

Electrochemical impedance spectroscopy of the poly-*o*-aminophenol film

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The technique of electrochemical impedance spectroscopy has been employed to study the conductivity of poly-*o*-aminophenol film under different conditions and to test the validity of the transmission line model. In this regard, the effect of dc offset potential, film thickness, temperature and pH on the conductivity of the film has been studied. It is shown that reduced form of the polymeric film is more conductive than oxidized form. The semiconductivity is revealed to be *p*-type through the application of the Mott-Schottky equation.

Electrical conductivity of the π conjugated polymeric films have attracted much interest¹ because of its controlling effect on the electrocatalytic², ion selective³ and other⁴ properties. The mechanism of the charge transport process⁵ and the dependency of the conductance on parameters such as pH (ref. 6) and solvent has been studied. For example the ionic conductivity of the poly-*o*-aminophenol is lost in solution^{2a} of pH > 5.

Many electrochemical techniques have been used to investigate the polymer's properties such as electrochemical quartz crystal microbalance⁶ and differential pulse voltammetry⁷. The electrochemical impedance spectroscopy (EIS) is also one of the most valuable techniques⁸. This method has proved that polypyrrole is a *p*-type semiconductor⁹ and the transmission line network could be applied to account for the conductance path fairly successfully¹⁰.

The electrochemical properties of the poly-*o*-aminophenol (POAP) film have been studied by several researchers¹¹, but still some challenging points remain to be investigated. In the present paper we shall attempt to present a detailed understanding of the electrochemical behaviour of the POAP film, taking into consideration the porous structure of the polymeric film¹⁰.

The conductivity studies were carried out by the method of impedance spectroscopy under varieties of conditions such as film thickness, dc potential and solution pH. Transmission line mod-

el was employed to rationalize the impedance results.

Materials and Methods

o-Aminophenol (OAP), aniline (An), CuSO₄, sodium hydroxide and sulphuric acid used in this work were all of Analar grade of Merck and were used without further purification. All solutions were prepared in doubly distilled water.

Electropolymerization and subsequent electrochemical studies were carried out in a thermostated conventional three electrode cell powered by a fully computerized EG & G electrochemical system capable of running cyclic voltammetry and impedance spectroscopy (IS). The glassy carbon electrode was employed as the working electrode and its potential was recorded against saturated calomel electrode (SCE) with a large Pt plate forming the auxiliary electrode. Cyclic voltammetry studies were performed using EG & G model 273A potentiostat/galvanostat, run by an IBM PC/valuepoint computer through 270/250 software while impedance studies were carried out by the Solartron SI 1255 frequency response analyser supported by the 273A potentiostat/galvanostat and run by the mentioned computer through M398 software. The impedance results were analysed with Boukamp equivalent circuit.

Poly-*o*-aminophenol (POAP) was prepared through anodic oxidation of 0.1 M monomer solution in sulphuric acid media onto a glassy car-

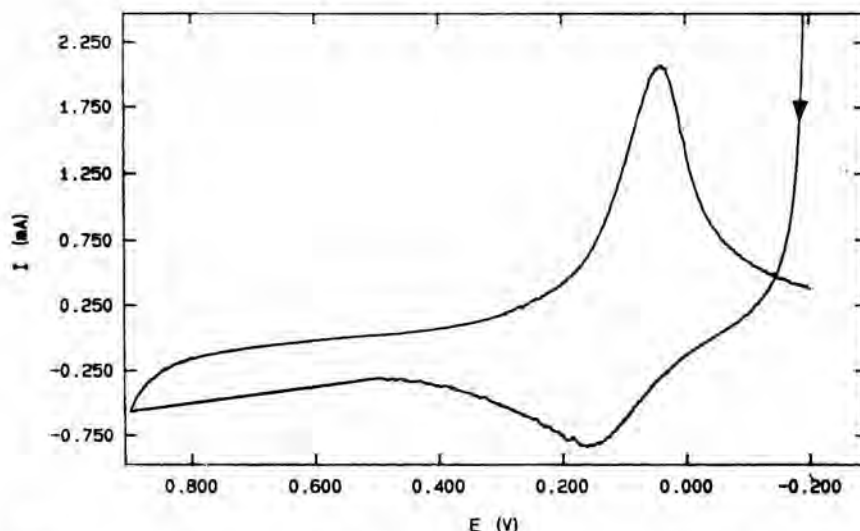


Fig. 1—Cyclic voltammogram of the POAP film in H_2SO_4 solution, $\text{pH}=0.5$, scan rate 100 mV/s

bon electrode by cycling the potential between -0.2 to 0.90 V/SCE (ref. 11). The resulted electrode was washed with dilute sulphuric acid and transferred to the monomer free acidic solution to investigate the electrochemical properties of the film.

