elimination step combined with a reversible electron transfer process [10]. In addition, the electrochemical studies shown that the extended potentiodynamic cycling of the POAP film electrodes strongly reduced the electron transport rate at POAP film and results in the deactivation of the polymer conductivity [10, 15, 16]. However, the conductivity of the POAP can be maintain when the upper potential reaches 0.5 V (vs. SCE) while the film experiences irreversible conductivity loss when the potential extends to values higher than 0.5 V (vs. SCE) [16, 17]. Recently, more studies have been performed to clarify the electrochemical polymerization of OAP in different medium [10, 15], however there is still deficiency in understanding of the chemical polymerization of OAP, particularly the oxidation of o-AP in neutral medium. This work reports the synthesis of electroactive and robust poly(o-aminophenol) POAP film through oxidative-free radical polymerization in neutral medium using ammonium persulfate as an initiator and followed by an electrochemical activation in an acidic media. The electrochemical and capacitance behavior of the polymer is characterized by cyclic voltammetery (CV) and electrochemical impedance spectroscope (EIS).

2. EXPERIMENTAL

2.1 Materials

O-aminophenol (o-AP, pure, M.Wt = 109.13, m.p = 170-175 ^{o}C), analytical grade H_2SO_4 (98%), ammonium persulphate (pure > 99%, M.Wt = 228.19) and ethanol (analytical standard) were purchased from Sigma-Aldrich. Dimethylformamide (DMF, Fine-Chem Limited India) was used directly without any additional distillation and the solutions were prepared using purified water that has a resistivity of 18.2 MΩ cm.

2.2 Preparation of poly (o-aminophenol) (POAP)

The POAP was prepared by dissolving 0.02 M (2.18 g) of o-aminophenol in 50 ml ethanol and mixed using magnet stirring for half an hour. Then the ammonium persulfate solution 0.02 M (4.56 g) dissolved in 25 ml distilled water was gradually added to o-aminophenol solution with constant stirring and the reaction is kept for 24 hours for completion. The mixture of POAP then was filtered and the solid polymer was washed with deionized water for several times.

2.3 FT-IR and electrochemical characterization

The FT-IR spectra of the polymer were measured in the range of 4000 to 400 cm^{-1} using FT/IR-4100 Spectrometer (Jasco analytical instruments, Japan). Glassy carbon (GC) disk with 3.0 mm diameter (SIGRADUR, Germany) sealed in glass was employed as working electrode. Before the experiment, the GC electrode was polished with (1.0 and 0.5 µm) wet alumina powder to a mirror finish followed by sonication in deionized water to remove any remaining alumina particles then dried up in air. For the electrochemical characterizations, a 50 mg of chemically prepared polymer was taken and suspended in 1.0 ml DMF. For the electrochemical experiments, a 15 µl of the polymer suspension is casted onto (GC) electrode then the electrode was left to dry in air at room temperature. The electrochemical experiments were executed using VSP multichannel Potentiostat/galvanostat (BioLogic) operated with EC-Lab software and using conventional three electrodes glass cell with platinum foil and a saturated calomel electrode (SCE) as counter and reference electrode respectively. Before the measurements, nitrogen gas was purged for 15 min to remove any dissolved oxygen in the solution. The polymer electrochemical activation was achieved by cycling the potential between –0.4 and 0.8 V vs. SCE at scan rate of 100 mV s^{-1} for about 50 cycles and a stable cycle were obtained. The activated polymer films then were characterized by cyclic voltammetry in 1.0 M H_2SO_4 solution and electrochemical impedance spectroscopy (EIS) was conducted in the frequency range from 100 mHz to 200 kHz.

3. RESULTS AND DISCUSSION

Fig. 1 shows the FTIR spectra of the POAP chemically prepared in the neutral solution using ammonium persulfate oxidizing agent. The FTIR peaks wave number and assigns is reported in table 1. The FTIR spectrum shows the strong absorption peaks at 750 cm^{-1} corresponding to N-H out of plane in aromatic amine. The existence of the absorption peak at about 3430 cm^{-1} is indicated that the POAP does not have a complete ring closure structure. Peaks at about 752 cm^{-1} and 866 cm^{-1} were assigned to 1,2- di-substituted and 1,2,3 tri-substituted benzene structures.

