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Applications of conducting polymers as sensors

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This article provides an overview of the tremendous technological potential of conducting polymers as sensors. Their electroactivity coupled with the ability to be switched from an insulating to conducting state makes these polymers attractive for use as sensors.

Introduction

Organic conducting polymers have emerged as a new class of electronic materials with a variety of applications[1]. They impart a blend of interesting optical and mechanical properties because of which it is possible to use them in situations where inorganic materials are unsuitable. Recently, synthetic capabilities as well as fabrication techniques have been developed to such an extent that molecular electronic devices based on conducting polymers can be designed and fabricated, marking evolution of a sophisticated technology in the field of microelectronics[2]. These electroactive materials cover a broad spectrum of applications from solid-state technology to biotechnology[3].

An important area of application for these materials is the development of sensors for chemical and biochemical species. Sensors based on conducting polymers, known so far can be broadly classified into two types, namely conductometric and amperometric sensors.

Conductometric sensors

The electronic conductivity of these polymers is strongly dependent on their electrochemical state[4]. For example, the conductivity of polyaniline is a function of *p*H and electrochemical potential[5] (Fig. 1). The conductivity is high at low *p*H and a potential 0.5V vs SCE. The conductivity decreases rapidly with increase in *p*H at a given potential. Similarly, at a given *p*H, the conductivity changes as the potential changes. This property has been utilized to develop sensors for various gases and biomolecules.

Gas sensors

Bartlett and co-worker[6] have described a number of sensors for organic vapours based on polypyrrole, poly-N-methylpyrrole, poly-5-carboxyindole and polyaniline.

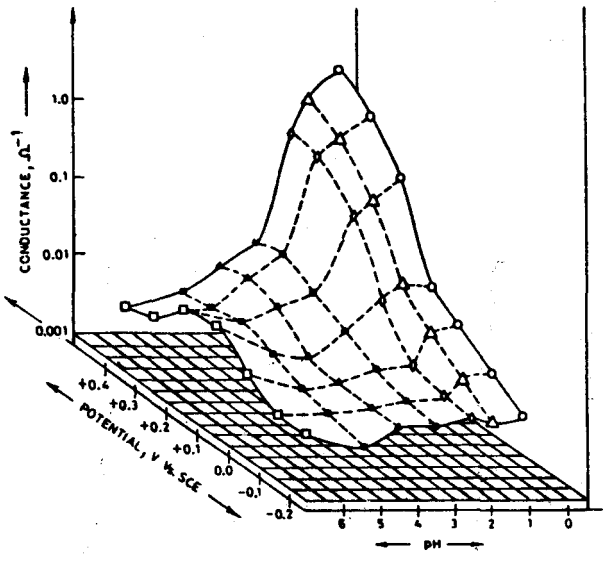

Fig. 1—A conductance surface 'state diagram' of polyaniline (ref. 4)

The sensors were formed by the electrochemical deposition of the appropriate polymer across a gap of 12 μm between two gold microband electrodes[7]. The polymer films were initially oxidized to a known extent potentiostatically. Upon exposure to the vapours, the polymers show conductivity changes that are rapid and in general reversible at room temperature.

Exposure to the organic vapours decreases the conductivity of the polymer films. The conductivity is restored on re-exposure of the polymer to air. The change in the conductivity probably results from a reversible reduction of the polymer on exposure to the organic vapour as well as change in the moisture content in the film. Though Bartlett *et al.*[7] have not reported the influence of relative humidity on the conductivity of the sensors, it is known that moisture content is important in determining the conductivity of polyaniline.