Results and Discussion

The cyclic voltammogram (CV) of the polymeric film was obtained between -0.2 to 0.9 V/SCE and showed a couple of reversible peaks, a broad anodic wave around 0.15 and a sharp cathodic wave around 0.04 V/SCE, as indicated in Fig. 1. This is the characteristic CV pattern of the POAP film in acidic media and in fact demonstrates the potentials at which proton-anion insertion/expulsion at the polymer solution interface occurs during the course of oxidation/reduction process¹¹. The shape and position of the anodic/cathodic peak of the polymeric film was used as a criterion to ensure the stability of the film during impedance measurements, where CV's of the films were compared before and after measurements.

Conductive polymeric films are believed to show the behaviour of porous electrodes¹⁰. On anodic scanning, positively charged polarons are formed inside the pore walls and the electroneutrality is preserved by the anions which are either penetrated into the solution side of the pores or are surface-adsorbed on the pore walls. On cathodic cycling, only surface adsorbed anions are removed. This behaviour may account for a broad anodic and a sharp cathodic peaks. A similar mechanism had already been reported for the CV of polypyrrole¹⁰.

The shape of the CV of the film is pH dependent, and the film is almost inactive^{2a} in $\text{pH} > 5$. This behaviour confirms the role of proton in the electroactivity of the polymeric film. On the other hand the shape of the CV of the film was independent of the rotation speed of the electrode. So, we suggest that oxidation/reduction process takes place at the polymer/solution interface or in a layer inside the film near the solution. Since protons are always available inside the pores, the reaction is not controlled by proton diffusion but by electron transfer through the bulk of the polymer. This reaction location is in agreement with the kinetic model proposed by Alberly *et al.*⁸. But it should be reminded that proton (and its insertion/expulsion) is preserved as a charge balancing species in the entire oxidation/reduction process.

The impedance of the POAP film was investigated under different conditions. As a first step in this direction, it is essential to present the equivalent circuit of the film. For this purpose the impedance of the film was obtained in an acidic solution ($\text{pH}=0.5$), under 0.15 V/SCE dc-offset potential (oxidation process) between 100 kHz to 10^{-4} Hz. As indicated in Fig. 2, the Nyquist plot contains a very small semicircle terminated to a large one. The first semicircle is clearly observable in the expanded portion of the high ω region, insert of Fig. 2. This is in contrast with the previously reported results¹² where in the medium to low ω region a straight line of ca 80 degrees slope has been observed. The appearance of the straight line was attributed to the charge leakage across the walls of the pores¹⁰.

The following equivalent circuit was proposed

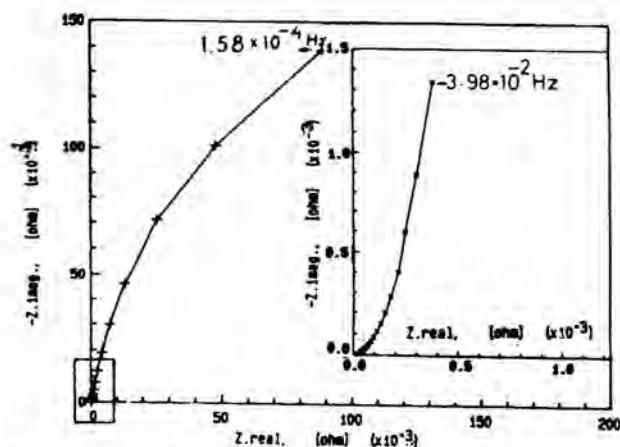


Fig. 2—Nyquist plot of the POAP film in the range of 100 kHz to 10^{-4} Hz, $E = 0.15$ V/SCE

to account for the impedance results and the values of each semicircle were found using Boukamp equivalent circuit software¹³.

