

***In situ* resistance measurement of a conducting polymer electrode[§]**

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Abstract. The resistance of a conducting polymer film electrode was measured *in situ* using a simple configuration. The data so generated have been used to construct a two-dimensional conductance surface 'state-diagram'. An attempt is made to correlate the electrochemical activity of these electrodes with their resistance-potential behaviour.

Keywords. Conducting polymer film electrodes; conductance-electrochemical activity relationship; *in situ* resistance measurement.

1. Introduction

Conducting polymers form a growing class of new synthetic materials with exciting technological possibilities. These materials are of special interest to electrochemists because a number of them can be easily synthesized electrochemically (Tourillon and Garnier 1982; Diaz and Logan 1980). Electrochemical oxidation/reduction of these materials can lead to large changes in their conductivity (Diaz and Clarke 1980; White *et al* 1984; Kittlesen *et al* 1984; Paul *et al* 1985). It can be expected that when used as electrode materials they will produce interesting electrochemistry for two reasons: (1) the 'organic' surface of these materials will perhaps exhibit selectivity and specificity in terms of reaction products which may be quite unlike that observed with conventional inorganic electrode materials; and (2) the potential dependent conductivity will be an additional variable in determining reaction rates.

Since the resistance of these materials is a sensitive function of the electrochemical potential (Paul *et al* 1985) and also the chemical environment (e.g. pH of electrolyte), MacDiarmid *et al* (1985), *in situ* resistance measurement is an essential input in the study of electrode kinetics. Kittlesen *et al* (1984) have reported such measurements for polypyrrole and Paul *et al* (1985) for polyaniline. We report here alternative and simpler configurations for obtaining such data.

Salaneck *et al* (1986) have recently suggested the use of a 2-dimensional conductance surface to describe the state of polyaniline as an aid in discussion of the properties of polyaniline. Using the data obtained by our procedure we shall attempt to generate such a conductance surface 'state-diagram'.

2. Experimental

Two configurations have been used for these measurements. The first configuration is shown in figure 1a. It consists of a 1 cm² Pt-foil on which the polymer under

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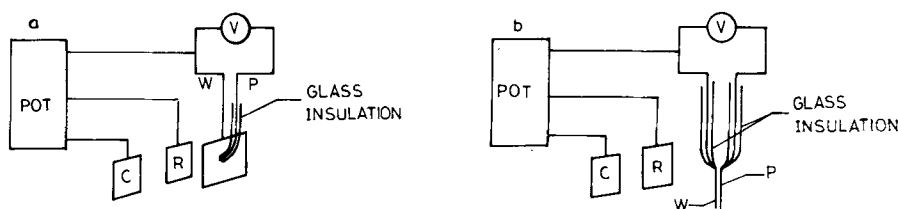


Figure 1. Schematic illustration of the electrode configuration used for measurement of polymer resistance. (a) Polymer deposited on a foil electrode, (b) Polymer deposited on and between two parallel wires.

investigation can be deposited. An insulated Pt wire (diameter = 1 mm) probe is positioned close to the foil surface such that when a polymer of sufficient thickness is deposited on the foil, the probe tip is just embedded in the polymer. This probe can be used to monitor the surface potential of the polymer. A similar configuration has been used by Fan *et al* (1984) to determine the surface potential of conducting layers on semiconductors. The resistance of the polymer film is determined as follows. When the polymer is under potentiostat control a current i flows across the polymer/electrolyte interface. This causes a voltage drop, V , across the polymer film due to the resistance of the polymer. This voltage drop V is measured between W and P . The resistance of the polymer is given by V/i .

The second configuration figure 1b is adapted from that used by Paul *et al* (1985). It consists of two parallel platinum wires (diameter = 1 mm) aligned very close to each other. When polymerization is carried out simultaneously on both the wires, the polymer layer grows on the two wires and eventually bridges the gap between the wires. One of the wires is then used for potentiostatic control of the polymer (W) and voltage drop in the polymer is measured using the second wire (P). The resistance of the polymer is obtained as before by taking the ratio of voltage drop to potentiostatic current.