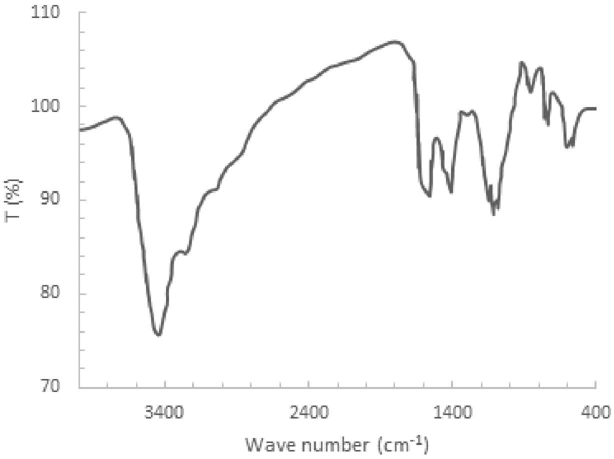
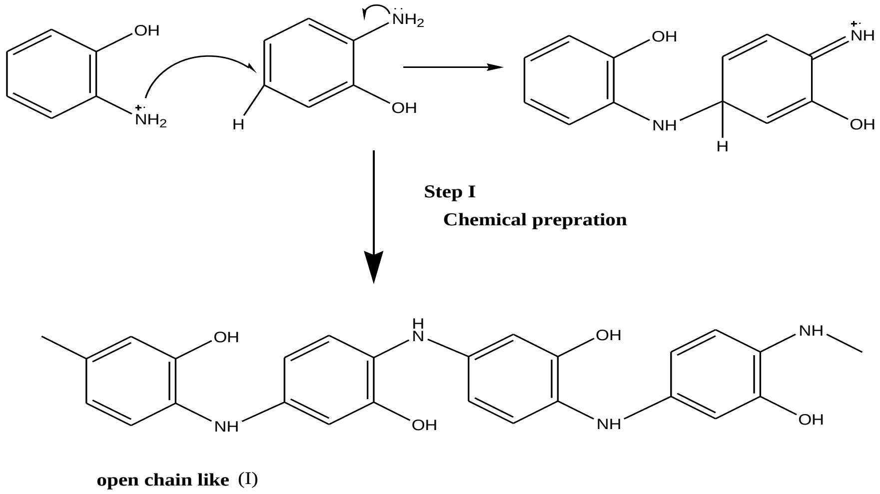


Figure 1. FTIR spectra for POPA polymer obtained by chemical oxidation in neutral solution.

Table 1. FTIR peaks assignment for POPA polymer.

Vibration assignments	Wave number, cm^{-1}
N-H Stretching	3242
N-H bending	1572
C=C of aromatic ring	1613
C-N Stretching of aromatic ring	1284
O-H Stretching in phenol	3432
O-H bending in phenol	1419
N-H out of plane	750

The chemical oxidation process of o-AP is complex and undergoes through more than one mechanisms because the existence of two susceptible functional groups of –OH and $–NH_2$. Many reports suggested the formation of ladder polymer structure of 3-aminophenoxazone (3-APZ) which plays the essential role in the formation of POAP [18]. Others studies suggested the formation of liner polymer via NC coupling [19] as shown in scheme 1 below.



Scheme 1. Suggested mechanism for the formation of liner POAP polymer via NC coupling [20].

The obtained POAP polymer then activated electrochemically by cycling in 1.0 M H_2SO_4 and Fig. 2A shows the cyclic voltammetry (CV) at 100 mVs^{-1} of the chemically prepared POAP film coated on GC electrode during extended cycling in1.0 M H_2SO_4 solution at potential from −0.4 to 0.8 V vs. SCE. Initially, during the first cycle only small oxidation peak (c) was observed around 0.45 V may be due to the formation of the ($OAP^{\bullet+}$) radical cations from unreacted monomers and/or oligomers [12]. In successive sweeps, peak (c) shifts to more positive potential as shown by red arrow then develop to a broad peak at 0.6 V vs. SCE.