$$R_1(R_2Q_2)(R_3Q_3)$$

where $R_1 = 2.10$ ohm, resistance of the solution; $R_2 = 203$ ohm, resistance due to charge transfer reaction at the polymer/solution interface; $Y_0^2 = 1.6 \times 10^{-3}$ mho, adjustable parameter containing diffusion coefficient related to Q_2 ; $n_2 = 0.6$, parameter related to Q_2 ; $R_3 = 4.9 \times 10^5$ ohm, film resistance; $Y_0^3 = 2.2 \times 10^{-3}$, parameter related to Q_3 ; and $n_3 = 0.8$, parameter related to Q_3 . Constant phase element Q , has been utilised in this equivalent circuit which is identified with Y_0 /mho, an adjustable parameter containing diffusion coefficient and n , a dimensionless and adjustable parameter¹³. For $n = 0$, it represents a resistance, for $n = 1$ a capacitance, and for $n = 0.5$ a Warburg (semi-infinite transmission line).

The previously reported double layer capacitance C_{dl} of the film is $8 \mu\text{F cm}^{-2}$ (ref. 12), and in the present work, the double layer capacitance due to the first semicircle as indicated in Fig. 2, is calculated to be around $30 \mu\text{F cm}^{-2}$. Such a capacitance could be attributed to space charge layer which is in agreement with the independency of the shape of the CV of the film with the speed of rotation. The space charge region arises from saturation of the pores with protons and it is accompanied by a small charge transfer resistance. The second and larger semicircle which may be observed as a line at medium to mHz frequencies is due to bulk capacitance of the film with a large ohmic resistance. Simulated patterns of Z_{real} and Z_{imag} are well in agreement with experimental ones.

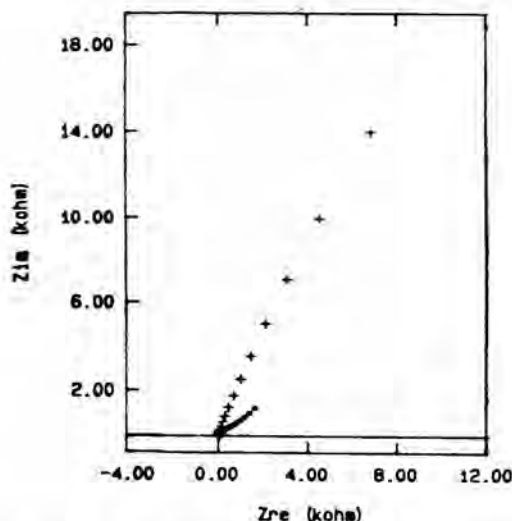


Fig. 3—Nyquist plots of the POAP (+) film & POAP/Cu (■), in the range of 100 kHz & 10 mHz, $E = -0.1$ V/SCE

If the polymer/solution interface could be blocked by a metallic coating, the electronic conductivity of the polymeric film could be obtained by impedance measurements of the polymer/metal/solution interface. In an attempt to eliminate polymer/solution interface (ionic conductivity), Cu was deposited onto the polymeric electrode. For this purpose the previously deposited and washed POAP film was immersed in an acidic solution containing 0.1 M CuSO_4 . The Cu deposition was carried out by the potentiostatic method at $-0.3/\text{SCE}$ for 1000 seconds. The CV of this electrode did not show the characteristic peaks of the POAP film in acidic solution, indicating full coverage of the film by the deposited Cu. The impedance of the POAP/Cu film was compared with the POAP film (in the range of 100 kHz to 10 mHz) in Fig. 3. In this plot the impedance of POAP/Cu is much smaller than impedance of the POAP film. Interestingly, the presence of Cu seems to make a short circuited path for conductance, providing open ended pores. The same behaviour was also observed when Cu was deposited onto the POAP film for 1 second. Similar effect was also seen in the case of PAn film coated with Cu. This result is in contrast to the ladder network model proposed by Flecher¹⁰, in which the pores inside the polymeric film are close ended.

In order to separate the contributions of electronic and ionic parts of the conductivity of the POAP film, we require both close ended pores as well as the blocking of the polymer/solution interface by a metallic substrate.

