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Conducting polymer based biomolecular electronic devices

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Abstract. Biomolecular electronics is rapidly evolving from physics, chemistry, biology, electronics and information technology. Organic materials such as proteins, pigments and conducting polymers have been considered as alternatives for carrying out the functions that are presently being performed by semiconductor silicon. Conducting polymers such as polypyrroles, polythiophenes and polyanilines have been projected for applications for a wide range of biomolecular electronic devices such as optical, electronic, drug-delivery, memory and biosensing devices. Our group has been actively working towards the application of conducting polymers to Schottky diodes, metal–insulator–semiconductor (MIS) devices and biosensors for the past 10 years. This paper is a review of some of the results obtained at our laboratory in the area of conducting polymer biomolecular electronics.

Keywords. Conducting polymers; LB films; biosensor microactuators; monolayers.

PACS Nos 68.18; 68.47.p; 72.80; 87.80

1. Introduction

Electronic technology has made rapid progress during the past 10 years. The aim is to produce simple, faster and smaller electronic devices for our daily routine. Most of the devices are presently based upon the semiconductor silicon. The advanced silicon chip can store about 16 million bites of information within an area of 1 cm^2. This is the practical limit of the storage of derived information on a silicon chip. If the physical dimensions are decreased, the overheating and the cross-talk between the components tend to decrease the performance of the electronic devices. These technical difficulties have led to the evolution of an interdisciplinary field named biomolecular electronics (BE) or molecular electronics (ME). In biomolecular electronics biological molecules, particularly proteins and lipids are used to perform the basic properties necessary for the functioning of the biomolecular electronic devices. These biological materials conduct current, transfer molecules from one location to another, are capable of major color changes on application of an electric field or light and can produce cascades that can be used for amplification of an optical or an electronic signal. All these properties can be applied to electronic switches, gates, storage devices, biosensors, biological transistors etc.

Among organic materials, conducting polymers have attracted much attention towards the application in biomolecular electronics [1–7]. The main characteristic of a conducting polymer is a conjugated backbone that can be subjected to oxidation or reduction by

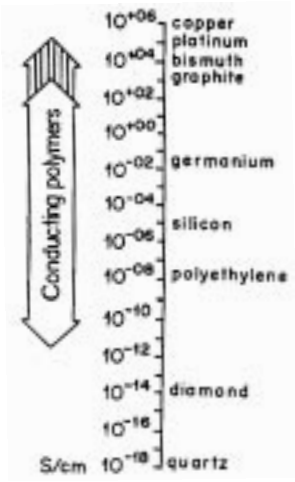

Figure 1. Conductivity chart for various conducting polymers.

electron acceptors or donors, resulting in what are frequently termed as p-type or n-type doped materials, respectively. The formation of a complex between the polymer and the dopant results in considerable increase in electron mobility resulting in enhanced electrical conductivity. Electrical conductivities can be varied by as much as 15 orders of magnitude by changing dopant concentrations so that electronic property control is feasible over the entire range from insulator to semiconductor and then to metal.

The electrical conductivity range of several conducting polymers are comparable to conventional metals, semiconductors and insulators as shown in figure 1.

Metals conduct electricity via mobile electrons in the conduction band that travel across atoms in the lattice. The equivalent situation in organic materials is provided by the delocalized π-electrons since conventional insulating polymers do not possess electrons in suitable orbitals. Thus the backbone of polyethene comprises sp^3-hybridized carbon with valance electrons confined to σ-bonding between adjacent atoms, while the π-electrons in the pendant atomic rings of polystyrene are unavailable for travel along the chain. Electrically conducting polymers have in common a significant overlap of delocalized π-electrons along the polymer chain. A number of polymer synthesis techniques are available, and many of them are used routinely by the polymer chemist. Among these are the stepwise synthesis routes, such as those using Ziegler–Natta catalyst [8], polycondensation [9], metal-catalysed polymerization [10], chemical [11] and electrochemical techniques [12].