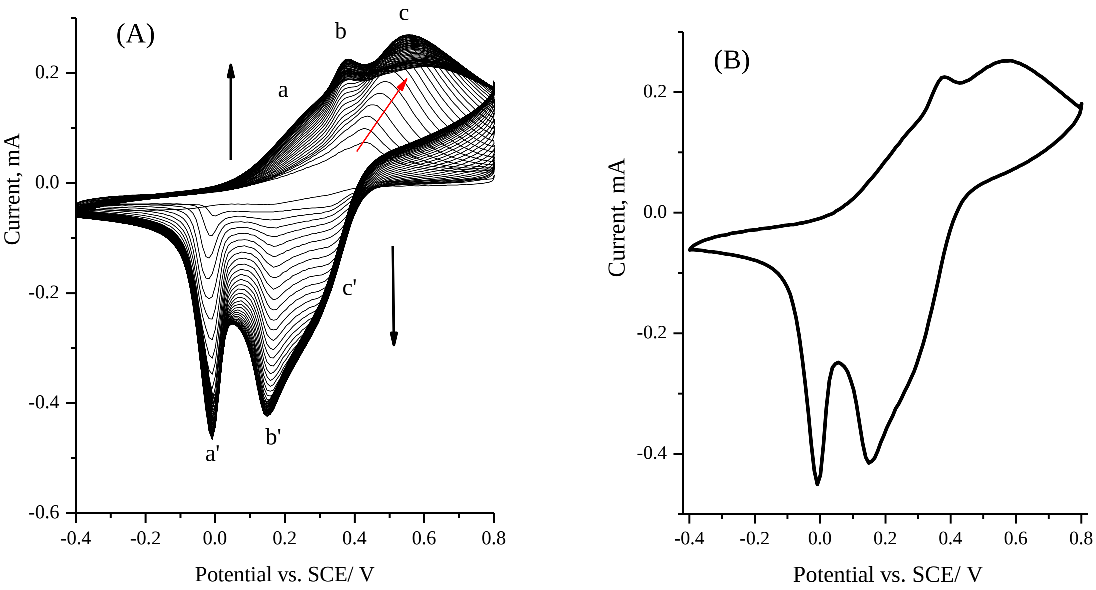
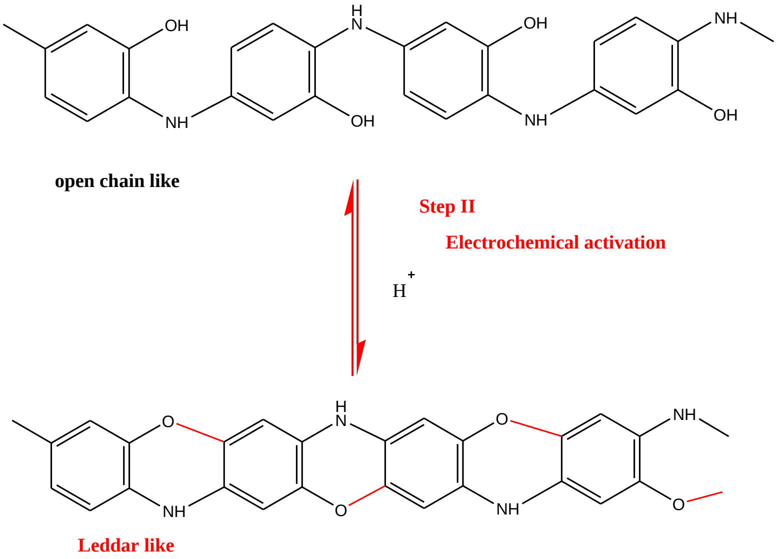


