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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 (Cu^{++}) in aqueous medium. The device reported here is an electrochemical transistor that consists of two platinum electrodes separated by 100-μm spacing and bridged with an anodically grown polycarbazole film. The undoped polycarbazole film 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. This 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 2.5×10^{-6} *M* Cu(II) ions and reaches a saturation region above a concentration of 10^{-4} *M* Cu(II) ions. In this concentration range, the plot of I_D vs log[Cu(II)] is linear. The selectivity of the device for other metal ions such as Cu(I), Co(II), Fe(II), Fe(III), Zn(II), and Pb(II) is also studied.

Index Entries: Conducting polymers; electrochemical transistor; sensor.

Introduction

In recent years, several devices based on conducting polymers have been developed for the detection of chemical species in electrochemical or biological environments *(1–5)*. Among these devices, ion-selective field effect transistors and microelectrochemical transistors *(4,5)* 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 polymers, which result owing either to oxidation/reduction

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of polymers in the presence of specific chemical species or to change in their configuration. Devices were also developed by incorporating some enzymes/ionophores or a separate ion-selective film into or onto the polymer itself *(6)*. These devices could detect specific chemical species depending on either their encounter with an ion-selective membrane (ionophores) or the response to specific enzymes.

In this article, we present some new findings concerning the Cu(II) ions' selectivity of polycarbazole film immersed in an aqueous solution and demonstrate the fabrication of a Cu(II) ion–selective transistor based on polycarbazole. The new device reported here is significant because it gives linear response in the range of 2.5×10^{-6} to 10^{-4} *M*.

In our earlier publication *(7)*, we reported on an electrochemical transistor based on the potential dependent conductivity of polycarbazole. In the present article, we report the results of a study of an ion-selective microelectrochemical transistor responsive exclusively to Cu(II) ions.

Materials and Methods

The device described here consists of two parallel platinum wire electrodes embedded 100 μm apart over a glass substrate. These electrodes were used as "source" and "drain" for the device. Polycarbazole deposition was carried out in dichloromethane (CH_2Cl_2) (Glaxo, India) solution containing 60 m*M* carbazole (Aldrich) and 0.1 *M* tetrabutylammonium perchlorate (TBAP) (Sigma) at a constant potential of 1.4 V vs Ag/AgCl electrode as described earlier *(7)*. The polymerization was carried out on both electrodes simultaneously until the polymer film bridged the gap between the two. In a completed device, one of the polymer-connected platinum electrodes was used as a source and the other as a drain, while a Ag/AgCl wire that established contact with polymer film through the electrolyte served as "gate." Figure 1 presents the configuration of the device. The transistor configuration is essentially the same as used by Kittelson et al. *(8)*. All electrochemical characterizations of polycarbazole electrodes were done using a Tacussel dual potentiostat (Type B1-PAD), and the data were recorded on a Hewlett-Packard 7035B X-Y recorder. The steady-state measurements were carried out at 25°C. Electrochemical characterizations were done using a platinum foil (area of 1 cm^2) and an Ag/AgCl wire as counterelectrode and reference electrode, respectively. Both cyclic voltammetry and chronoamperometry were performed for a nonaqueous solution of 0.1 *M* TBAP in CH_2Cl_2.

The characteristics of the transistor were first obtained for the aforementioned device in aqueous solution of 0.1 *M* $LiClO_4$/Tris-HCl buffer (pH 7.0) devoid of any Cu(II) ions. Before using the device for sensing Cu(II) ions, polycarbazole was dedoped electrochemically (only once after the formation of the film) by allowing a small current (~2 μA) to pass in reverse direction (keeping the polycarbazole electrode as the cathode) for half an hour and then washed in distilled water. This device was used

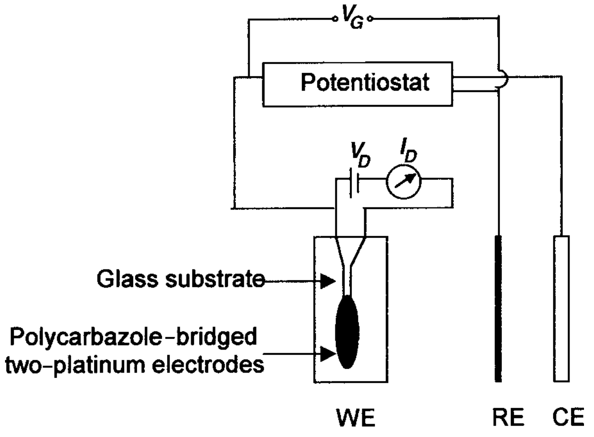

Fig. 1. Schematic diagram of a microelectrochemical transistor, in which WE indicates working, RE reference, and CE counterelectrode.

