A New Kind of Chemical Sensor based on a Conducting Polymer Film

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An anion doped polypyrrole film exhibits a stable potential response for the doping anion in solution and the response behaviour is closely related to the nature of the ion.

Organic conducting polymers have become attractive new materials[1] and various organic conducting polymers such as polyacetylene,[2,3] polypyrrole (PPy),[4] polythiophene,[5] polyaniline,[6] poly(*p*-phenylene),[7] and poly(*p*-phenylene sulphide)[8] *etc.* have been synthesized by chemical and electrochemical methods. The conduction mechanism and their application as anodic materials in chemical cells has been extensively investigated.[1] Also, the release of ions and drugs has been reported by 'doping' and 'undoping' reactions of conducting polymers.[9] Also, authors have investigated the interaction between the chain of the conducting polymer and the doping anion, and doped PPy exhibits a stable potential response for the doping ion in solution and the response behaviour is related closely to the nature of the ion. Study of this characteristic is interesting for two reasons: i, understanding the interaction of the doping ion with the conducting polymer and exploring the conduction mechanism; ii, possible applications as an active material in ion selective electrodes and new types of chemical sensors. This type of chemical sensor has possible attractive advantages such as low resistance, fast response, easy production and anti-poison ability in organic solvents. It may be useful in preparing biological electronic sensors. This paper reports the response behaviour of a PPy film electrode prepared by electrochemical polymerization, and discusses the relationship between the response behaviour of the electrode potential and the nature of the doping ion. We have prepared successfully several anion potential sensors with the advantages of low resistance, fast response, and insolubility in organic solvents.

The pyrrole (Py) used was a reagent of analytical grade, purified by distillation with CaH_2, and restored under N_2 in a low temperature vessel protected against light. A PPy polymer film electrode was prepared by electrochemical polymerization[10] in an aqueous solution containing Py and doping ion on glassy carbon (GC). Polymerization experiments were performed on a RDE 4 potentiostat with a three electrode system. The process of polymerization and thickness of the polymer film was controlled by polymerization time, scan times, and potential range in cyclic voltammetry (CV), and density of current and polymerization time in a constant current method. After it was immersed and activated in the doping ion solution, the electrode potential of the PPy polymer film electrode was measured on a Beckman φ60 pH meter *vs.* standard calomel electrode (S.C.E.) whose out-tube was filled with 0.1 M K_2SO_4 to avoid interference from the solution. All potentials given are *vs.* S.C.E.

The PPy polymer film electrode prepared in aqueous solution containing Py and doping ion shows a stable electrode potential response behaviour for the doping ion in solution. When PPy polymer film electrodes which were doped separately with anions such as Cl^-, Br^-, NO_3^-, and ClO_4^- *etc.*, were immersed in a 10^{-2} M solution of the doping ion, the electrode potentials drop steeply with time at first, then change gradually to reach a stable potential after a longer time. Figure 1 gives a variation curve of the electrode potential with time when the Br^- doped PPy electrode is immersed in a 10^{-2} M Br^- solution. After stablizing, the electrode potentials have a linear Nernst response for 10^{-1}—10^{-4} M Br^- solutions with a detection limit of 6.0×10^{-5} M, and a gradient of *ca.* 60 mV/pBr. In the same way, we have prepared several chemical sensors for Cl^-, NO_3^-, and ClO_4^- etc. Their properties are given in Table 1. The results are encouraging for Br^-, Cl^-, NO_3^-, and ClO_4^- sensors but for I^-, when Py is polymerized, redox reaction of the I^- anion takes place, so the PPy film cannot be obtained uniformly. A PPy film can be made in a doping 5-sulphosalicylate$^-$ (SSA^-) solution, but its response for SSA^- solutions with different concentrations is not linear and does not obey the Nernst equation. During the process of electropolymerization, Py is polymerized to form a conjugated chain cation doped with anion in solution at the same time. According to the literature,[10—12] it is thought that 3 or 4 Py rings contain one positive charge. Since the PPy cation is a large conjugated cation with strong hydrophobility, when in contact with an aqueous solution an interface between the