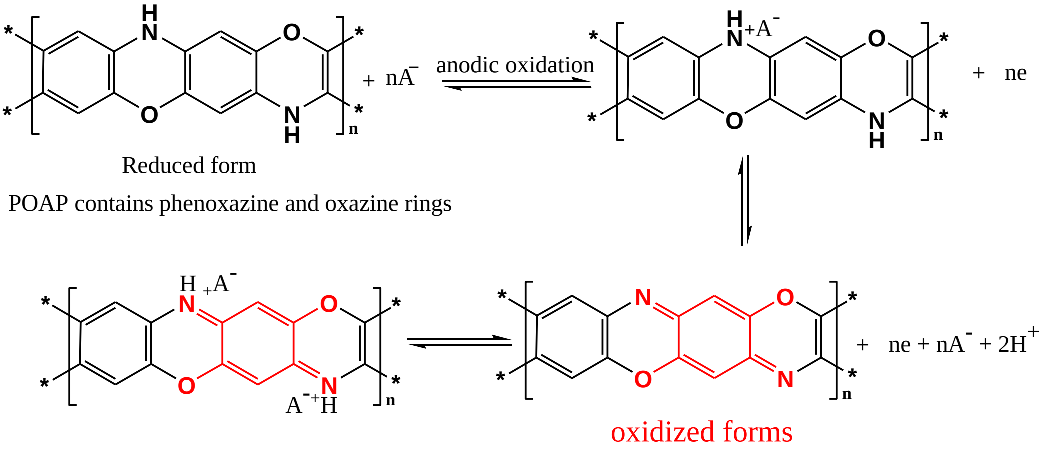
Figure 2. (A) multi-cyclic voltammograms at 100 mVs^{-1} obtained for POAP films in 1.0 M H_2SO_4, and (B) cyclic voltammetry of freshly activated POAP electrode in 1.0 M H_2SO_4.



Scheme 2. Mechanism proposed for the transformation of linear POAP to ladder structure by electrochemical activation.

After a few scans, the oxidation peak (b) around 0.37 V began to appear may be attributed to the formation of ladder polymer of 3-aminophenoxazone that is formed by a sluggish cyclization reaction of the oxidized C-N chain of o-AP cation radical. The peak (b) increases sharply then stabilized after long cycling. Also not appear at lower scan rate for the same polymer film indicating the complete conversion of the obtained polymeric intermediates to the ladder polymeric form as shown in scheme 2. Moreover in anodic scan and after long cycling the voltammogram developed a wave (a) around 0.25 V which can related to the oxidation of phenoxazine redox center in the polymer [20, 21].

Therefore, it can concluded that the formation of POAP occurs through; firstly the formation of liner polymeric intermediate via NC coupling during chemical polymerization in neutral medium using oxidative-free radical roots as shown in scheme 1. There is no electrochemical activity appears for the polymer during few first cycles in H_2SO_4. In the second step, the ladder polymer of 3-aminophenoxazone was obtained by the electrochemical oxidation in acidic solution as shown in scheme 2. The o-AP chemical oxidation was discussed in the literatures [19] and the full FTIR spectral analysis was reported which suggested the formation of mixture from Poly (3-aminophenoxazine) as a cyclic products and liner (open chain like I) polymer. During the cathodic scan the CV shows the presence concomitant reduction wave (c′) at 0.35 V and two well defined reduction peaks (b′, a′) at 1.6 and 0.0 V vs. SCE respectively, which suggested a complex redox behavior for the activated POAP. The peak (c′) appear around 0.35 V in the reverse scan may be related to the reversible redox center of the -OH group of some unconverted liner chain POAP and the corresponding oxidation peak should be merging but only brood oxidation peak (c) appears in the forward scan. The other two reduction peaks (b′, a′) appear at 0.16 and 0.0V may be attributed to the redaction process of the full oxidized POAP as shown in scheme 3 [22, 23] and the corresponding oxidation peaks merged to a broad peaks of (b) and (a) respectively.



Scheme 3. Reaction scheme for oxidation-reduction of phenoxazine, both reduced and oxidized forms can be protonated and the H^+ exchange can also occurs.