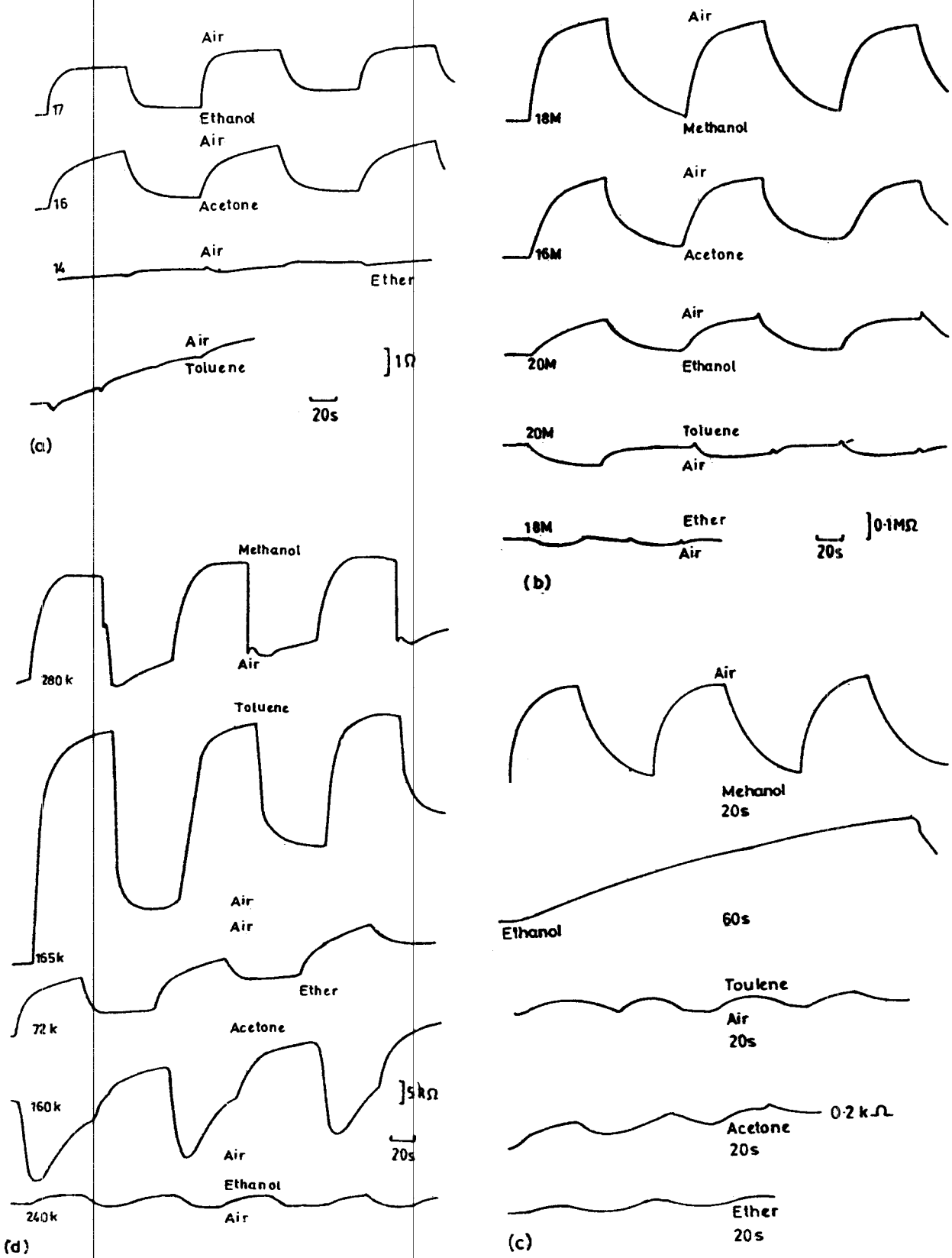

Fig. 2—(a, b, c, d) Typical responses (change of conductance) of polypyrrole, poly-N-methylpyrrole, poly-5-carboxyindole and poivaniline on exposure to saturated vapour at 25°C in a flowing system. The devices were cycled repeatedly between saturated and clean air (ref. 6).

Of the four polymers studied, poly-5-carboxyindole was found to give the most reproducible response. Typical responses of these polymers to the above organic vapours are shown in Fig. 2 (a, b, c and d).