In an attempt to prepare a polymeric film with

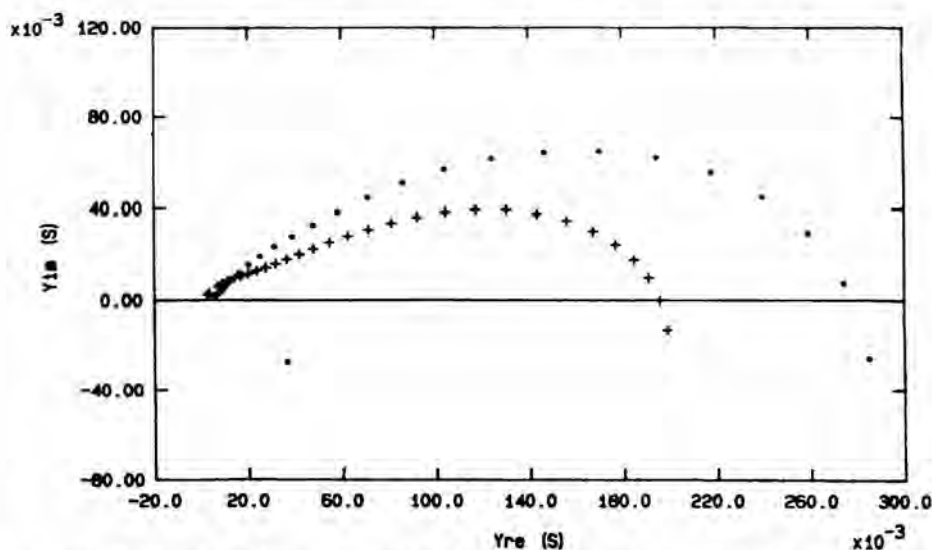


Fig. 4—Admittance plots of PAN/POAP film (■) & PAN/POAP/Cu (+) in the range of 100 kHz & 10 mHz, $E = 0.1$ V/SCE

close ended pores, polyaniline (PAN) was deposited onto glassy carbon electrode by cycling the potential between -0.2 to 0.9 V/SCE of $0.1M$ monomer solution in sulphuric acid media and then POAP was deposited onto it by 20 times cycling of the PAN electrode in a solution containing OAP monomer. Finally, when this electrode was transferred to monomer free acidic solution, neither the characteristic peaks of the POAP, nor the characteristic peaks of PAN were observed. The structure of the synthesised polymeric film is unknown, but it could be a combination of PAN and POAP. This electrode was subsequently immersed in $0.1M$ $CuSO_4$ solution and Cu was deposited on the film at -0.3 V/SCE for 300 seconds. The impedance of this electrode was obtained at -0.1 V/SCE and compared with the impedance of PAN/POAP at the same offset potential. Short circuited pathway by Cu deposition was not observed, Fig. 4. The above coating method with different monomers resulted in forming of a new polymeric film with close ended pores.

The Nyquist plot of PAN/POAP film is compared with PAN/POAP/Cu film. The first semicircle of Cu deposited polymeric film is much smaller than Cu undeposited film. This result shows that the space charge capacitance due to proton-anion exchange between polymer and solution is considerably reduced and anion movements are stopped inside the bulk of the polymer.

So, it could possibly be suggested that the difference between the real component of admittances of PAN/POAP and PAN/POAP/Cu at 63.10 kHz, i.e. 70×10^{-3} s, arises from electronic conduction of the PAN/POAP film, Fig. 4.

Effect of DC potential on the impedance of POAP

Plots of Z_{real} versus ω for POAP at oxidation potential (ox) of 0.115 V/SCE and reduction potential (red) of 0.040 V/SCE are obtained. Due to total electronic conduction at high ω , $Z_{real}(ox) = Z_{real}(red)$ in the range of 100 kHz to 3.980 kHz. Afterwards, $Z_{real}(ox) > Z_{real}(red)$ down to 6.31 Hz. At oxidizing potential, polarons are trapped and stabilized by anions and their movements are impeded, so showing lower conductivity relative to the reduced form. At lower ω the trend is changed. Presumably the effect can be attributed to the take over of the capacitance of the film (Q_3) in the low ω domain.