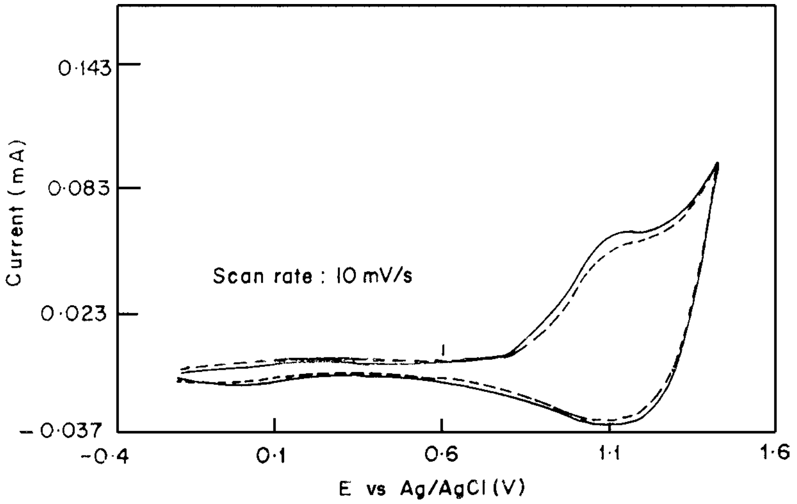

Fig. 2. Cyclic voltammograms of polycarbazole-coated single platinum (——) and split platinum electrodes (– – –).

as an ion sensor in 0.1 *M* Tris-HCl buffer (pH 7.0) by applying gate potential $V_G = 0.8$ V and biasing at $V_D = 50$ mV. Drain current I_D was recorded by varying the concentration of Cu(II) ions in the solution. Cu(II) acetate was used to change the Cu(II) concentration from 10^{-6} to 10^{-3} *M*.

Results and Discussion

Figure 2 depicts the cyclic voltammograms of polycarbazole-coated single platinum and split platinum electrodes covered with polycarbazole,

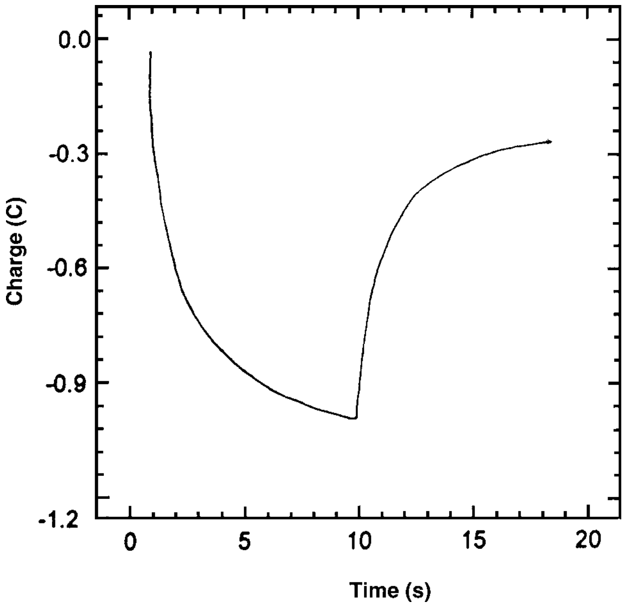

Fig. 3. Chronoamperometric curve of polycarbazole-coated split platinum electrodes in 0.1 *M* TBAP/CH_2Cl_2 for a time period of 10 s.

at the scan rate of 10 mV/s. As seen, the magnitude of current of cyclic voltammograms corresponding to the polycarbazole-coated single platinum electrode and the polycarbazole-connected split platinum electrode is the same. The identical nature of cyclic voltammograms suggests that the effect of external potential is the same for polycarbazole-coated single platinum and polycarbazole connected split platinum electrodes. In other words, this implies that the polycarbazole film, which bridges the gap between two platinum electrodes, works as a conducting channel of which one end can be considered as the source and the other as a drain.

As revealed in Fig. 3, the total charge introduced into the polycarbazole film connecting the two platinum electrodes is nearly 900 mC, for a charging time of 10 s, whereas the amount of charge given out of the polymer film is 877 mC for a similar time period. This reversible charging-discharging characteristic of the polycarbazole-connected platinum electrodes is important from a device point of view.

The transfer characteristics of the polycarbazole transistor were studied in both electrolytes: 0.1 *M* $LiClO_4$ and Tris-HCl buffer. It is clear from Fig. 4 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) value of the polycarbazole transistor was 0.28 S/cm for the channel width of 100 µm at $V_G = 50$ mV. This value is fairly high and indicative of the better sensitivity of the device. The high g_m value and the wide potential window of the device make it possible to use the device over a larger potential range. Therefore, an attempt was made to use it as an ion sensor in 0.1 *M* Tris-HCl

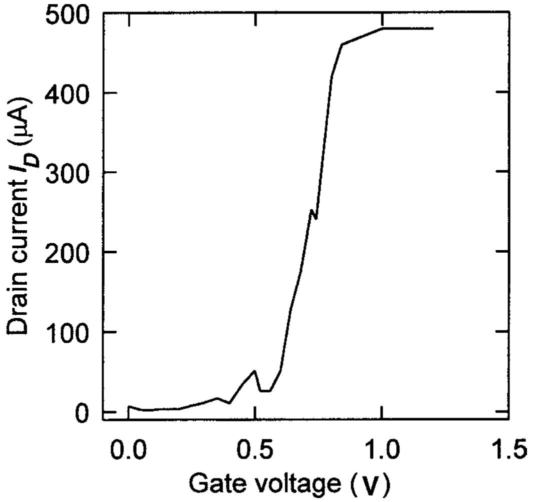

Fig. 4. Drain current (I_D)/gate voltage (V_G) curve of the polycarbazole-based microelectrochemical transistor in Tris-HCl buffer (pH 7.0) at drain voltage (V_D) = 50 mV.

