

Potentiometric iodide ion sensor based on a conducting poly(3-methylthiophene) polymer film electrode

A. Ersin Karagözler¹, O. Yavuz Ataman², Ahmed Galal³, Zhi-Lun Xue, Hans Zimmer
and Harry B. Mark, Jr. *

Department of Chemistry and Edison Sensor Technology Center, University of Cincinnati, Cincinnati, OH 45221-0172 (USA)

(Received 12th October 1990)

Abstract

A potentiometric iodide-selective electrode based on a poly(3-methylthiophene) (PMeT) film was developed. Graphite electrodes were first coated with PMeT and then iodine was incorporated (doped) into the polymer film by electrochemical oxidation of iodide at +0.70 V. The effects of various electroactivation parameters such as doping potential, polymer film thickness, dopant concentration and doping period were examined in relation to the slope and linearity of calibration graphs. The performance of the electrode with respect to electrode reproducibility, response stability, appropriate pH range and response time was also examined. The polymer-based iodide-selective electrode was found to be suitable for the measurement of iodide concentrations down to 1×10^{-6} M and its selectivity coefficients for most of the potential interferences were of the order of 1×10^{-3} . However, certain species that deplete the iodine in the polymer matrix adversely affected the electrode response.

Keywords: Potentiometry; Iodide; Ion-selective electrodes; Poly(methylthiophene) conducting film

Organic conducting polymers are not only interesting from the industrial point of view [1,2], but are also important for chemical modification of electrode surfaces for sensitive and selective electrochemical measurements. Surface modification is usually adopted for voltammetric measurements and organic conducting polymers constitute only a small fraction of many schemes available for surface modification [3].

Electrochemically synthesized conducting polymers are obtained in their oxidized form and, for electroneutrality reasons, they are "doped" with anions. Original doping occurs with the anions of the electrolyte in which the electrochemical

synthesis is carried out. It is also possible to replace the original dopant anions by simply dipping the electrode in a different electrolyte solution.

This property of doping of conducting polymers can be exploited in various ways from an analytical chemistry application point of view. For example, a polymer can be doped with an electroactive substance and the thermodynamic equilibrium potential that exists between the doped substance and some particular species in a second phase can form the basis of a potentiometric method of analysis. In fact, the construction of chloride [4] and perchlorate [5] ion-selective electrodes based on polypyrrole conducting polymers that utilize the aforementioned approach has been previously described.

Compared with voltammetric applications, the use of conducting polymers for fabrication of sensors for potentiometric measurements is rela-

¹ On leave of absence from İnönü University, 44069 Malatya, Turkey

² Present address: Department of Chemistry, Middle East Technical University, Ankara, Turkey.

³ On leave of absence from Cairo University, Cairo, Egypt

tively rare. In addition to the aforementioned references, a poly(benzylpropargylamine)-based membrane was described as a non-specific potentiometric sensor for ion chromatographic anion detection [6]. The use of a poly(*N,N*-dimethylaniline)-poly(*o*-chloroaniline) dual-layer coated electrode for a selective response to iodide ion has also been reported [7].

We have been studying the synthesis, characterization and application of conducting polymers electrochemically produced from thiophene oligomers. The electrochemical behaviour [8] and spectroelectrochemical characteristics [9] of some of these conducting polymers have been reported. The use of poly(3-methylthiophene) coatings as working electrode materials in amperometric detection of inorganic anions [10] and some biologically important compounds [11] has also been described.

This paper reports the construction and properties of an iodide ion-selective electrode based on a poly(3-methylthiophene) (PMeT) conducting polymer film. The electrode is easy to prepare and compares favorably with a commercial, heterogeneous solid membrane iodide electrode in terms of selectivity coefficients, working range and response time.