The potential range of the conductivity of POAP film was elucidated by measuring total impedance at different dc offset potentials, in the range of 100 kHz– 10 kHz. Then the total impedance was plotted against dc potential at each frequency. A typical plot is represented in Fig. 5, illustrating lowest impedance in the range of 30 to 150 mV/SCE. In this potential window the POAP film is also most electroactive consistent with the CV studies.

Thickness effect

POAP was deposited onto glassy carbon electrode at constant potential (0.9) V/SCE for 300, 600 and 1000 seconds to assure, depositing various and largely different film's thickness. The impedance of the films obtained at 0.15 V dc offset potential. The plots of Z_{real} and Z_{imag} vs ω , Fig. 6, show that increasing the thickness increases Z_{real} and Z_{imag} . According to the modified porous electrode model¹⁰, capacitance arises in the pores walls and not in the bulk of the solid polymer or

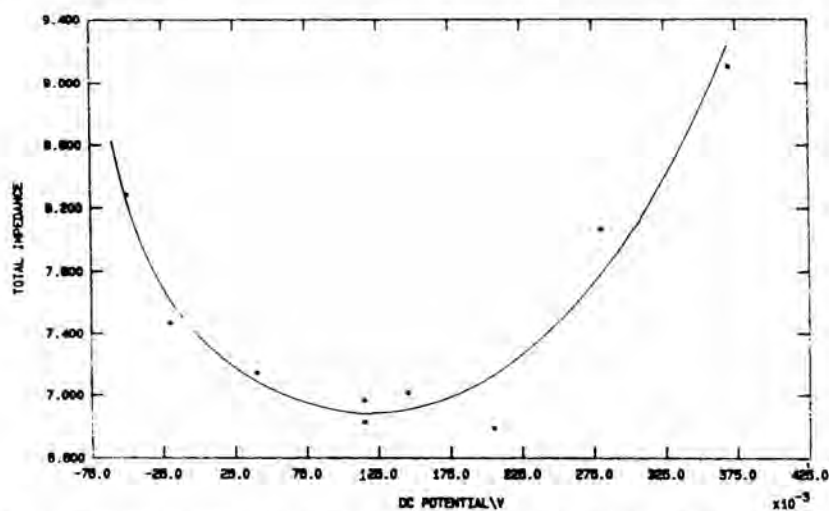


Fig. 5—The plot of total impedance versus dc potential for the POAP film, $\omega = 1$ kHz