Polyaniline films were produced by the procedure described by Diaz and Logan (1980). All chemicals were AR grade. Aniline was further purified by distillation under nitrogen. Sulphuric acid was purified by distillation under dry air. 0.5 M H_2SO_4 used as supporting electrolyte for resistance measurements was purified by pre-electrolysis for 48 hours. The following solutions were used for measuring the pH dependence of resistance: pH = 0.74, 0.5 M H_2SO_4 ; pH = 1–2, chloride buffer; pH = 3–5, phthalate buffer; pH = 6.5, phosphate buffer.

Potential control was done using a PARC 362 Scanning Potentiostat and potentiodynamic data were recorded on a Hewlett-Packard 7035B X–Y Recorder. Voltage drop across the polymer was measured using HIL 2161 Digital Multimeter.

Polymerization was carried out by potentiodynamic cycling between -0.2 V to $+0.8$ V vs SCE in 0.1 M aniline + 0.1 M H_2SO_4 at 50 mVsec $^{-1}$. Polymerization time of 30 minutes produced a film of thickness sufficient to provide contact between W and P . All measurements were made with 30 minute films.

3. Results and discussion

The resistance of polyaniline films measured using the first configuration is shown in figure 2. The polymer is highly resistive at -0.2 V and anodic polarization results

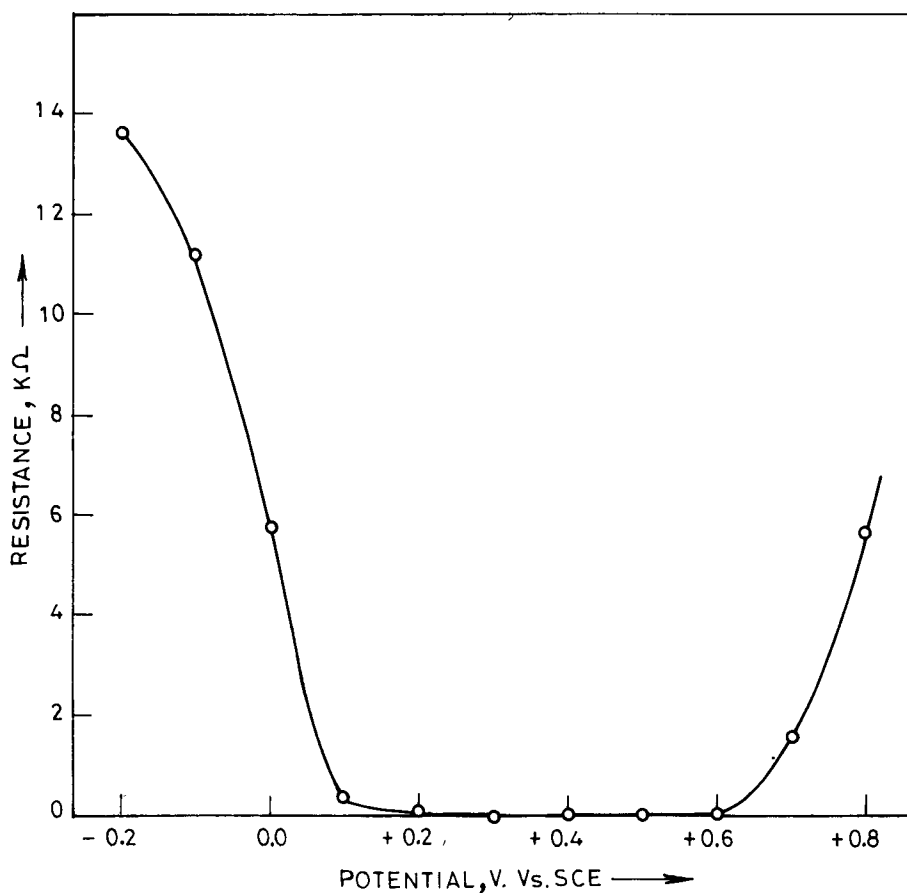


Figure 2. Resistance of a supported polyaniline film as a function of applied electrochemical potential in 0.5 M H_2SO_4 (pH = 0.74).

in decrease of the resistance. A broad minimum in resistance is observed between +0.1 V and +0.6 V with sharp increase in resistance on further anodic polarization. These observations are in agreement with the results reported by Paul *et al* (1985). The resistance change with our films is generally of the order of 10^4 . Paul *et al* (1985) have reported a change in resistance of $> 10^6$. This difference may be partly due to the fact that our films are thicker ($\approx 100 \mu\text{m}$) than those used in the earlier study ($\approx 5 \mu\text{m}$). Identical results were obtained when the second configuration was used for resistance measurement.