Similarly, a polypyrrole-based sensor for hydrazine and ammonia has been described[8]. An ultra thin film of polypyrrole was coated on a non-conducting substrate e.g., acrylic, by dipping into a colloidal suspension of polypyrrole. This thin coating reversibly combines with low concentrations of ammonia or hydrazine with a concomitant reversible increase in resistance, 0.1 μg cm^{-3} of ammonia can be readily be detected with 1 cm^2 area of sensor. Sensors for ammonia are therefore required which are sensitive at the threshold limit of 25 μg cm^{-3}, i.e., the concentration in air to which workers can be exposed day after day without ill effects. A very important reason for monitoring workplaces with analytical devices for hydrazines is that the olfactory threshold for these vapours is above the concentration at which permanent damage can be caused.

Gas sensors based on thiophene and polyacetylene have been reported by Schmidt *et al.*[9]. It was found that polythiophene films exposed to NO showed an increase in conductivity by more than two orders of magnitude (Fig. 3). On the other hand, exposure to CO and N_2O resulted in little change in conductivity. A similar effect was observed when polyacetylene was exposed to these gases (Fig. 4).

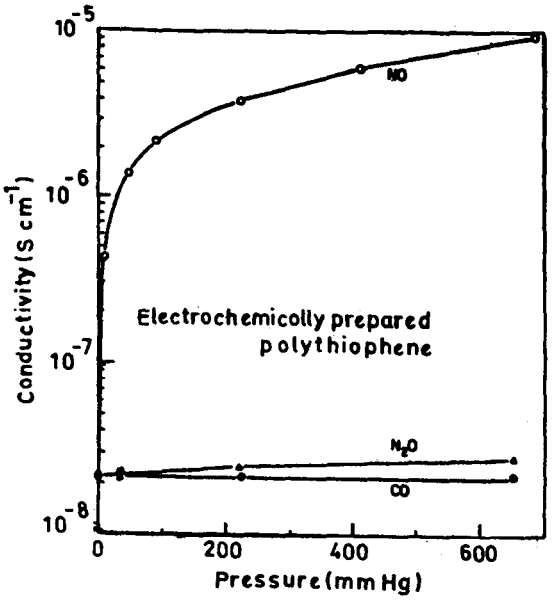

Fig. 3—Dependence of the electrical conductivity of polythiophene film on gas pressure (ref. 9)

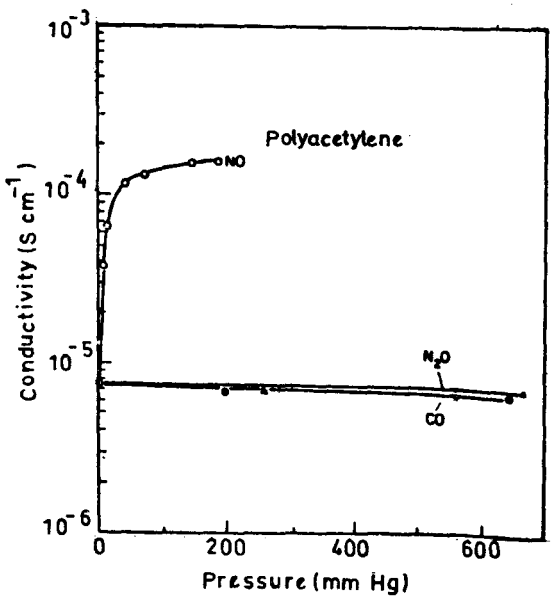

Fig. 4—Dependence of electrical conductivity of polyacetylene film on gas pressure (ref. 9)

Biosensors

A biosensor[10] is an analytical device incorporating a biological or biologically derived material, either intimately associated or integrated within a physico-chemical transducer. The aim is to produce an electronic response that is proportional to the concentration of the analyte. The advantage of a biosensor lies in its exploitation of biological specificity which potentially endows the device with the ability to detect low concentrations of analyte in complex matrices. The change in electronic conductivity of conducting polymers in response to change in *p*H has been made use of in fabricating sensors for biomolecules. Specificity to the desired molecule can be achieved by immobilising the appropriate enzyme into the polymer matrix.