EXPERIMENTAL

Fabrication of the electrode

A copper wire was screwed in and fixed by means of silver paste to one end of a spectroscopic-grade graphite rod (Paco Graphite, Decatur, TX; grade AXFSQBL). The rod (diameter 4.4 mm, height ca. 4 cm) was then inserted towards the tapered end of a glass tube (5.9 mm i.d.) and sealed to the glass by Torr Seal (Varian). The glass collar and the solidified resin were ground down with coarse emery paper until the tip of graphite was seen. A male pin was soldered to the copper wire at the top end of the glass tubing. The base of the pin was then secured to the glass with heat-shrink PVC. Final polishing of the electrode was effected with 600-grid acetone-wetted emery paper, ultrasonication and then repolishing on an acetone-wetted fine filter-paper. Several electrodes

were prepared in the same fashion and only those having similar background cyclic voltammograms in 0.1 M KNO₃ were chosen for experiments. Voltammetric background checking and the two-step polishing were repeated before preparation of polymer surface and any of the ion-selective electrode studies.

Electroactivation of the electrode

Conducting polymer coatings on the graphite electrodes were achieved in a three-electrode single compartment cell containing 100 mM 3-methylthiophene and 100 mM tetrabutylammonium tetrafluoroborate (as electrolyte) dissolved in acetonitrile. The graphite electrode was functionalized as the working electrode; the counter electrode was a 1 × 1 in platinum foil and a Ag/AgCl (3 M NaCl) electrode (BAS, MF2020, West Lafayette, IN) was employed as a reference electrode.

Film coatings were normally formed under constant-potential conditions (1.65 V vs. Ag/AgCl). Coating could also be achieved by repeated potential cycles between -0.1 and +1.8 V. Coated electrodes were rinsed with acetone, air dried for ca. 3 min and immersed in a three-electrode single compartment cell containing aqueous KI solution. Iodide was oxidized and simultaneously incorporated into the polymer film as iodine or triiodide ion at potentials greater than +0.6 V. Electrodes activated by the above procedure were rinsed with water and subjected to air drying for at least 20 min.

Potential measurements and the reagents

Potential measurements were made with an Orion Model 601A ionalyzer using an Orion Model 90-02 double-junction reference electrode with a 10% KNO₃ solution in its outer chamber.

The iodide-selective electrode was connected to the measuring device with a coaxial cable. Before the actual measurement of potentials in iodide solutions, the electrodes were conditioned in stirred water until a steady potential value was obtained, which usually took 0.5–1 h. Standard solutions of iodide were prepared by serial dilutions of 1 N KI. All test solutions contained 10⁻³ M HNO₃ as an ionic strength adjuster, except in

the experiments where the interferences and the pH effect were investigated. 3-Methylthiophene and tetrabutylammonium tetrafluoroborate (Aldrich) were used as received. The acetonitrile was dried over 4A molecular sieve. All the other chemicals mentioned were of analytical-reagent grade and were obtained from either Aldrich or Fisher. Distilled, deionized water was used throughout the experiments, which were conducted at $23 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Effect of electroactivation parameters on electrode response

Choice of doping potential. The oxidation potential of a given I^- solution at an inert electrode such as platinum can be calculated from the standard electrode potential of the $\text{I}_2(\text{s})/\text{I}^-$ couple (0.535 V [12]) and by approximating the potential of the Ag/AgCl (3 M NaCl) reference electrode to that which is prepared with saturated KCl (0.197 V [13]). For instance, the oxidation potential range of 0.1–0.001 M I^- solutions at a platinum electrode is calculated to be within 0.673–0.555 V. However, as the oxidation peak potential values in a cyclic voltammetric experiment of a given iodide solution at a PMeT electrode is shifted slightly with each scan to more positive potentials, experimental determination of the doping potential of iodide into the polymer matrix was deemed to be necessary. Figure 1 demonstrates the effect of doping potential on the response of electrodes coated for 60 s and doped with 1×10^{-2} M KI solution. The electrode that was doped at +1.50 V did not produce an acceptable calibration graph. Although the correlation coefficients of the data for the electrodes doped at +0.50 and +1.0 V were similar (e.g., 0.996 and 0.997, respectively), the slope of the calibration graph obtained with the electrode doped at +1.0 V for the concentration range $1 \times 10^{-1} - 1 \times 10^{-6}$ M was 56.6 mV per decade. This is closer to the expected value of 58.7 mV per decade (at 23°C) than 49.2 mV per decade obtained with the other electrode doped at +0.5 V. However, as the starting of a second iodide oxidation peak observed in