It has been recognized that the chemistry of polyaniline is sensitive to pH. The open-circuit potential of polyaniline electrodes is pH-dependent (Jozefowicz *et al* 1969) as also the conductivity (MacDiarmid *et al* 1985). It has been suggested that polyaniline may have application as a pH sensor in a limited range. Thus it is of interest to obtain a quantitative dependence of conductivity on pH.

The dependence of polymer resistance on the pH of the supporting electrolyte is shown in figure 3. The anodic potential excursion was limited to +0.4 V in order to avoid the slow oxidative degradation of the polymer which occurs at more positive

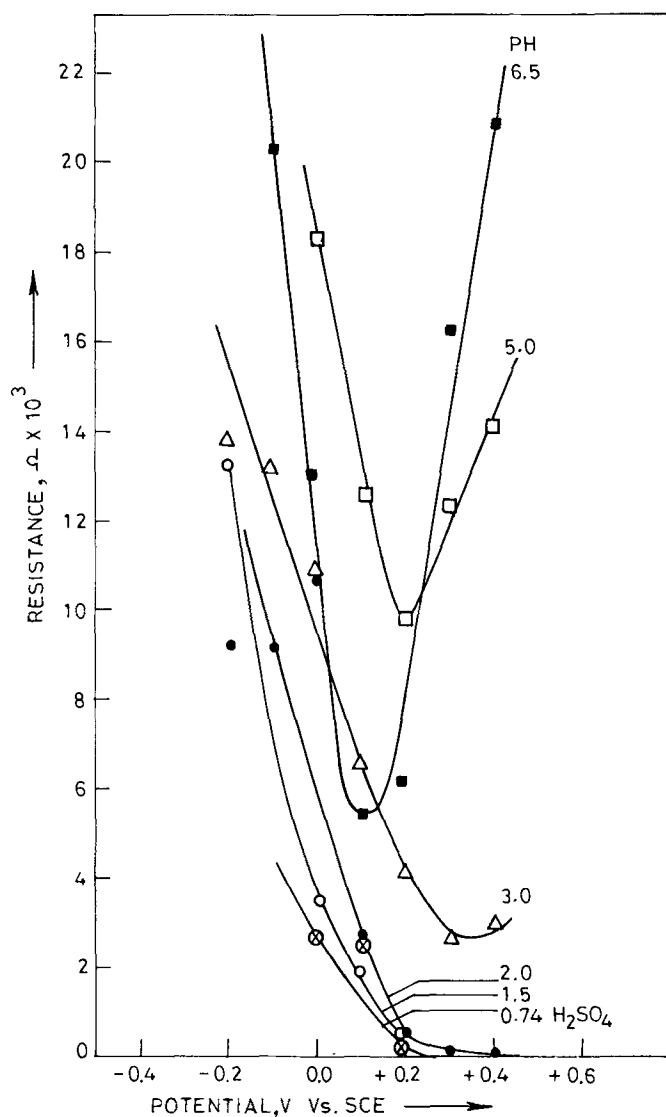


Figure 3. Resistance of a polyaniline film as a function of applied electrochemical potential in buffers of various pH.

potentials. The resistance of the polymer increases with pH in agreement with the earlier report. There is a slow evolution in the resistance-electrochemical potential behaviour with the resistance minimum becoming sharper at higher pH.

These data were used to generate a conductance surface, 'state-diagram' as shown in figure 4. Such a 'state-diagram' has been suggested as an aid in the discussion of various properties of polyaniline. Salaneck *et al* (1986) have proposed a surface curvature based on the data at pH = 1 and the pH-dependent resistance of emeraldine. The surface curvature shown in figure 4 is in close agreement with that surface.