The above concept has been utilised and demonstrated for the detection of glucose[11], urea, triglycerides and hemoglobin[12]. The conducting polymer used in these cases was polyaniline. The corresponding enzyme was immobilized in the polymer by physical entrapment. Thus the polymer acts as the immobilisation medium as well as the transducer for converting a biochemical signal to an electronic signal. Sensor response is typically derived as a result of changes in the chemical microenvironment occurring due to the enzymatic reaction.

The sensor configuration used in these studies is shown in Fig. 5. In the polyaniline-glucose oxidase system, the sensor showed change in resistance with concentration of glucose upto 10 m*M*

(Fig. 6). The change in resistance was reversible and reproducible. The resistance of the polymer decreased with increase in concentration of glucose. The specificity of the sensor to glucose has also been shown. The results show that after an initial fall in activity, the sensor response is stable for more than 14 independent measurements with a standard deviation of less than 10% (Fig. 7).

Similarly, a penicillin sensor[13] based on a microarray electrode coated with *p*H-responsive polypyrrole has been described. The enzyme reaction acidifies the polypyrrole membrane, resulting in increase in the electrical conductivity of polypyrrole. The conductivity changes were detected by the increase in the current (I_d) between the arrays at a constant applied voltage (V_D).

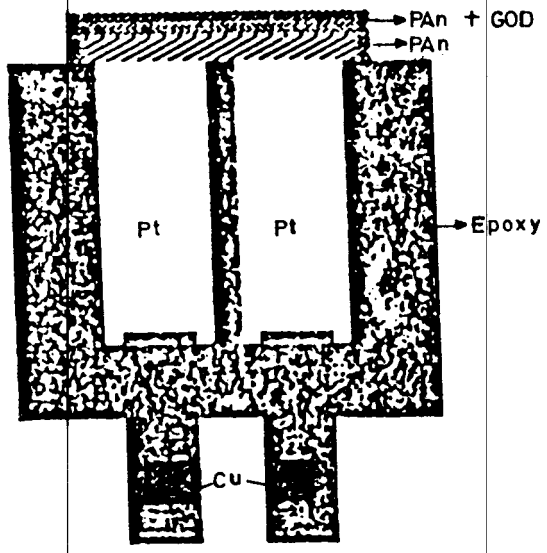

Fig. 5—A schemematic representation of sensor structure (ref. 11)

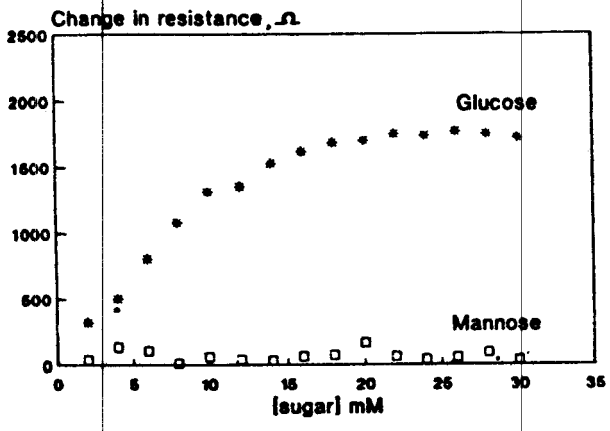

Fig. 6—Sensor response to solutions (phthalate buffer *p*H 4.0) containing various concentrations of (i) D-glucose and (ii) D-Mannose (ref. 11)

Recently an enzyme switch responsive to glucose was reported[11] The switch (Fig. 8) was constructed by immobilising glucose oxidase in an electropolymerized film of poly(1,2-diaminobenzene) grown on top of a polyaniline film. The switch employed tetrathiafulvalene (TTF) as a redox mediator capable of shuttling charge between the enzyme and the conducting polymer. In the oxidised state, polyaniline, at +0.5 V vs SCE (*p*H 5.0) is insulating. On addition of glucose, polyaniline is reduced. The reduced form being conducting, there is a rapid increase in current, operation of the switch is shown in Fig. 9.