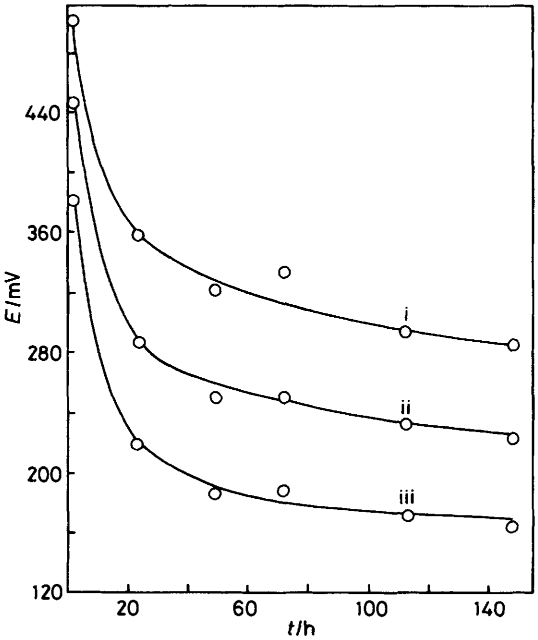

Figure 1. Potential change curves for a Br^- doped PPy polymer film electrode after being immersed in a 10^{-2} M Br^- solution. Conditions of polymerization: 0.2 M Py and 0.1 M KBr, current density 1.6 mA cm^{-2}, time 10 min, concentrations of Br^- solutions: i, 10^{-3}; ii, 10^{-2}; iii, 10^{-1} M.

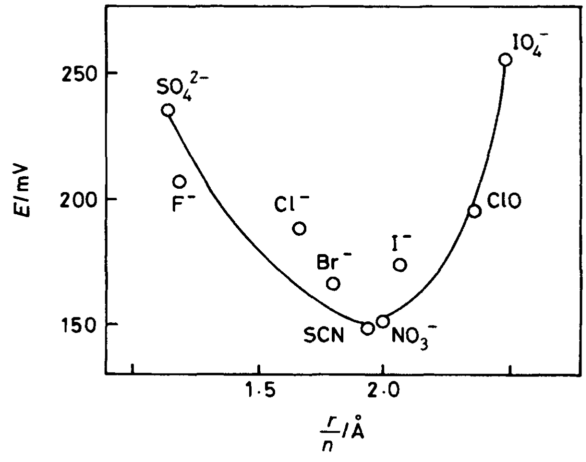

Figure 2. Relationship between the potential of Br^- doped PPy electrode and the radius of an anion with unit negative charge.

Table 1. Response properties of ion-selective electrodes based on PPy polymer films.

Electrode	Linear range /M	Detection limit /M	Gradient (mV/pX)	pH range	Resistance /kΩ
NO_3^-	1×10^{-1}—1×10^{-4}	3.2×10^{-5}	54	3—8	<10
Cl^-	1×10^{-1}—1×10^{-4}	4.5×10^{-5}	56	2.5—6	<10
Br^-	1×10^{-1}—1×10^{-4}	7.0×10^{-5}	61	3.5—8	<10
ClO_4^-	1×10^{-1}—1×10^{-4}	4.5×10^{-5}	50	3.8—8	<10
SSA^-	non-linear response				
I^-	film is not uniform				
SCN^-	film not well formed				

hydrophobic PPy film and the aqueous solution can be formed and an equilibrium distribution of the anion occurs across the interface to produce the membrane potential of the PPy film. The more easily a doping ion can enter the hydrophobic PPy film phase from the water phase, the better the film electrode that can be prepared. Because the PPy cation should have different interactions with different anions, different performances of the PPy polymer film can be anticipated. This difference can be characterized by the differing potentials of the PPy film electrode in different kinds of doping ion solutions with the same concentration, as shown in Figure 2 for a Br^- doped PPy film electrode. Because PPy polymer films form a hydrophobic phase, ions with a larger radius and small charge, or a small hydrating ability enter the hydrophobic phase more easily by association with the PPy conjugated chain cation. So it appears that the potentials of SO_4^{2-}, F^-, Cl^-, and Br^- solutions change negatively until reaching a radius of *ca.* 2.00 Å, and then the potential becomes most negative. But when the radius increases continuously, the potential shifts to more positive again. This may result from steric interactions. When the PPy film is prepared under Br^- doping conditions, a channel just suitable for Br^- is formed. Although larger radius ions enter the polymer film more easily due to association, the ion is restricted by steric resistance at the same time, and a parabola-like curve showing the change of potential with nature of ion is obtained, see Figure 2.