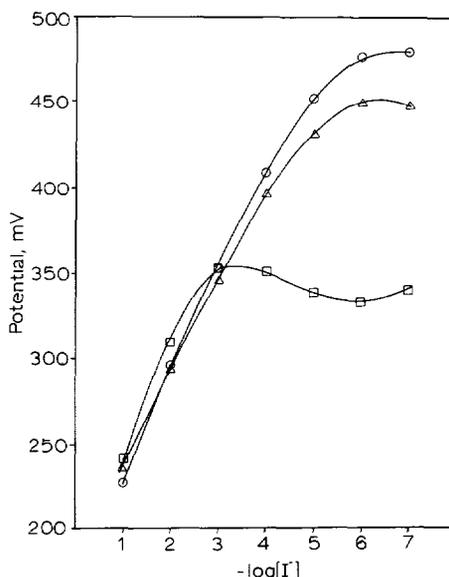


Fig 1. Effect of doping potential on the response of PMeT-coated iodide-selective electrode. Doping potential: (Δ) 0.50 V; (\circ) 1.00 V; (\square) 1.50 V. Film thickness, 60 s; dopant, 1×10^{-2} M KI (in 0.1 M NaNO_3); doping period, 60 s

cyclic voltammetry corresponds to values around +1.0 V, a potential of less than +1.00 V was deemed to be preferable and, therefore, all subsequent experiments were done with electrodes doped at +0.70 V.

Effect of PMeT film thickness. Figure 2 illustrates the effect of film thickness on the potentiometric response of the electrodes. The correlation coefficients and slope values given in Table 1 for different concentration ranges indicate that all three electrodes (films were grown using deposition times of 30, 60 and 90 s, which correspond to 78, 143 and 200 mC cm^{-2} as deposition charges, respectively; film thicknesses are subsequently expressed in this fashion) produce acceptable calibration graphs, with the thinnest film having the closest slope value to the expected Nernstian slope.

Effect of dopant concentration. The effect of concentration of iodide as dopant was investigated with electrodes having 30-s film thicknesses. The potential applied and electrolysis period were 0.70 V and 60 s, respectively. As seen from Fig. 3 and Table 1, with increasing dopant concentration the

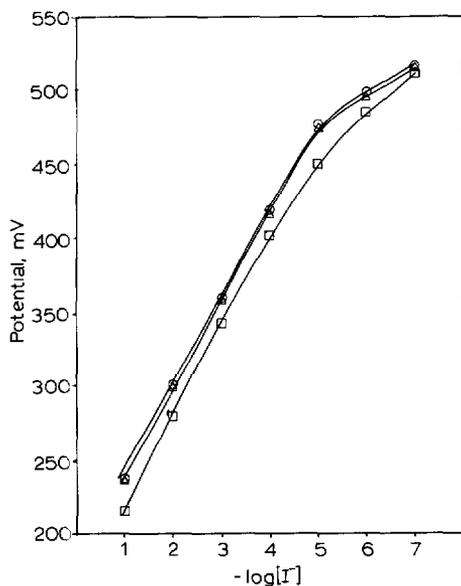


Fig. 2 Effect of film thickness on the response of PMeT-coated iodide-selective electrode. Film thickness: (□) 30 s; (○) 60 s, (△) 90 s. Dopant, 1×10^{-2} M KI (in 0.1 M NaNO_3); doping potential, +0.70 V.