Before the addition of glucose $i_{drain} = 0$ because at +0.5 V vs SCE at this *p*H, the polyaniline is in its insulating state. On addition of glucose, there is an initial lag followed by a rapid increase in the drain current, which then levels off to a constant value. Figure 10 shows a typical set of results for one device for a range of glucose concentrations. The speed of response of the device, as defined by the time taken for i_{drain} to reach half of its final value $t_{1/2}$, and the slope of the steepest

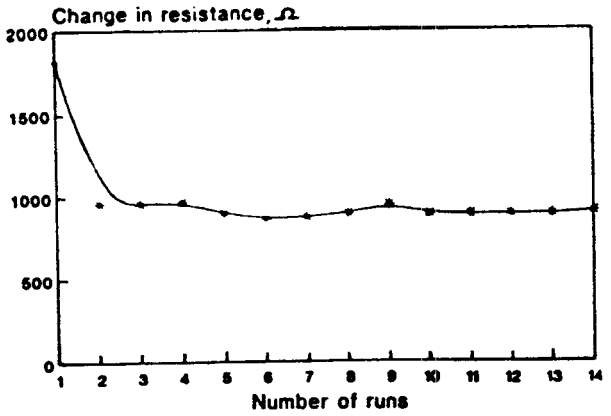

Fig. 7—Sensor response to a solution of 10 m*M* glucose concentration as a function of the number of independent measurements (ref. 11)

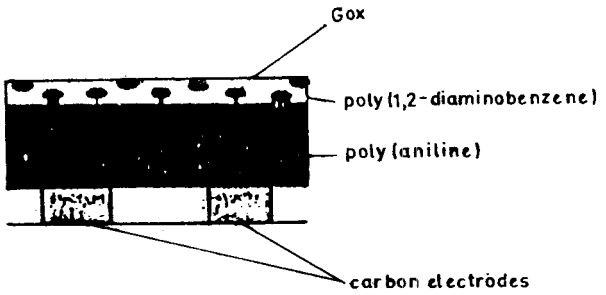

Fig. 8—Enzyme switch responsive to glucose. The enzyme glucose oxidase is immobilized in a thin insulating film of poly (1,2-diaminobenzene) deposited on top of the polyaniline film (ref. 14).

part of the curves S_{max}, depend on glucose concentrations. The inset in Fig. 10 shows S_{max} as a function of glucose concentration. In the absence of glucose the device turns on slowly ($t_{1/2}$ = 360 s) due to the reduction of the polyaniline film by TTF present in solution. In blank experiments, where either glucose oxidase or TTF was omitted no response to glucose was obtained.

A similar switch sensitive to NADH is already known[15]. A microarray electrode coated with pyrrole-N-methylpyrrole co-polymer containing diaphrose shows an on/off response upon addition of NADH, since diaphrose catalyses the reduction of polymer by NADH from a conductive to an insulating state.

These sensor concepts will open up the possibility for miniaturization and integration using microelectronic fabrication technology to produce inexpensive chips for sensing a range of biomolecules.

Amperometric sensors

In an amperometreic sensor, a constant potential is maintained between the sensing electrode and the reference electrode. The current generated by the redox reaction of the analyte at the sensing electrode is directly proportional to the analyte concentration at the electrode surface (Fig. 11).

Umana and Waller[16] reported for the first time a novel approach to electrode immobilisation of an enzyme, glucose oxidase, by electropolymerization of pyrrole in the presence of the enzyme. The enzyme becomes entrapped by the polypyrrole film growing on the electrode surface. The electropolymerized enzyme was active and served as the basis for a glucose electrode system that remained active for several days.

It was found that stable polypyrrole modified electrodes could be prepared and used in aqueous media for glucose determinations and polypyrrole modified electrodes are effective working electrodes for the indirect amperometric determination of H_2O_2 via I_2 reduction at 0.0 V. From experiments performed using polypyrrole/glassy carbon electrodes, it was shown that under optimum conditions GOx can be incorporated into polypyrrole films during their formation and that such electrodes can be used in the determination of glucose in aqueous solutions for a period of upto 7 days (Fig. 12).