Conducting polymers can be obtained by using a doping agent, i.e., by using anodic oxidation, a technique that leads directly to materials with high conductivity. Various methods such as chemical, electrochemical, photochemical doping and ion implantation methods are available for the doping of conducting polymers [13–15].

Characterization of conducting polymers has been considered to be very important for investigating the electronic processes occurring in molecular electronic materials. A variety of techniques such as electrochemical, optical, electron spin resonance (ESR), scanning electron microscopy (SEM), atomic force microscopy (AFM), gel permeation

chromatography (GPC) etc. have been widely used to delineate the physical properties of the conjugated polymers [16–20]. Information on morphological changes has been found to be very helpful towards the fabrication of lightweight batteries [21]. Electrochemical characterization provides information regarding redox behaviour, number of electrons in the redox reaction and diffusion coefficient estimation of conducting polymers [22]. Thermal techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TGA) reveal valuable information on the thermal stability and degradation of these organic molecular electronic materials [23]. It is emphasized that the experimental data accumulated as a result of characterization plays a significant role for the application of a desired conducting polymer to molecular electronics.

Due to the unique electrical, electronic and optical properties of these conjugated materials, several potential, technological and commercial applications such as fabrication of batteries, electronic devices, displays, sensors, functional electrodes etc. have been reported [24–26]. The present review is based on some of the recent research findings in the field of biomolecular electronics obtained in our laboratory.

2. Preparation of conducting polymer films

Ultrathin films of controlled thickness have drawn the attention of several scientists and technologists, the major advantage being the miniaturization, which has helped in enormous developments on very large scale integrated circuit (VLSI) devices specially of the organic semiconductors. Conducting polymers, which are organic semiconductors, have challenged the reign of the inorganic semiconductors. The simplicity in preparation and the cost effectiveness followed by the tailoring of properties of these organic molecules have attracted the attention of biotechnologists, physicists and chemists and technologists leading to the evolution of potential field of molecular electronics.

Conducting polymer films have been prepared by several techniques, e.g., spin coating, cast coating, self-assembled monolayer, Langmuir–Blodgett (LB) methods etc.

The LB film deposition technique is known to be capable of giving highly ordered monolayer films with a densely packed structure and precisely controlled thickness. Organized ultrathin films of controlled thickness deposited on solid substrates by the LB technique have attracted much attention because of their inherent suitability to functional molecular devices such as metal–insulator– semiconductor (MIS) devices, non-linear optical, electro-optic switches, modulators, memories and biosensors.

3. Langmuir–Blodgett films

Langmuir–Blodgett (LB) films are formed by first dispensing a small quantity of an amphiphilic material dissolved in a volatile organic solvent onto the surface of purified water (sub-phase). As the solvent evaporates, a monolayer is formed as dictated by the amphiphilic nature of the molecules; the head group is immersed on the water surface and the tail group remains outside (figure 2).

The molecules in their closest packed arrangement (solid phase) are removed from the surface of water by suitably dipping and raising a desired substrate through air/water interface.

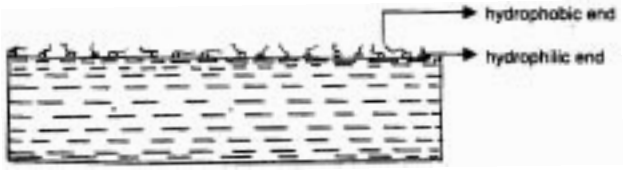

Figure 2. Monolayers of fatty acids on air–water interface.

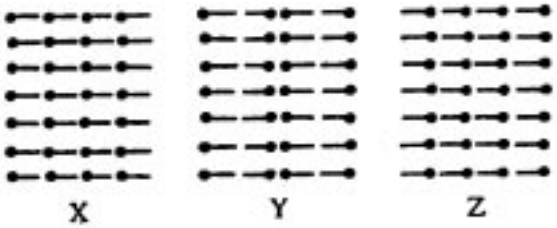

Figure 3. Schematic of X-, Y- and Z-type of deposition.

