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A comparative study of a polyindole-based microelectrochemical transistor in aqueous and non-aqueous electrolytes

Received: 6 April 1999 / Accepted: 24 August 1999

Abstract The behaviour of a polyindole-based microelectrochemical transistor in aqueous and non-aqueous electrolytes is described. The polyindole film was grown onto two closely spaced (100 μm) platinum microelectrodes by anodic oxidation of indole (10 mM) from 0.1 M tetrabutylammonium perchlorate in dichloromethane at 1.1 V vs. Ag/AgCl. The polymerization was carried out for a sufficiently long time in order to connect both Pt microelectrodes, which operated as a transistor when immersed in an electrolytic solution. In this transistor, one microelectrode was a “source” and the other a “drain”; the Ag/AgCl wire reference electrode was used as a “gate”. The drain current (current between source and drain) was modulated by varying the gate potential (potential between source and gate) at a fixed drain potential (potential between source and drain). The transconductances of the transistor were estimated as 0.98 mS/cm and 20.6 mS/cm of channel width (separation between two microelectrodes) in aqueous and non-aqueous solutions, respectively.

Key words Conducting polymer · Polyindole · Electrochemical transistor

Introduction

In recent years there has been enormous interest in the development of semiconducting devices based on conducting polymers, because of their unique electrical and electronic properties. The conductivity of these polymers

can be controlled by changing their redox state by means of chemical or electrochemical reduction or oxidation accompanied by insertion of counter ions. This means that the characteristics of electronic devices based on conducting polymers can be modified on request. This behaviour promises the utilization of conducting polymers as active components in the fabrication of semiconducting devices. So far, a number of devices have been developed using conducting polymers, which include field effect transistors (FETs), metal-insulator-semiconductor field effect transistors (MISFET), Schottky diodes, light emitting diodes, microelectrochemical transistors [1–5], etc. Among these electronic devices, microelectrochemical transistors are very important because of their applications. In recent years, microelectrochemical transistors have been developed for detection of chemical and biological substances [6, 7], which shows that conducting polymers are promising materials for sensing devices.

Earlier work on polyindole, showed poor yield, air instability and low conductivity [8], which precluded the use of this material for electronic device construction. Recently, we reported on a modified polyindole of high stability, electroactivity and conductivity [9], which seems to be promising for various applications [10, 11]. In the present paper we report on the behaviour of the polyindole-based microelectrochemical transistor both in aqueous and non-aqueous electrolytes.

Experimental

The transistor described here consisted of two closely spaced platinum microelectrodes, which were used as “source” and “drain”. Polyindole was grown by electropolymerization onto Pt microelectrodes under constant potential conditions, as described earlier [9]. The polymer deposition was carried out at 1.1 V vs. Ag/AgCl from 10 mM indole containing 0.1 M tetrabutylammonium perchlorate (TBAP), in CH_2Cl_2 . All the chemicals used were from Sigma/Aldrich. The polymerization was carried out on both microelectrodes simultaneously until the 100 μm gap between them was bridged. In the completed device, a third electrode (Ag/AgCl

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wire) was used as a "gate" which was contacted to the polymer film through the electrolyte. The electrochemical deposition of the polymer and characterization of the microelectrochemical transistor was done using a model RDE4 Bi-Potentiostat (Pine Instruments) and a 7035B X-Y recorder (Hewlett-Packard). All measurements were carried out at room temperature (25 °C). The transistor characteristics in both aqueous (0.1 M LiClO₄) and non-aqueous (0.1 M TBAP, CH₂Cl₂) solution were compared.

Prior to use as a pair of microelectrodes, each microelectrode wire was tested with an ohmmeter to make sure that it is not shorting. Then, each microelectrode was tested by cyclic voltammetry (CV) in a solution of 0.1 M TBAP in CH₂Cl₂. Next, the microelectrodes were coated with polyindole and the coated microelectrodes were then examined by CV in 0.1 M TBAP in CH₂Cl₂, in order to assess the coverage of the polymer and to determine if the polymer bridged both microelectrodes completely.