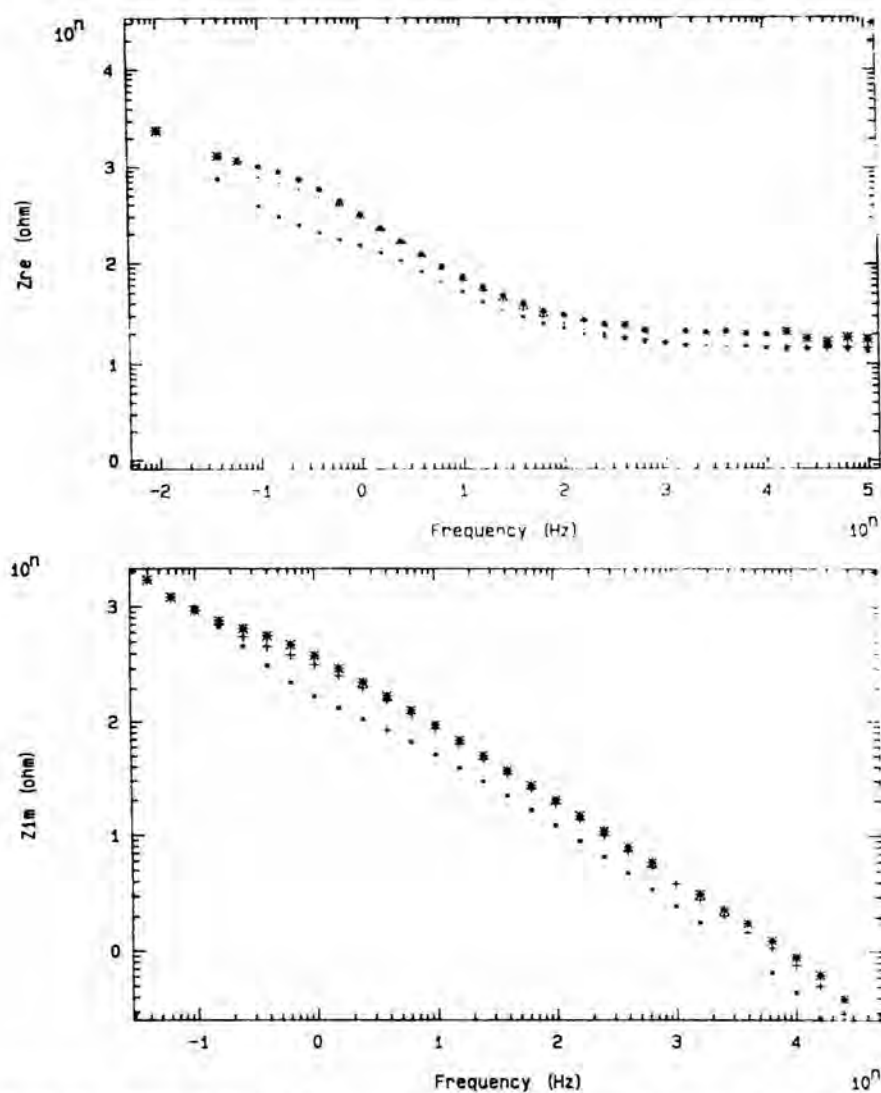


Fig. 6—The plot of (a) Z_{real} versus ω & (b) Z_{imag} versus ω of the POAP films deposited for 300 (■), 600 (+), 1000(*), $E = 0.15/\text{SCE}$

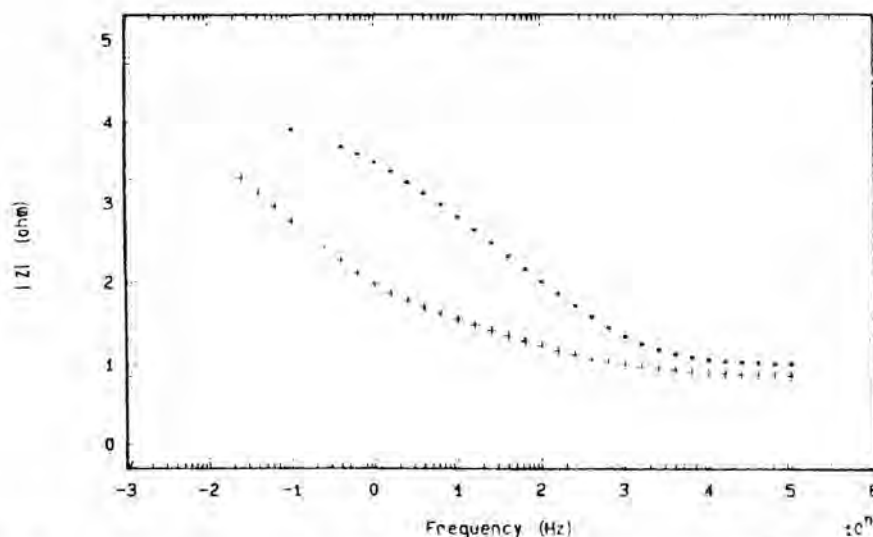


Fig. 7—The plot of Z_{real} versus ω of the POAP film at $pH=0.5$ (+) and $pH=12$ (■), $E=0.15V/SCE$

