

## SHORT COMMUNICATION

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**Copper(II) ion-selective microelectrochemical transistor**

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**Abstract** A device has been developed for the measurement of copper(II) ions ( $\text{Cu}^{2+}$ ) in aqueous medium. The device reported here is an electrochemical transistor which consists of two platinum electrodes separated by 100  $\mu\text{m}$  spacing and bridged with an anodically grown film of polycarbazole. Polycarbazole film (undoped form) is observed to be highly selective for the Cu(II) ions. In a completed device, the conductivity of the polycarbazole film changes on addition of Cu(II) ions. The change in conductivity is attributed to the conformational changes in the polymer phase on occupation of the Cu(II) ions, without affecting electron/proton transfer. The device turns on by adding  $2.5 \times 10^{-6}$  M Cu(II) ions and reaches a saturation region beyond  $10^{-4}$  M Cu(II) ion concentrations. In the above concentration range, the device response [ $I_D$  vs.  $\log$  Cu(II) ion concentration] is linear. The selectivity of the device for other metal ions such as Cu(I), Ni(II), Co(II), Fe(II), Fe(III), Zn(II) and Pb(II) is also studied.

**Key words** Copper(II) ions · Polycarbazole · Electrochemical transistor

**Introduction**

In this article we wish to present some new findings concerning the Cu(II) ion selectivity of polycarbazole immersed in an aqueous solution and to demonstrate the fabrication of a Cu(II) ion selective transistor based on polycarbazole. We recently reported [1] a solid state

Cu(II) ion-selective electrode (ISE) based on polycarbazole with a lowest detection limit of  $\sim 10^{-4}$  M. The new device reported here is significant because it gives a linear response in the range of  $2.5 \times 10^{-6}$  M to  $10^{-4}$  M.

In recent years, several devices based on conducting polymers have been developed for the detection of chemical species in electrochemical or biological environments [2–6]. Among these devices, the ion-selective field effect transistor (ISFET) and microelectrochemical transistor [5, 6] have attracted considerable attention owing to the possibility of making miniaturized devices with high selectivity, sensitivity and durability. These sensing devices were made by making use of the significant conductivity changes of the conducting polymer, which happens either due to oxidation/reduction of the polymers in the presence of specific chemical species or to a change in their configuration. Devices were also developed by incorporating some enzymes/ionophores or a separate ion-selective film into/onto the polymer itself [7]. These devices could detect specific chemical species, depending upon either the ion-selective membrane (ionophore) or the response to a specific enzyme.

In our earlier publication [8] we reported an electrochemical transistor based on the potential-dependent conductivity of polycarbazole. In the present paper we report the results of a study of an ion-selective microelectrochemical transistor (ISMET) responsive to Cu(II) ions.

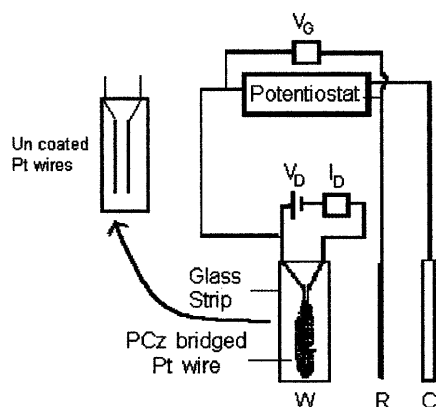
**Experimental**

The device described here consists of two parallel platinum wire electrodes embedded 100  $\mu\text{m}$  apart over a glass strip. These electrodes were used as the “source” and “drain” for the device. Polycarbazole deposition was carried out in dichloromethane (Glaxo, India) solution containing 60 mM carbazole (Aldrich), 0.1 M tetrabutylammonium perchlorate (TBAP) (Sigma) at a constant potential of 1.4 V vs. an Ag/AgCl electrode as described earlier [8]. The polymerization was carried out on both electrodes simultaneously until the polymer film bridged the gap between the

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two electrodes. The device was completed by using a third electrode (Ag/AgCl wire) as a "gate", which was in contact with the polymer film through the electrolyte as shown in Fig. 1. The transistor configuration is essentially the same as used by Wrighton and co-workers [9]. All electrochemical characterizations were done using a Pine Instruments Bi-Potentiostat (model RDE4) and data were recorded on a Hewlett-Packard 7035B X-Y recorder. The measurements were carried at 25 °C. The transistor characteristics were first obtained for the above device in an aqueous solution of 0.1 M LiClO<sub>4</sub>/Tris-HCl buffer (pH 7) in the absence of any Cu(II) ions. Before using the device for sensing Cu(II) ions, polycarbazole was dedoped electrochemically by passing a small current (~μA) in the reverse direction for half an hour and then washing in distilled water. This device was used as an ion sensor in 0.1 M Tris-HCl buffer (pH 7) by applying a gate potential  $V_G = 0.8$  V and biasing at 50 mV. The drain current  $I_D$  was recorded with variation of the concentration of Cu(II) ions in the solution. Cu(II) acetate was used to obtain the Cu(II) concentration from  $10^{-6}$  M to  $10^{-3}$  M.