Results and discussion

Figure 1 shows the cyclic voltammogram, at 20 mV/s in 0.1 M TBAP in CH₂Cl₂, of the polyindole-coated single microelectrode (one wire) and a pair of the microelectrodes (both wires). The current of both voltammograms was the same, indicating that only one electrode is capable of oxidizing all the polyindole

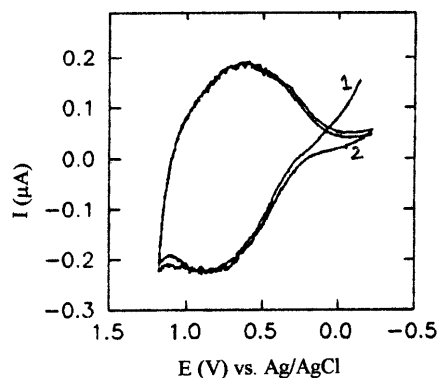
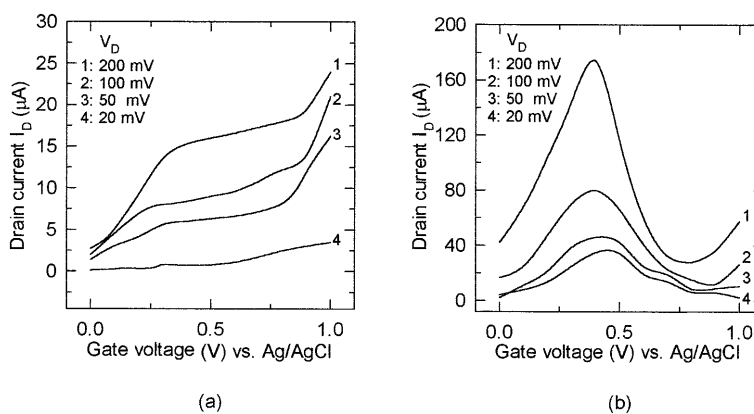


Fig. 1 Cyclic voltammogram at a scan rate 20 mV/s in 0.1 M TBAP in CH₂Cl₂ of the polyindole transistor for only one microelectrode connected (curve 1) and both microelectrodes connected (curve 2)

Fig. 2 Drain current vs. gate potential characteristics of the polyindole-based microelectrochemical transistor for **a** 0.1 M LiClO₄ aqueous solution and **b** 0.1 M TBAP in CH₂Cl₂ at various drain potentials, V_D



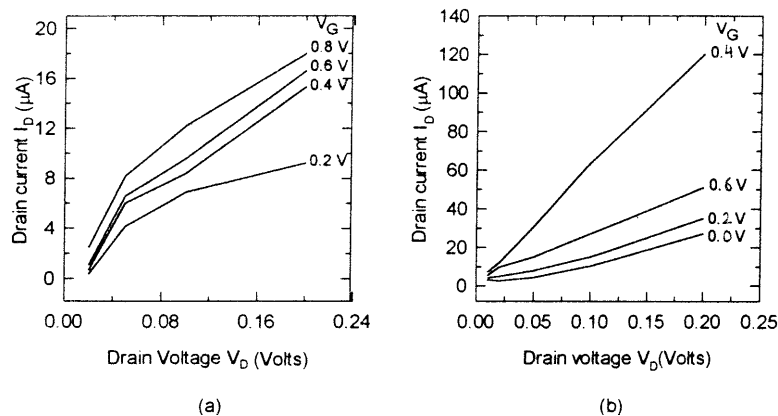
present over the microelectrodes. Additionally, if both microelectrodes bridged with polyindole are externally connected, then the cyclic voltammogram is the same as if potential is applied to only one of the microelectrode.