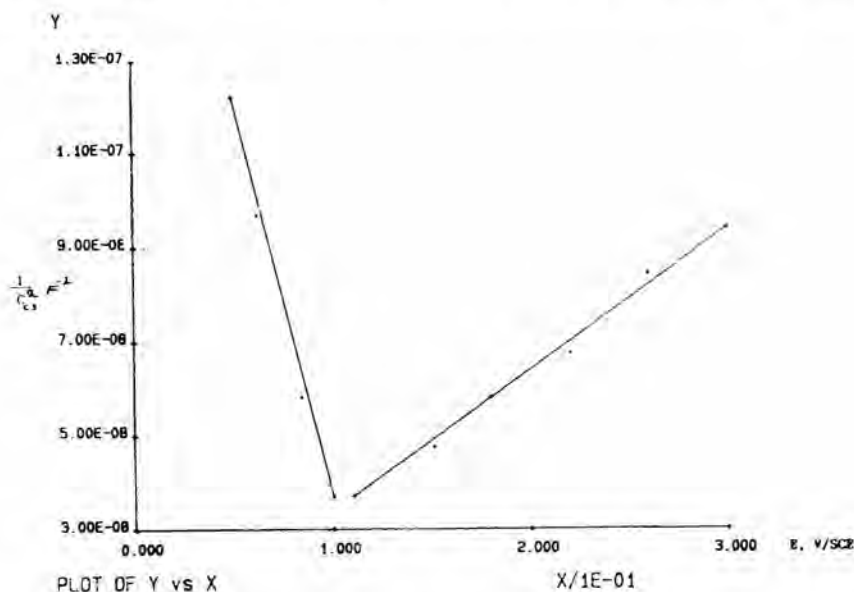


Fig. 8—Mott-Schottky plot of the POAP film

in solution inside the pores. As the thickness increases, number of pores increases, the greater the number of pores in parallel, the greater the total impedance.

pH and temperature effects

The impedance of POAP film was obtained in acidic and alkaline solutions containing 1M Na_2SO_4 . The plots of total impedance, $[Z]$ versus ω in $pH=0.5$ and $pH=12$ are compared. According to Fig. 7, at high ω , $[Z]$ of the film in acidic and alkaline solutions are the same as expected. At lower ω down to 1.585Hz, total im-

pedance in acidic solution is less than in alkaline solution due to higher conductivity of the film in acidic media.

The impedance of the POAP film was also obtained in acidic and alkaline solution at different temperatures. Z_{real} in acidic solution decreases with increasing temperature from 10 to 80°C, because ionic conductivity is enhanced as the temperature is raised. In alkaline solution the trend is reversed.

The following data is obtained from the Nyquist plots and C_{sc} was calculated from the maxima of the first semicircle.

$$[R_{ct} = 126 \, \Omega, pH = 0.5] \ll [R_{ct} = 8160 \, \Omega, pH = 12]$$

$$[C_{sc} = 29 \, \mu F cm^{-2}, pH = 0.5] \gg [C_{sc} = 0.130 \, \mu F cm^{-2}, pH = 12]$$

Due to proton exchange in acidic solution, small R_{ct} is accompanied by large surface charge capacitance. In basic solution large R_{ct} is accompanied by a small capacitance, which is in fact a double layer capacitance, since C_{sc} cannot be formed in the absence of protons, because under this condition the polymeric film is inactive. This reasoning is in agreement with the presented equivalent circuit and assigning the first semicircle to C_{sc} . Also, C_{sc} is due to a high concentration of proton at the film/solution interface that makes the shape of the CV independent of ω (speed rotation of the electrode).

The Mott-Schotky equation⁹ was employed to obtain the type of the semiconductivity and flatband potential of POAP film by plotting $1/C_{sc}^2$ versus dc potential as shown in Fig. 8. The x intercept provides the flatband potential value of -0.012 V/SCE. The negative slope of this line is an indication of the *p*-type semiconductivity of the POAP film. The pattern changes slope above the potential of 0.15 V/SCE to positive values indicative of either *n*-type bulk semiconductivity of the film or the appearance of an inversion layer. Closer inspection of the C_{sc} values for the domain of the *p* type behaviour is strongly in favour of the formation of the inversion layer as signable difference of the values of C_{sc} in either side of the inversion potential.

Based on the results obtained in this work it is concluded that:

i. The POAP film is a *p* type semiconductor and an inversion layer is observed above the potential of 0.15 V/SCE; ii. the reduced form of the polymeric film is more conductive relative to the oxidized form in the range of 3.98 kHz to 6.31 Hz; iii. electron diffusion through the bulk of polymer has the controlling effect upon the conductance but the presence of proton is essential for the electroactivity of the film, because electroactivity is lost in solution of $pH > 5$; iv. oxidation/reduc-

tion processes take place at the polymer/solution interface or in a layer inside the film near to the solution; v. a surface charge capacitance is established at the film/solution interface which explains many behaviours of the film such as *pH* effect, independency of the shape of the CV with the speed rotation of the electrode, thickness effect and so on; and vi. some aspects of the transmission line model are confirmed by the pores inside the polymer are open ended.

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