Three deposition types, viz. X, Y, Z deposition (figure 3) are possible depending on the nature of the substrate. If the substrate is hydrophilic, the first monolayer is transferred as the substrate is raised through the sub-phase and these molecules stack in a head-to-head and tail-to-tail configuration. This deposition mode is referred to as Y-type deposition. This results in an odd number of monolayers being transferred onto the solid substrate. However, if the solid substrate is hydrophobic, a monolayer will be deposited as it is first lowered into the sub-phase, thus a Y-type film containing an even number of monolayers can be fabricated. The Y-type deposition in the Langmuir trough is shown in figure 4. If a monolayer is deposited on the substrate when the solid substrate enters the sub-phase, then it is called an X-type deposition. On the other hand, if a monolayer is deposited on the substrate when it is withdrawn from the sub-phase, it is called Z-type deposition.

The value of the photocarrier mobility obtained by the time-of-flight (TOF) measurements in P3HT-SA LB films sandwiched between metal (Al) and ITO-coated glass was determined to be 1.8×10^{-5} cm^2/V-s at an applied field of 1.3×10^6 V/cm [27]. Agbor and co-workers [28] have reported the effect of various gases (NO_2, H_2S, CO, SO_2, N_2 and CH_4) on surface plasmon resonance of Langmuir–Blodgett films of polyaniline. Stella *et al* have characterized olive oil using an electronic nose based on polypyrrole [29]. Li *et al* [30] fabricated polyaniline composite ultrathin films with isopolymolybdic acid and demonstrated that the conductivity of the films is sensitive to humidity, NO_2 and NH_3. Besides this, the use of conducting polymer films for the development of biosensor has attracted significant attention.

A biosensor 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 analyte. Specificity of the desired molecule can be achieved by immobilizing the appropriate enzyme into the polymer matrix. Immobilization of the enzyme in several matrices has been used for the fabrication of biosensors for the estimation of glucose [31,32], urea [33,34], cholesterol [35] etc.

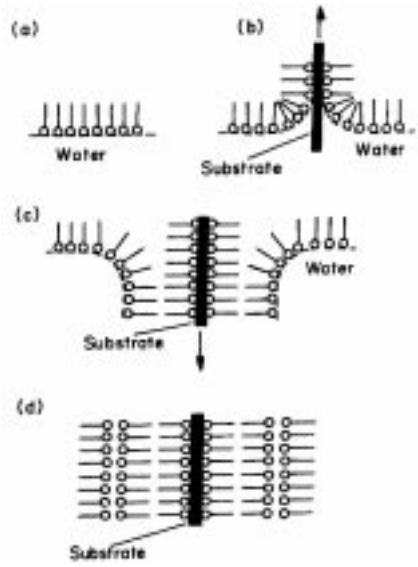

Figure 4. Schematic of Y-type deposition in a Langmuir trough. (**a**) Compressed monolayer of molecules on water surface, (**b**) deposition of first monolayer withdrawn on hydrophilic substrate, (**c**) deposition of second monolayer on insertion of hydrophilic substrate, (**d**) deposition of third monolayer in head-to-head and tail-to-tail configuration.

The immobilization of monolayers, or sub-monolayers, of enzymes on electrode surfaces forms the basis of molecular level fabrication of enzyme biosensors. Monolayer enzyme electrodes have been fabricated via covalent or electrostatic binding of the recognition molecule onto electrodes modified with Langmuir–Blodgett films [36,37]. Owaku *et al* [38] fabricated protein A molecular membrane on a quartz surface by LB method. Protein A has specific efficiency to the fc part of anti-human IgG antibody. The antibodies were self-assembled onto a protein A LB film. These films can be used for optical immunosensing. Chen and co-workers [39] found that chemically synthesized poly (*o*-anisidine) could form stable monolayer on the water surface. These monolayers transferred onto quartz crystal microbalance (QCM) can be used as organic vapor sensor. The advantage of using LB films is that this technique provides well-defined surface for protein immobilization [40].