buffer (pH 7.0) under steady-state conditions. The drain current, I_D, was recorded with varying concentrations of Cu(II) in the solution. As shown in Fig. 5, there was a sharp rise in the drain current above a concentration of 2.5×10^{-6} *M*, and it reached a plateau above a 10^{-4} *M* Cu(II) ion concentration. The slope of the linear curve for the plot of I_D vs [Cu(II)] was estimated to be 1.07 mA/concentration. Although the response of the device was confined to a short concentration range, the sensitivity was found to be very high. To verify that the response of the device is specifically for Cu(II) ions and not for the other cations, similar characterization was done for Cu(I), Co(II), Fe(III), and Pb(II). No significant change in the drain current was observed on addition of cations other than Cu(II). This device could be reused after 10 min of incubation in distilled water. The distilled water should be changed two to three times during the incubation period. This process removes weak-binded Cu(II) ions from the cavities of polymer matrix and was found to provide reproducible results.

Change in conductivity (or, equivalently, the drain current of the transistor) of polycarbazole can be understood by the secondary doping concept proposed by MacDiarmid and Epstein *(9)*. The Cu(II) ions change the conformation of the polycarbazole chains from "compact coil" to "expanded coil." In light of these results, it can be inferred that the polycarbazole exhibits a reversible type of linkage that may be defined as a new type of host-guest linkage. It has been shown, in our earlier publication, that a very thin film of polycarbazole formed potentiostatically reveals regular and well-arranged polymer matrix *(10,11)*, although the number of such cavities may be fewer. The selectivity of Cu(II) ion may be owing to those cavities/holes in the polymer matrix, which are surrounded by nitrogen atoms of carbazole units of the chain similar to that of the Cu phthalocynine.

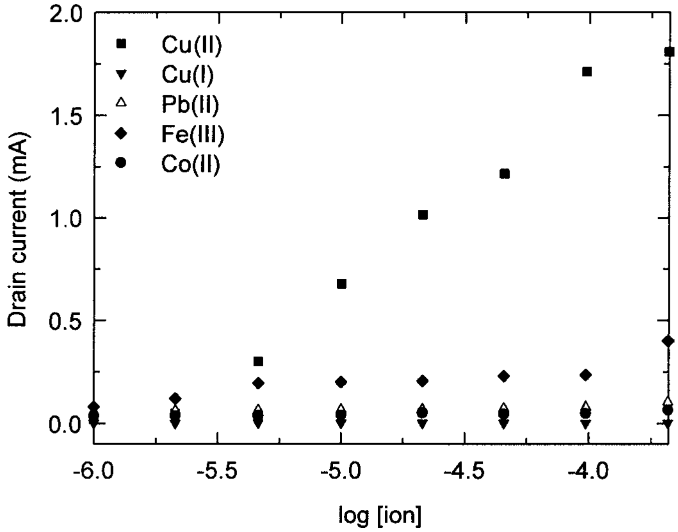

Fig. 5. Drain current/log [ion] characteristics for the polycarbazole-based microelectrochemical transistor. The fitting equation for Cu(II) ions is $y = 1.0714x - 0.125$. The potential V_G (=0.8 V) is the potential of the polycarbazole with respect to the Ag/AgCl electrode, and V_D (=50 mV) is the drain potential applied across the polycarbazole-connected platinum electrodes.

Table 1
Ionic Radius of Various Elements *(12)*

Serial Number	Element	Ionic radius (A°)
1	Cu(II)	0.69
2	Cu(I)	0.96
3	Co(II)	0.72
4	Fe(II)	0.74
5	Fe(III)	0.64
6	Zn(II)	0.92
7	Pb(II)	0.84

Such a type of matrix, when undoped, is supposed to provide a definite geometry of cavities, which, in turn, may provide the host-guest linkage. The size and stabilization energy of such types of cavities is specifically suitable for Cu(II) ions. As seen from Table 1, the ionic radius of cations, Cu(I), Co(II), Fe(II), Fe(III), Zn(II), and Pb(II) is either smaller or bigger than that of Cu(II) ions. Therefore, these cavities select only Cu(II) ions. The evidence for such cavities is supported by the poor response of the doped polycarbazole toward Cu(II) ions. 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 was found to give a very poor response. The host-guest linkage is not only dependent on the cavity size and cation radius but also the stabilization energy owing to ionic interaction of Cu(II) cation and lone-pair electrons of nitrogen atoms.

Conclusion

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 polymer phase, which are a consequence of a high local electrostatic field owing to the occupation of Cu(II) ions by polymer matrix. The occupied Cu(II) ions enhance the alignment of the polymer chains and thus also 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 it does not require any additional ion-selective membrane and thus is simple to fabricate.

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