These POAP redox peaks are really stable and reproducible at prolonged cycling. After the electrochemical activation was completed, the POAP electrode was removed from the electrolyte and rinsed with deionized water and a fresh cycle voltammetry was recorded. Figure 2B shows the cyclic voltammograms for the fresh activated POAP films at 100 mVs^{-1} in 1.0 M H_2SO_4. Clearly the CV shows the presence of typical redox peaks of POAP observed in Figure 2A which confirm the stability of the POAP film. Interestingly, in our case the CV for POAP contains a broadened oxidation peaks (a, b, c), reduction shoulder (c′) and two well defined reduction peaks (a′, b′). Moreover, the overall current of the redox peaks considerably increases with potential cycling and reached stability after around 40 cycles.

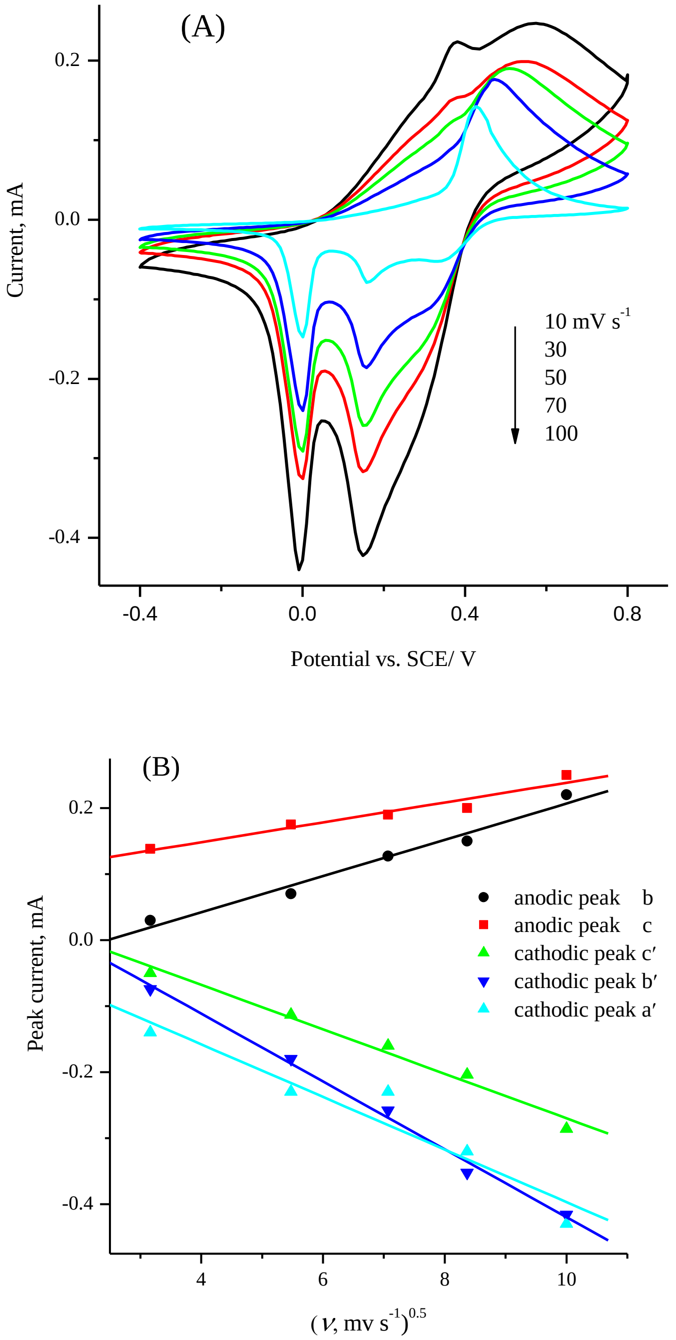


Figure 3. (A) Cyclic voltammetry at different scan rate of POAP film in 1.0 M H_2SO_4, and (B) plot for the relationship between peaks current and square root of the potential scan rate.

This behavior of activated POAP is different from the electro-polymerized o-aminophenol in acidic media which is developed only one redox center at longer cycling [10, 15]. In addition the elecro-polymerized POAP film suffers from conductivity loss under prolonged potential cycles in the region from -0.2 to 0.5 V (SCE).