4. Application of conducting polymer films in biomolecular electronics

4.1 *Lactate biosensor based on sol–gel polyaniline film*

Figure 5 shows the response curve for sol–gel/PANI/LDH electrodes, before and after PVC coating. The reaction mixture (5 ml) consists of lactate and NAD (0.02 M). LDH immobilized on the electrodes, catalyses the conversion of lactate on reaction with the co-enzyme NAD^+ to pyruvate and NADH. NADH thus produced was oxidized to NAD^+ on the sol–

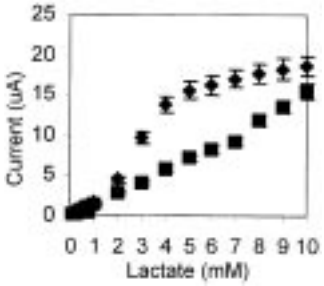

Figure 5. Calibration curve for sol–gel/PANI/LDH electrodes as a function of lactate concentration before PVC coating (♦) and after PVC coating (■).

gel/PANI electrodes, at a bias voltage of 0.4 V. PANI entrapped within the sol–gel can act as an electron acceptor and the current produced was recorded through an electrometer.

$$\text{NADH} \xrightarrow{0.4\text{ V}} \text{NAD}^+ + \text{H}^+ + 2e^- \tag{1}$$

$$\text{PANI}_{\text{ox}} + 2e^- \longleftrightarrow \text{PANI}_{\text{red}}. \tag{2}$$

The calibration curve of the sol–gel/PANI electrodes without PVC coating shows a linear increase in response with increasing lactate concentration (1 mM to 4 mM) whereafter a very small increase in the response current was observed leading to the steady state response [41]. When the response measurements were carried out with sol–gel/PANI electrodes coated with an external PVC layer, the linearity was extended to 10 mM of *l*-lactate. This has been attributed to the reduced and uniform availability of the substrate to the enzyme as it has to diffuse through the external PVC layer indicating that the external PVC layer acts as a rate limiting layer during the reaction.

4.2 *Urea biosensor based on PNVK/SA LB film*

Urea is one of the most important end product of protein degradation in the body. The urea content of blood serum depends on protein catabolism and protein intake and is regulated by renal excretion. The serum concentration of urea provides information on kidney function and the estimation of urea is frequently performed in medical diagnostics. The normal level of urea in blood serum ranges from 3.6 mM to 8.9 mM. For detection of urea in blood or solution, various techniques such as spectrophotometry, potentiometry, flow injection technique, coulometry, amperometry, conductometry etc. have been proposed [42–50]. Potentiometric and amperometric methods of determination are however frequently used.

The urease was immobilized onto Langmuir–Blodgett films of poly-*N*-vinyl carbazole (PNVK)/stearic acid (SA) by Langmuir–Blodgett technique. About 7.35 mg of urease was mixed at room temperature (30°C) in 0.5 ml solution of stearic acid and poly-*N*-vinyl carbazole in chloroform results 1 IU/μl solution of urease. This solution was carefully loaded onto the surface of deionized water (Millipore 10 RTS) in the LB trough with a syringe at 30°C and at pH 7.0. Pressure–area isotherm of the urease-immobilized PNVK/SA films (figure 6) shows a gas–liquid phase transition at a surface pressure of 3.33 mN/m at the area/molecule of 65 Å^2. The liquid–solid phase transition occurs at a surface pressure of

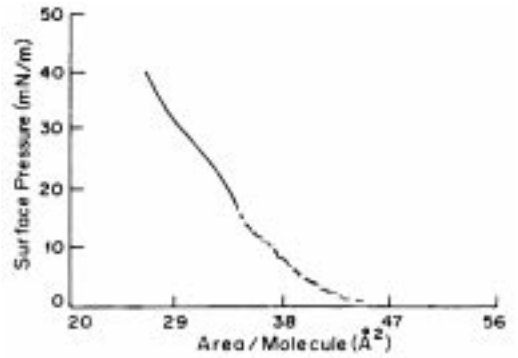

Figure 6. Pressure–area isotherm of mixed monolayers of poly-*n*-vinyl carbazole (PNVK) and stearic acid (SA) at a sub-phase temperature of 30°C and pH 7.0.