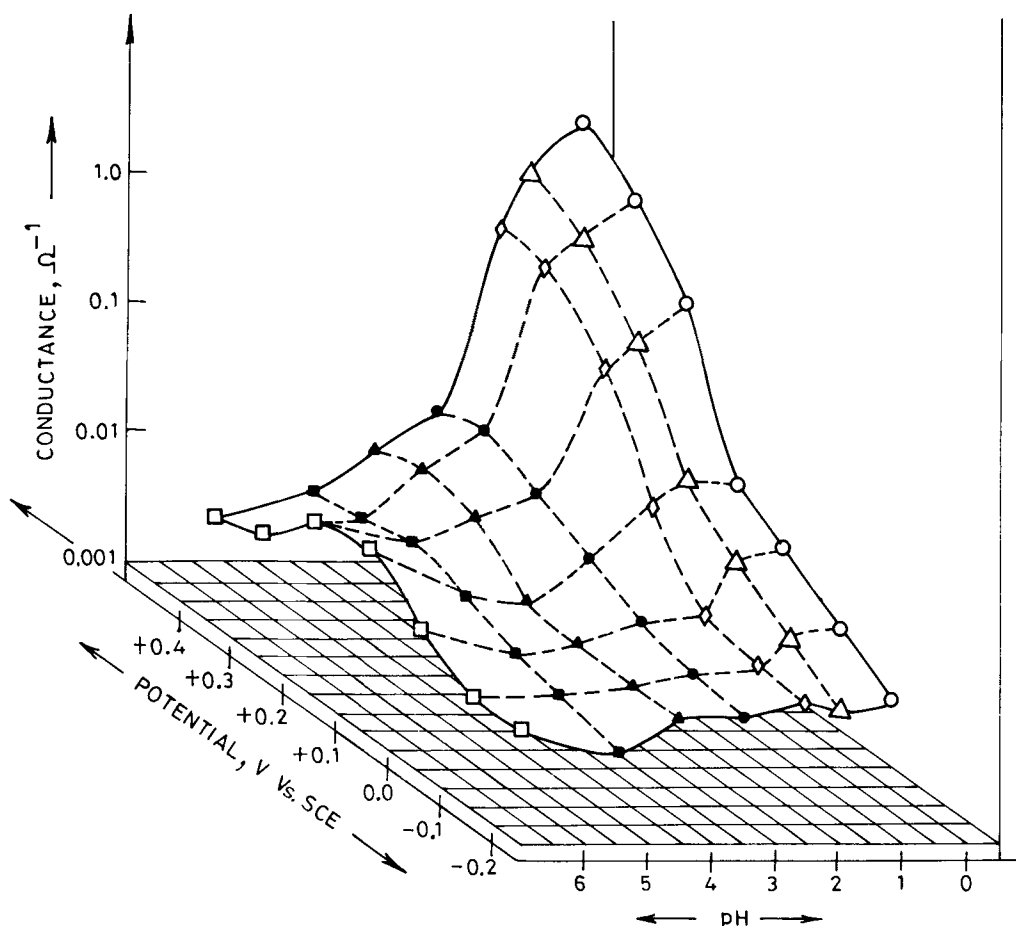


Figure 4. A conductance surface 'state-diagram' of polyaniline generated from the data shown in figure 3.

4. Polymer resistance and electrochemical activity

The cyclic voltammogram of polyaniline in 0.5 M H_2SO_4 and the steady-state resistance of the polymer in the same solution are shown in figure 5. It is apparent that the electrochemical activity of the polymer film occurs mainly in the resistance window between +0.1 V and +0.6 V. Similarly it has been observed by Oyama *et al* (1983) that the ability of the polymer to drive redox reactions is determined by the equilibrium redox potential of the couples concerned. Couples whose redox potential is within the range +0.1 V to +0.6 V exhibit reaction rates which are not substantially different from those observed at pyrolytic graphite. Couples whose equilibrium potentials are outside this range are inhibited.

A direct relation between polymer resistance and electrochemical activity is also observed when the pH of the electrolyte is varied. Figure 6 shows the cathodic scans for polyaniline in supporting electrolytes of varying pH. There are two types