Figure 3A shows the effect of scan rate on the redox behavior of activated POAP in 1.0 M H_2SO_4 and Figure 3B shows the plot for relationship between peaks currents and the square root of the scan rate.

Clearly the plots in Figure 3B show both anodic and cathodic currents are linearly increase with the square root of the potential sweep rate, which pointed to the electrochemical process occurs at POAP electrode is controlled by diffusion of the electroactive species. Nevertheless the plot intercept for anodic peak (c), cathodic peaks (b′) and (a′) are not pass through the origin suggesting the presence of contribution from kinetic restraint.

The capacitance behavior of activated polymer is investigated by electrochemical impedance spectroscopy (EIS) techniques in an aqueous solution of 1.0 M H_2SO_4. EIS has been used to investigate the electrochemical redox system of the POAP films and to evaluate their ionic and electronic conductivity as well as its specific capacitance [14, 17]. The EIS analysis of the electrochemical system has the capability of distinguishing the contribution from the individual components and the recorded data can be modelled into an equivalent electrical circuit. Therefore, the parameters of solution resistance (R), the electrochemical double-layer capacitance of film/electrolyte interface (C_{dl}), and the bulk faradic impedance of the polymer layer can be obtained. Figure 4 displays the Nyquist plot of POAP electrode in 1.0 M H_2SO_4 within the frequency range of 100 KHz to 10 mHz with the dc-offset potential of 0.1 and 0.4 V vs. SCE. Clearly, the shape of the impedance responses for POAP films changes significantly by changing the potentials from 0.2 to 0.4 V. This indicates that the electrochemical properties of POAP films are having distinct variations with applied potentials. In both cases, the polymer Nyquist plots have a small semicircle at high frequencies ended to a large one at the lower frequency part of spectrum. The semicircle at high frequencies is due to the parallel combination of charge transfer resistance, R1, and constant phase element (CPE1) that is related to the electron transfer at the polymer/electrode contact interface. The second large semicircle at lower frequency attributed to the charge transport, R2, in parallel with the CPE2, which may be ascribed to the anions insertion into the polymer film to compensate the positively charged centers in polymer phase [22, 24].

The suggested equivalent circuit for Nyquist plot is shown in the inset of Figure 4 and table 2 reports the value of the electrochemical parameters derived from the best-fit of the equivalent circuits using Z-Fit software. The data show that after the potential is increased to 0.4 V there is a decrease in charge transport resistance. The constant phase element behavior of interface has also ascribed to a fractal nature of the interface [23]. In case of rough surfaces, the relation between impedance, Z, versus frequency, *w*, often behaves as a CPE [25], therefore:

$$Z_{CPE} = T_{CPE}(j\omega)^{-n}{}_{CPE} \qquad (1)$$

where CPE is defined by:

$$Z_{CPE} = T_{CPE}(j\omega)^{-n}{}_{CPE} \qquad (2)$$

Where T and n are frequency-independent constants and ω is the angular frequency. The exponent n is a correction factor related to the roughness of electrode surfaces. The values for n are ranging between 0 and 1. $n = 1$ denotes the CPE element is an ideal capacitor, while $n = 0$ and 0.5, denotes a resistance and Warburg behavior, respectively.

The exponent n and, through it, the fractal dimension, D_r, obviously used to obtain the interfacial roughness.

$n = 1/(D_f - 1)$ (3)

The fractal dimensions of the POAP films were calculated from the CPE exponent of the first semicircle of the Nyquist plots, n1 (in Table 2), and Eq. 3. The D_r values are 2.22 and 2.28 for POAP-SO_4 films at 0.2 and 0.4 V vs. SCE, respectively. The increase of the fractal dimension of the films at 0.4 V indicates an increase in films porosity with increasing the potential to the oxidation peak region (c) which reflects the change in the chain structure of POAP at this potential. The specific capacity of the activated POAP film reaches about 280 Fg^{-1} which is comparatively similar to the capacitance reported for POAP fabricated by electrochemical deposition on high surface area graphene support [25].