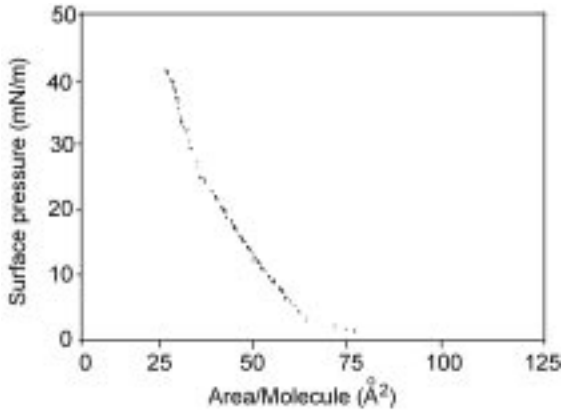

Figure 7. Pressure–area isotherm of mixed monolayers of poly-*n*-vinyl carbazole (PNVK), stearic acid (SA) and urease at a sub-phase temperature of 30°C and pH 7.0.

25 mN/m and at the area/molecule 34 $Å^2$. The compressibility for gas–liquid phase varies from 0.078 m/mN to 0.013 m/mN and for the liquid–solid phase transition it varies from 0.008 m/mN to 0.006 m/mN. The increase in the area/molecule of the PNVK/SA/urease as compared to PNVK/SA (figure 7) indicates the incorporation of enzyme urease into the PNVK/SA monolayers. Thirty monolayers of PNVK/SA/urease were transferred onto 40 monolayers of PNVK/SA which were transferred onto ITO-coated glass plates by vertical dipping method.

The activity of PNVK/SA/urease electrodes was measured in a measuring cell containing phosphate buffer (0.01 M, pH 7.0), using ammonium ion analyser (AR 25, Fisher Scientific). All measurements were taken at room temperature (28°C) using PNVK/SA/urease LB electrodes as working electrode and NH_4^+ sensing electrode as counter electrode. The urea solution of different concentrations (0.5 mM–93 mM) was prepared in phosphate buffer of pH 7.0 at 30°C. The concentration of NH_4^+ ion produced was measured in ppm and the resulting change in potential was measured in mV. The potentiometric response of a PNVK/SA/urease LB electrode is shown in figure 8. A good linear correlation between

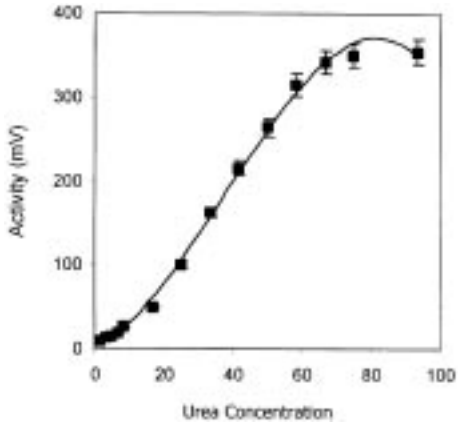

Figure 8. Response curve of PNVK/SA/urease LB films as a function of urea concentration, 0–93 mM.

potential sensed by an ammonium ion selective electrode and urea concentration was obtained in the range 0.5 mM to 93 mM when this electrode was used. Two linear ranges were obtained, viz. 0.5–10 mM and 10–68 mM (figure 8). In the first range the change in activity was insignificant. Above 10 mM, the sensor showed a good linear response upto a concentration of 68 mM. The response time of the urease/PNVK/SA LB electrode was about 2 min. The detection limit and the sensitivity for this electrode have been experimentally determined as 5 mM and 10 mV/mM urea, respectively. The measurements were repeated several times using the same electrode and consistent results were obtained for 10 repeat cycles, beyond which there was a large drop in the activity. Thus it was found that the PNVK/SA electrodes immobilized with urease could be used for 10 cycles.