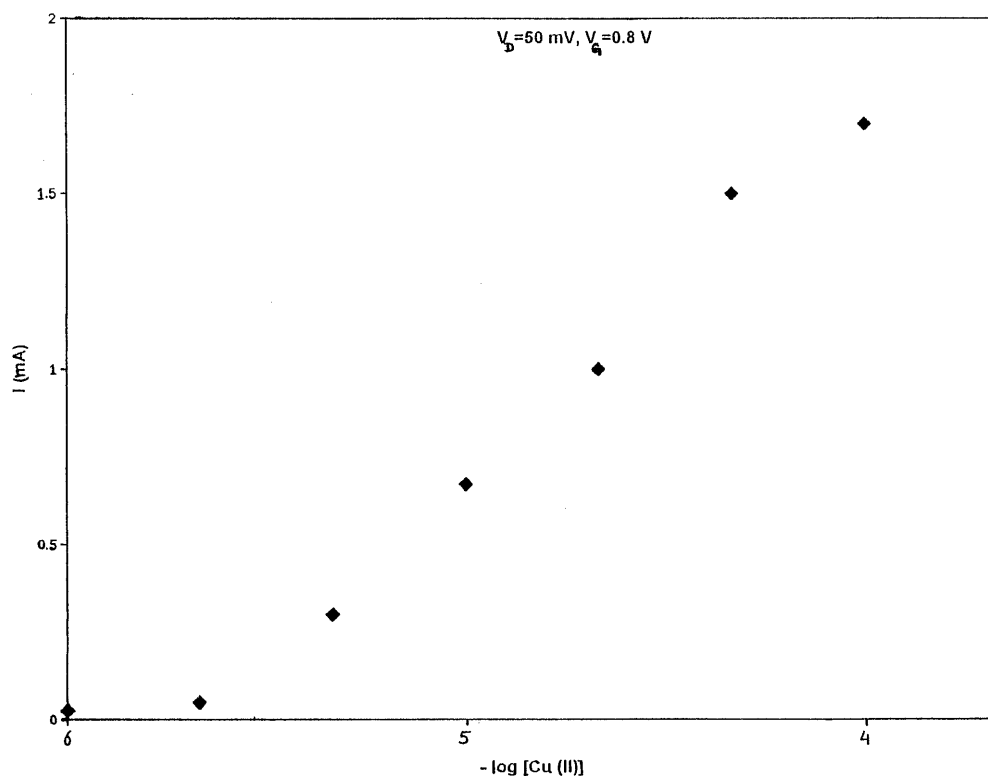


**Fig. 1** Diagram of the microelectrochemical transistor, where *W* indicates the working, *R* the reference and *C* the counter electrodes

## Results and discussion

The transfer characteristics of the polycarbazole transistor were studied in both electrolytes (0.1 M LiClO<sub>4</sub>/Tris-HCl buffer, pH 7). It was found that there is a significant change in the drain current ( $I_D$ ) after a gate potential  $V_G = 0.6$  V and it saturates after 1.0 V. The transconductance  $g_m$  of the device was estimated to be 0.28 S/cm of the gate width at  $V_D = 50$  mV, which is quite high and an indication of good sensitivity of the device. Also, the wide potential window (the region in which  $I_D$  does not change significantly) makes it possible to use the device over a large potential range. On the basis of the characteristics described above, the Cu(II) ion sensor was developed. Figure 2 depicts the drain current response of the device upon adding different concentrations of Cu(II) ions. The characterization was carried out in 0.1 M Tris-HCl buffer (pH 7.0) in a steady condition, where the value of  $V_G$  (0.8 V vs. Ag/AgCl) and  $V_D$  (50 mV) of the device were fixed. There was a sharp rise in the drain current above a Cu(II) ion concentration of  $2.5 \times 10^{-6}$  M and it reached a plateau beyond  $10^{-4}$  M. Though the response of the device is confined to a short concentration range, the sensitivity is very high. In order to verify that the response of the device is specifically for Cu(II) ions and not for the other

**Fig. 2** Drain current vs. log Cu(II) ion concentration for the polycarbazole microelectrochemical transistor in 0.1 M Tris-HCl buffer (pH 7). The potential  $V_G$  (0.8 V) is the potential at the polycarbazole with respect to the Ag/AgCl electrode and  $V_D$  (50 mV) is the drain potential applied across the polycarbazole bridged Pt wire electrodes



cations, similar characterization was done for Cu(I), Ni(II), Co(II), Fe(II), Fe(III), Zn(II) and Pb(II). No significant change was observed in the drain current on addition of cations other than Cu(II). This statement was also verified by measuring the potential of the polycarbazole electrode with respect to a saturated calomel electrode (SCE) in 0.1 M Tris-HCl buffer (pH 7.0) [1]. This device was reused after thorough washing with distilled water.

The conductivity change of polycarbazole can be understood by the secondary doping concept proposed by MacDiarmid and Epstein [10]. The Cu(II) ions change the conformation of the polycarbazole chains from a "compact coil" to an "expanded coil". The selectivity of Cu(II) ions may be due to those cavities/holes in the polymeric matrix, which are surrounded by nitrogen atoms from carbazole units of the chain. Such types of cavities can be compared with Cu phthalocyanine. In doped form, most of the nitrogen atoms of the polymer chains may be positively charged (depending on doping level) and also surrounded by dopant molecules. Hence such cavities are either positively charged or occupied by dopant molecules, which do not accept Cu(II) ions. This phenomenon was observed when a doped polycarbazole coated device was used for the Cu(II) sensor and it gave a very poor response.

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## Conclusions

We have shown that it is possible to make a Cu(II) ion-selective microelectrochemical transistor using

polycarbazole alone. The increase in  $I_D$  with increase in Cu(II) ion concentration is attributed to the conformational changes in the polymer phase, which are a consequence of a high local electrostatic field due to the occupation of Cu(II) ions in the polymer matrix. Inserted Cu(II) ions enhance the alignment of the polymer chains and thus the conductivity of the polymer. The device is reproducible for response only after a few washings with distilled water. The main advantage of the device is that no additional ion-selective membrane is necessary and hence simplicity in the fabrication.

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