Figure 2a and b show drain current (I_D) vs. gate potential (V_G) characteristics for the polyindole-based transistor operated in 0.1 M LiClO₄ aqueous solution and 0.1 M TBAP in CH₂Cl₂, respectively. As shown in Fig. 2a, the accessible potential window (the potential range in which the drain current does not change significantly) extends to a potential of 0.9 V. This result is in contrast to that shown in Fig. 2b, where the drain current and therefore the conductivity decreases significantly as the result of the polymer oxidation at a potential exceeding 0.4 V. This behaviour indicates that the polymer has a finite potential-dependent window. Consistently, a potential range of high conductivity is associated with a range where a potential shift is accompanied by a change of redox state of the polymer. Unlike the solid state transistors, the polyindole-non-aqueous electrolyte-based transistor shows a maxima at about 0.4 V on the I_D vs. V_G curves (Fig. 2b). In contrast, the polyindole-aqueous electrolyte-based transistor shows an increase of I_D as V_G is scanned positively, then I_D reaches a plateau at $V_G > 0.4$ V, and for $V_G > 0.8$ V it again increases. A large slope of the I_D vs. V_G plot for $V_G > 0.8$ V can be considered as over-oxidation of the polyindole (loss of electroactivity and redox reversibility).

Another important feature of the polyindole-based transistor is a larger maximum value of I_D for the non-aqueous solution than that for the aqueous solution. A typical value of the drain current is $I_D = 174 \mu\text{A}$ at $V_D = 200$ mV. This value is significantly higher than that for the aqueous solution, which is only $I_D = 21 \mu\text{A}$ at the same V_D . The higher I_D value indicates that the conductivity of polyindole in the non-aqueous solution is higher than that in the aqueous solution. Presumably, this result is due to the more efficient doping-dedoping of polyindole in the non-aqueous solution.

An important parameter, transconductance " g_m " [12] of the transistor defined as

Fig. 3 Drain current vs. drain potential characteristics of the polyindole-based microelectrochemical transistor for **a** 0.1 M LiClO₄ aqueous solution and **b** 0.1 M TBAP in CH₂Cl₂ at various gate potentials, V_G



$$g_m = \left[\frac{I_D}{V_G} \right]_{V_D = \text{constant}} \quad (1)$$

and it is calculated from the slope of the linear part of the I_D vs. V_G curve. For non-aqueous solutions the average value of $g_m \approx 20.6$ mS/cm is significantly larger than that for aqueous solutions, $g_m \approx 0.98$ mS/cm. The high g_m value for non-aqueous solutions indicates that the sensitivity of the transistor is high. Figure 3a and b show the output characteristics of the transistor, I_D vs. V_D , at various values of V_G , both for aqueous and non-aqueous solutions. Figure 3b shows a decrease of the slope of the characteristics for a gate potential exceeding 0.4 V. At zero potential applied to the gate ($V_G = 0$ V) the I_D value is small, and polyindole is expected to be insulating. If V_G is closed to 0.4 V, then a drain current is significant. However, the polymer is insulating again and the drain current decreases with the V_G increase at more positive potentials ($V_G \approx 0.6$ V). This behaviour is similar to that of polyaniline [5]. The behaviour of polyindole in aqueous solution (Fig. 3a) is entirely different than that in non-aqueous solution (Fig. 3b), where the slope of the I_D vs. V_D plots is larger the larger is the V_G value, similar to the behaviour of the solid state transistors.

Conclusions

Polyindole can be deposited onto a pair of Pt microelectrodes in a manner that allows its operation as a transistor-like electronic device. The conductivity change of the polyindole with the change of the applied potential is the basis of the functioning of this device. The polyindole-based transistor-like devices can be turned on and off by electrical or chemical signals that

oxidize/reduce the polymer. The polyindole-based electrochemical transistor reveals different types of transistor characteristics in aqueous and non-aqueous electrolytes. Relative high sensitivity and conductivity of the transistor are observed for the non-aqueous electrolyte, which were attributed to the relatively high electroactivity of the polymer in the electrolyte.

Acknowledgements The authors are thankful to Prof. K.S.V. Santhanam, Chemical Physics Group, Tata Institute of Fundamental Research, Mumbai, India, for providing his laboratory facilities and CSIR, New Delhi, India, for financial assistance.

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