The thermal stability of urease immobilized on PNVK/SA LB films was investigated by measuring the urease activity as a function of temperature by holding the film in a 1 ml phosphate buffer at varying temperatures of urea solution (10 mM) between 25 and 60 °C, maintained in a hot water bath for about 10 min. The films were then tested for urease activity by the method described earlier. A higher temperature (40 °C) optimum (figure 9) was obtained for PNVK/SA/urease electrode, which could perhaps be due to higher intermolecular interactions. About 75% activity was recorded at 45 °C after which a steady decrease was observed. This has been assigned to the denaturation of protein at higher temperatures. This decrease in activity was reversible until 49 °C indicating that the enzyme perhaps attains its near original conformation after returning to normal temperature. Activation energy is the amount of energy required for the catalysed reaction to proceed [51]. The activation energy before and after critical temperature (40 °C) was found to be 4027 and 7595 cal, respectively. These studies indicate that the PNVK/SA/urease LB films exhibit increased activity in the lower temperature region (<40 °C).

The detection limit and sensitivity of these electrodes was found to be 5 mM and 10 mV/mM, respectively. These PNVK/SA/urease LB electrodes were found to be stable up to 40°C and can be used for 10 times for urea estimation. The shelf-life of these electrodes was found to be about 5 weeks at 4°C.

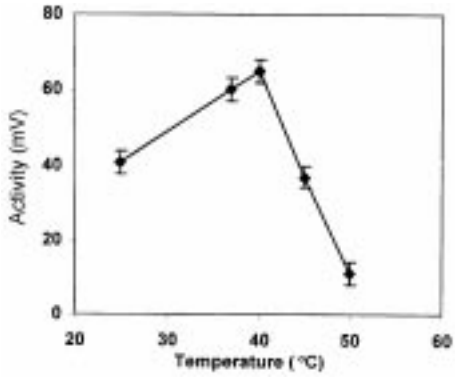

Figure 9. Effect of temperature (25–50°C) on the activity of urease immobilized in PNVK/SA LB films in phosphate buffer at pH 7.0.

4.3 *Glucose biosensor based on P3DT/SA LB films*

The monolayers of P3DT/SA were fabricated by dispensing a solution (1:1) of P3DT (1 mM) and stearic acid (2 mM) in chloroform onto water sub-phase containing $CdCl_2$ (2×10^{-4} M), using a Joyce–Loebl LB trough (model 4). The pressure–area isotherms of P3DT/SA monolayer were obtained at the barrier compression rate of 4 mm/min at different temperatures and pH. The monolayer stability onto the water sub-phase was measured at different surface pressures, temperatures and sub-phase pH, respectively. These monolayers were transferred onto the ITO-coated glass plates at a surface pressure of 30 mN/m at 30°C by vertical dipping method. The dipping speed was 5 mm/min during upstroke and downstoke. 5 mg (200 units/mg) of enzyme GOX was mixed in a solution of P3DT/SA in chloroform and this solution was spread onto air–water interface of the LB trough. Thirty monolayers were later transferred onto P3DT/SA-ITO glass plates.

The results of amperometric response determined for P3DT/SA/GOX LB films are shown in figure 10. All measurements were performed at room temperature using P3DT/SA LB film immobilized with enzyme (GOX) as working electrode polarized at 0.4 V and Pt as counter electrode. The working solution comprised phosphate buffer (pH 7.0) and glucose. The overall reaction of GOX with the LB/GOX electrode involves the catalytic oxidation of glucose by GOX,

$$\beta\text{-Glucose} + O_2 \xrightarrow{\text{Glucose Oxidase}} \beta\text{-Gluconic acid} + H_2O_2 \tag{3}$$

followed by the amperometric determination of H_2O_2 by electrochemical oxidation at 0.4 V Vs SCE,

$$2H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-. \tag{4}$$

P3DT/SA/GOX LB electrode shows linearity from 100 mg/dL to 400 mg/dL after which a limiting value of current was obtained.