The above result is important for improving the selectivity of chemical sensors, it yields a different selective order from ordinary liquid membrane ion selective electrodes, selectivity being improved by changing doping and polymerization conditions. An order of interference for a Cl^- doped PPy polymer film electrode is: Cl^-, $HCOO^-$, $NO_3^- > I^- > IO_4^- > Br^- > ClO_4^- > F^- > Ac^- > SSA^- > SO_4^{2-}$; for a NO_3^- doped PPy electrode is $NO_3^- > Br^-$, $I^- > HCOO^- > ClO_4^- > Cl^-$, $Ac^- > IO_4^- > SO_4^{2-}$; and for a Br^- doped PPy electrode is: Br^-, NO_3^-, $SCN^- > HCOO^-$, I^-, $IO_4^- > Cl^- > ClO_4^-$, SA^- (salicylate) $> Ac^- > BrO_3^-$, $F^- > SSA^- > SO_4^{2-}$.

In order to understand the influence of doping on the properties of a polymer film electrode, we prepared a PPy polymer film electrode doped separately with Br^-, SSA^-, SA^- and measured the potential responses for Br^-. The response behaviour of those PPy electrodes doped with SSA^- and SA^- anions for Br^- in solution are not so good as that doped with Br^-. It means that the interaction between the chain of PPy and doped anion is an important factor in affecting the performance of PPy polymer film electrodes.

Under our experimental conditions, cations in solution do not take part in the polymerization, and do not enter into the polymer film *i.e.* a PPy film is not accessible to cations. We have measured the electrode potentials for a Cl^- doped PPy polymer film electrode in the presence of different cations such as Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} *etc.* at the same concentration of Cl^- anion, and no apparent difference appears. The results are the same for Br^- and NO_3^- doped PPy film electrodes. The response curves of a Br^- doped PPy film electrode for Br^- in the presence of K^+ and tetramethylammonium$^+$ (TMA^+) are given in Figure 3, and shows the response behaviours of a Br^- doped PPy film electrode in the non-aqueous solvents acetonitrile and ethanol. In acetonitrile, the response is good with a linear range of 1.0×10^{-2}—1.0×10^{-4} M and a gradient of 40 mV/pBr. But in ethanol, the response is not linear, and the electrode potential first increases with decreasing Br^- concentration, then decreases below 10^{-4} M. Usually a conducting polymer is not soluble in organic solvents, so it can be used for potentiometry in organic solvents. This is advantageous to ordinary liquid and PVC membrane ion selective electrodes.

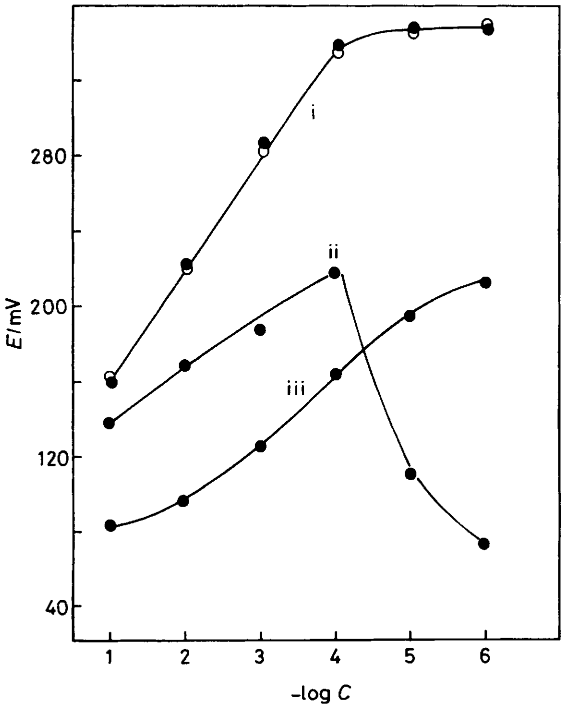

Figure 3. Response behaviour of Br^- doped PPy electrodes in different solutions: i, aqueous solutions containing KBr ● or TMABr ○; ii, ethanol containing TMABr; iii, acetonitrile containing TMABr.

This kind of chemical sensor is based on conducting polymer material. Electrode resistance is very small, and resistance of the measurement mainly depends on the resistance from the reference electrode and solution system. A PPy polymer film electrode has the advantages of being stable, a fast response etc. These properties make it suitable for use in preparation of ion sensitive electronic and bioelectronic devices.

The support of the National Science Foundation of China is gratefully acknowledged.

Received, 14th March 1988; Com 8/00995C

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