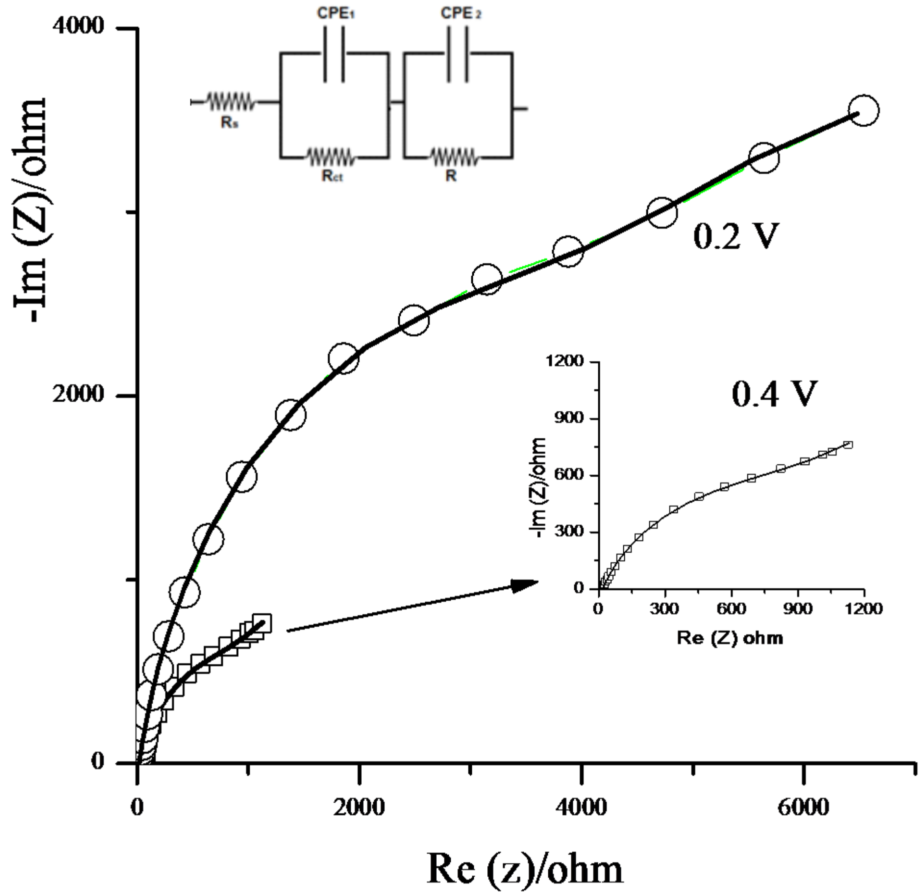


Figure 4. Nyquist plot for POAP in 1.0 M H_2SO_4 within the frequency range 200 kHz – 0.1 Hz at 0.2 and 0.4V, square represent the EIS results where solid line represent the fitted data and the inset shows the suggested equivalent circuit.

Table 2. The values of the electrochemical parameters of activated POAP films obtained from the equivalent circuits best-fit in Figure 4.

	0.2 V vs. SCE	0.4 V vs. SCE
R_1 (Ω)	16.58	16.74
CPE_1 (F)	$0.2e^{-3}$	0.327e-3
n_1	0.815	0.777
R_2 (Ω)	9000	1200
CPE_2 (F)	40.6e-6	2.1e-3
n_2	0.866	1
R_3 (Ω)	3896	1700

4. CONCLUSION

Electroactive and stable poly(o-Aminophenol) POAP film is obtained by oxidative-free radical chemical polymerization using ammonium persulfate oxidizing agent in neutral medium followed by an electrochemical activation step in acid solution. Electrochemical response of the obtained polymer reflects the high conductivity and stability of the obtained polymer film at high anodic potential of 0.8 V vs. SCE. Also the interfacial roughness was studied using EIS analysis and shown that the interfacial roughness of the prepared film was increased by increasing the applied potential and a specific capacity of 280 Fg^{-1} was achieved at 0.4 V. This procedure has the advantage of mass chemical production of conducting POAP for energy storage applications.

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