P3DT/SA/GOX LB films were tested for stability up to 40 days, under the same operating conditions as those for the response measurements. Figure 11 shows the amperometric

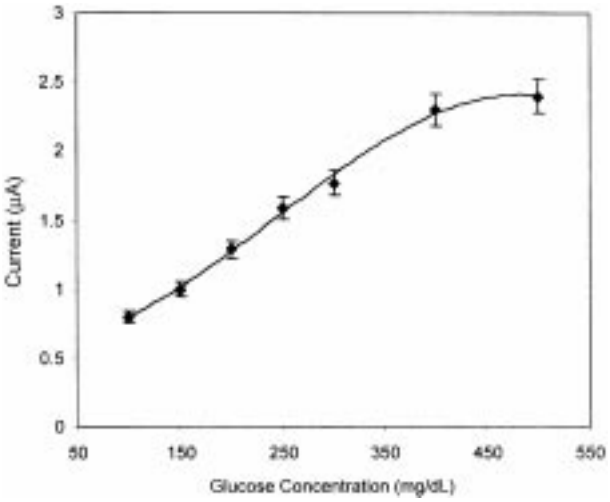

Figure 10. Amperometric response of P3DT/SA/GOX LB film in phosphate buffer (pH 7.0) at 0.4 V (bias voltage).

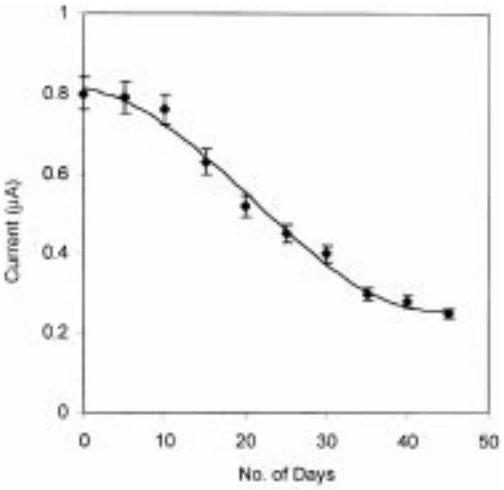

Figure 11. Response of P3DT/SA/GOX electrodes as a function of storage time in the presence of glucose (100 mg/dL) in phosphate buffer (pH 7).

response of the P3DT/SA/GOX LB films to 100 mg/dL glucose solution in phosphate buffer (pH 7) with time. It can be seen that the response of these electrodes remains almost same for about 10 days followed by a gradual decrease in its value up to about 40 days after which it becomes stable. The half-life of these electrodes P3DT/SA/GOX LB films has been determined to be about 25 days.

The effect of interferents in the presence of their physiological maximum levels with glucose was studied under similar conditions as those for response measurements. The response current for 5.5 mM glucose in the presence of ascorbic acid (0.1 mM) or uric

acid (0.5 mM) were within the range of relative error of 5% from the actual value without addition.

4.4 *Microactuators*

Conducting polymers can be driven reversibly between conducting and insulating state through electrochemical charge–discharge processes in an electrolyte solution or through chemical redox reaction in a solution or gaseous atmosphere. These charge–discharge processes are associated with the volume change of the conducting polymer. This property of volume change has been employed for fabrication of several devices like actuators and sensors [52]. Batra *et al* [53] have designed and fabricated an experimental set-up to study the electromechanical properties of solution cast polyaniline film ($\sim$50 μ) under load. Extension of the films versus voltages has been measured in terms of change in capacitance of parallel plate capacitor constituted by metal pan and a fixed metal plate. It was found that during the first cycle the length is enhanced by about 6% of the original value, while repetitive value of extension is $\sim$2.8%, in subsequent cycles.

5. Conclusions

It has been shown that conducting polymers can be used for the fabrication of various biomolecular electronic devices such as microactuators and biosensors. Further, it can be seen that stable monolayers of PNVK/SA and P3DT/SA can be formed at air–water interface. The enzyme GOX and urease can be immobilized in these monolayers of P3DT/SA and PNVK/SA, respectively. These enzyme immobilized monolayers can be transferred onto ITO-coated glass plates. These P3DT/SA/GOX and PNVK/SA/urease LB electrodes can be used for the estimation of glucose and urea in solution, respectively.

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