Optical sensors

Electrochemically synthesized conducting polymers like polyaniline films[17] possess high redox reactivities in aqueous acidic solutions, and oxidized and reduced forms of the films exhibit vivid green and yellow colours respectively. Such colour changes in the film caused by redox reaction can be used for developing a redox sensor because of its fast response and high durability. Electrochromic devices using this property have been described[18] but there are as yet no reports of their application as redox sensors.

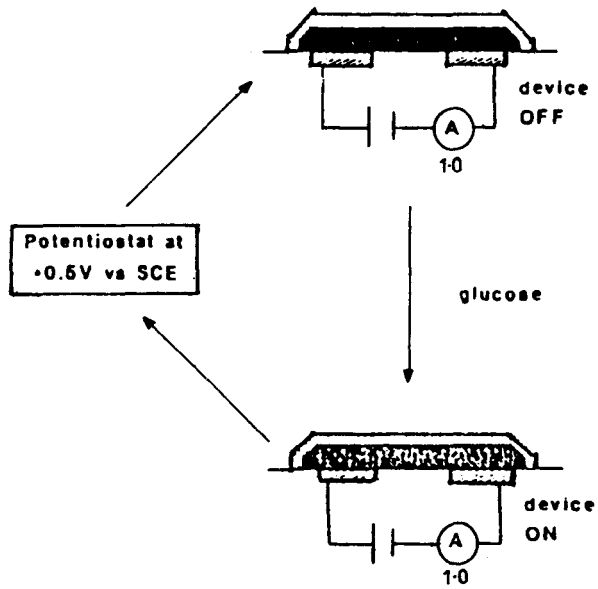

Fig. 9—Operation of the switch. Upon exposure to glucose the switch is turned from "off" to "on". The switch is reset by holding the film at +0.5 V vs SCE in a background buffer solution (ref. 14).

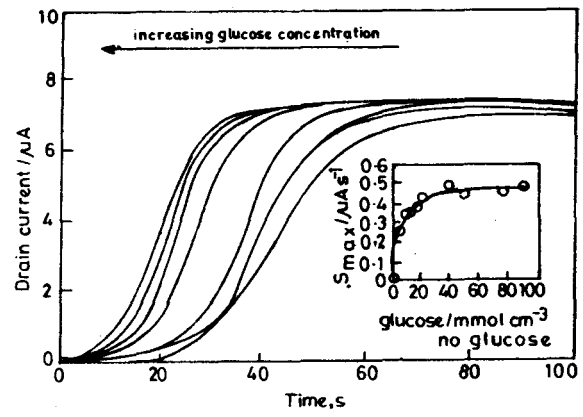

Fig. 10—Plots of drain current, I_{drain}, recorded for a 20 mV bias as a function of the time following addition of aliquot of glucose of a citrate/phosphate *p*H 5.0 buffer solution containing 0.5 mol dm^{-3} Na_2SO_4/0.5 vol % Triton X 100 and saturated with TTF. Between each measurement the device was washed and reoxidized at +0.5 V vs SCE. The inset shows a calibration plot of S_{max} as a function of glucose concentration (ref. 14).