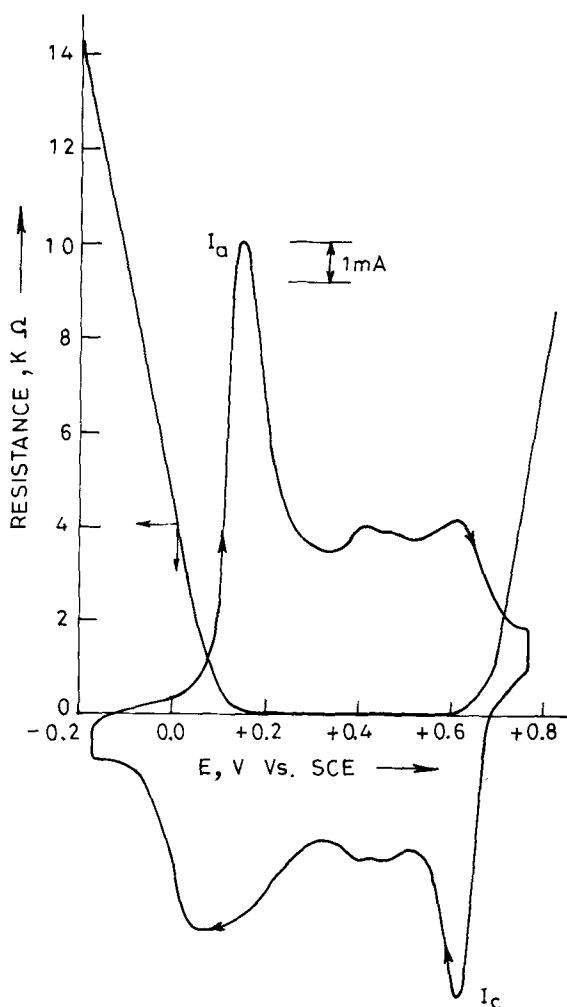


Figure 5. Cyclic voltammogram of polyaniline in 0.5 M H_2SO_4 and corresponding resistance profile. The resistance was obtained from steady-state measurements.

of changes which can be observed with increasing pH. The i - V curve in $\text{pH} = 0.74$ (figure 5) is quite complex and at least four peaks can be distinguished. With increasing pH some of these peaks coalesce or disappear and at $\text{pH} = 5.0$ a single peak is observed. Simultaneously, the potential range in which high currents are observed becomes narrower and at $\text{pH} = 5.5$ the polymer is virtually electroinactive. These changes are in qualitative agreement with resistance measurements where the resistance window becomes higher and narrower with increasing pH.

Polyaniline has been used as a protective coating for the prevention of passivation/dissolution of small band gap semiconductors such as n -Si. The polymer films were found to function satisfactorily when used to drive redox reactions such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ or I_3^-/I^- but were virtually inactive for oxidation of water (Noufi *et al* 1980, 1982; Skotheim *et al* 1981). This behaviour can now be understood in terms of

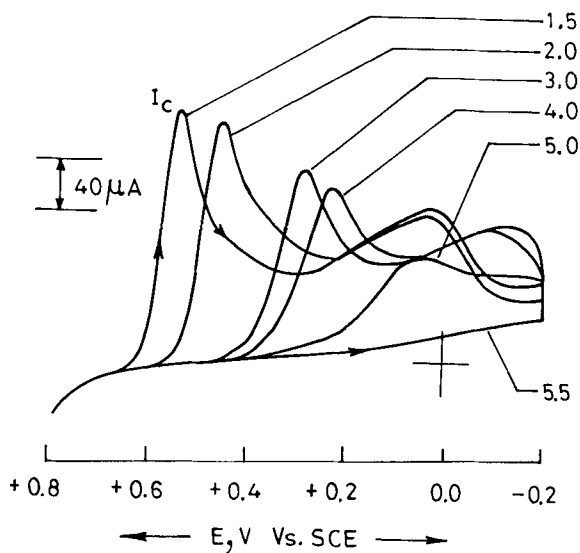


Figure 6. Cathodic scans of polyaniline in buffers of various pH.

the change in resistance of polyaniline. The equilibrium potential of the redox couples are within the resistance window between +0.1 V and +0.6 V while the equilibrium potential of water oxidation (+1.0 V) lies in a region where the polymer is highly resistive.

5. Conclusion

It has been shown that resistance of conducting polymer films can be measured *in situ* by a procedure which is simpler than has been used earlier. The worth of such studies in understanding electrode kinetics has been seen particularly in relation to the variation of pH. However, a more quantitative analysis of the influence of resistance on the electrochemical behaviour is required.

In situ resistance measurements in the presence of redox couples should be of interest in understanding their kinetics. Such studies are currently in progress in our laboratory.

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