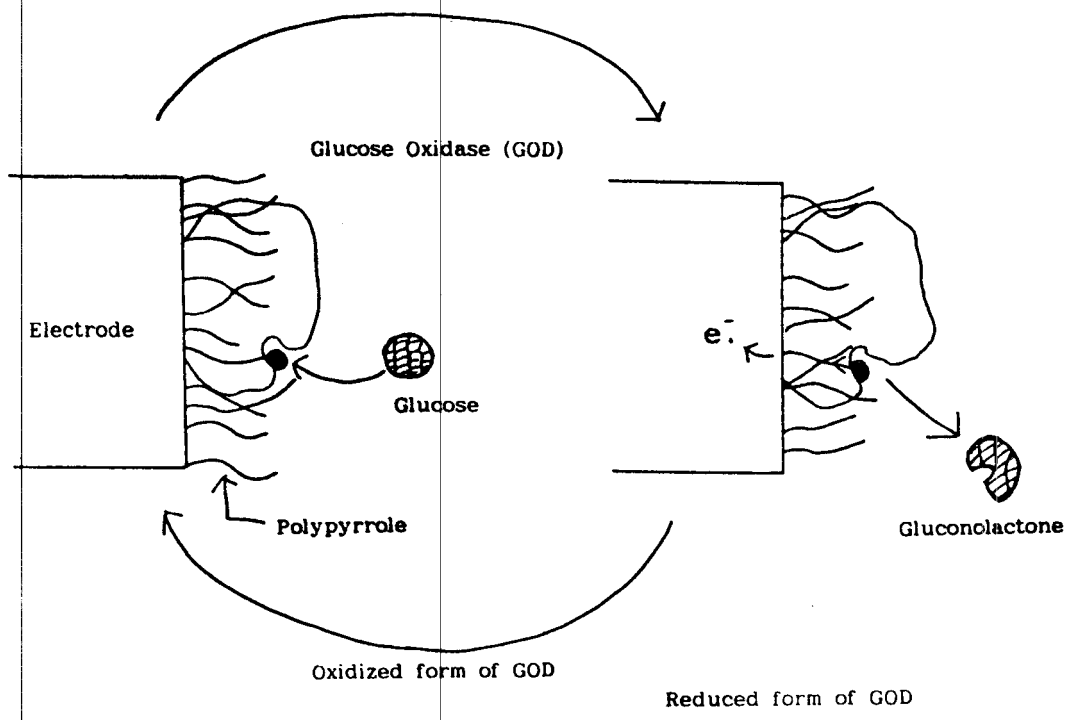

Fig. 11—Electron transfer of GOD entrapped in a conducting polymer membrane (ref. 16)

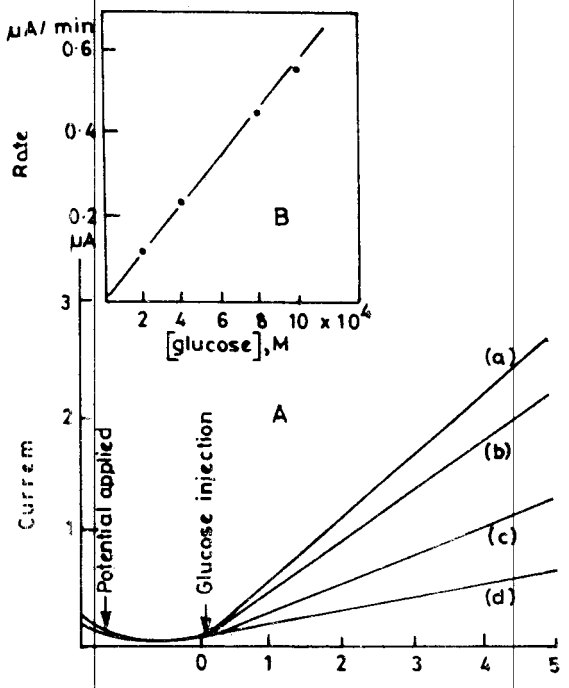

Fig. 12—Amperometric determination of glucose in the presence of 1 unit/ml glucose oxidase at 0.0 V using a PP/GC electrode: (A) current vs time curves at (a) 1×10^{-3} *M*, (b) 8×10^{-4} *M*, (c) 4×10^{-4} *M*, and (d) 2×10^{-4} *M* glucose); (B) initial rate of glucose oxidation as a function of [glucose] (ref. 16)

Conclusions

It has been seen that conducting polymers have tremendous technological potential as sensors. The advantages of conducting polymer based sensors are that they are inexpensive, can be miniaturized and can be easily fabricated as compared to other miniaturized sensors like FETS e.g., CHEMFETS, ISFETS, ENFETS etc. Also the primary output of these sensors is electrical in nature and hence easier to integrate into a single chip for further signal processing. The above advantages may lead to the development of 'multiple sensors' or 'sensor arrays'. In due to course these sensors are bound to find their way from the laboratory to commercial markets.

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