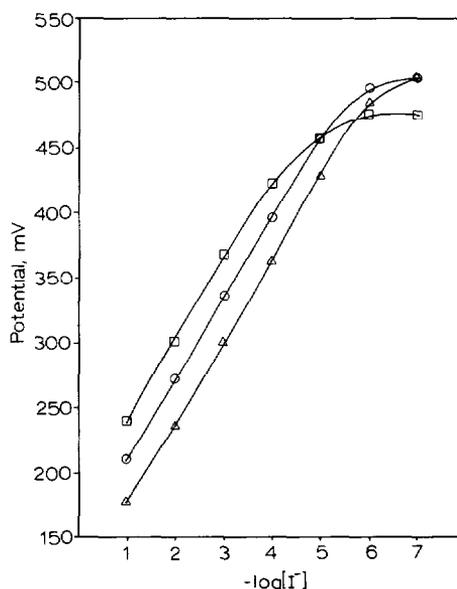


Fig. 3. Effect of dopant concentration on the response of PMeT-coated iodide-selective electrode. Dopant concentration (□) 1×10^{-1} M, (○) 1×10^{-2} M, (△) 1×10^{-3} M. Film thickness, 30 s; doping potential, 0.70 V; doping period, 60 s.

useful working range of the electrodes tends to become narrower.

Effect of doping period. For a given film thickness of 30 s and a concentration of 1×10^{-2} M KI, the effect of the doping period on the working range and slope of the electrode were also ex-

amined. For the given set of conditions, the optimum doping period was found to be 60–120 s, as illustrated by Fig. 4 and Table 1.

The data presented so far indicate that in order to obtain an electrode with a wide working range and a Nernstian slope, there must be an optimum

TABLE 1

Effect of various electroactivation parameters on the correlation coefficients (R) and slope (S) of calibration graphs for different concentration ranges

Parameter	Value	Concentration range (M)					
		$10^{-1}-10^{-4}$		$10^{-1}-10^{-5}$		$10^{-1}-10^{-6}$	
		R	S	R	S	R	S
Film deposition times (s)	30	1.000	62.0	1.000	60.9	0.993	55.5
	60	1.000	60.2	1.000	59.5	0.993	53.9
	90	1.000	59.9	1.000	59.5	0.993	53.9
Dopant concentration (M)	1×10^{-1}	0.999	62.0	0.993	55.6	0.982	48.7
	1×10^{-2}	1.000	62.5	1.000	61.9	0.998	58.5
	1×10^{-3}	1.000	62.3	1.000	63.1	1.000	62.3
Doping period(s)	15	1.000	68.6	0.995	62.2	0.979	53.6
	60	1.000	62.5	1.000	61.9	0.998	58.5
	120	1.000	60.7	1.000	59.6	0.994	54.6
	600	1.000	60.7	0.991	54.0	0.979	47.1

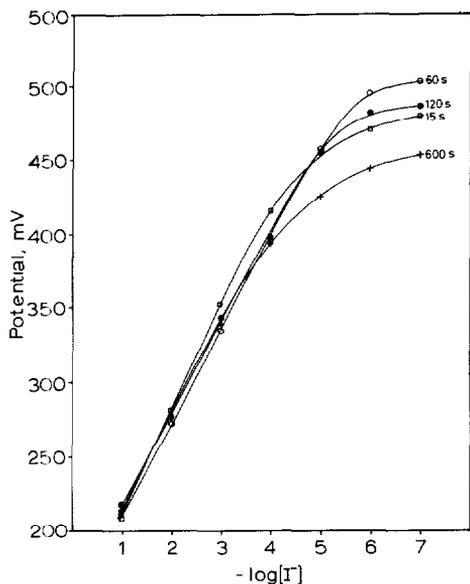


Fig 4 Effect of doping period on the response of PMcT-coated iodide-selective electrode. Doping period: (□) 15 s; (○) 60 s; (●) 120 s; (+) 600 s. Dopant, 1×10^{-2} M KI (in 0.1 M NaNO_3); doping potential, 0.70 V; film thickness, 30 s.

amount of iodine incorporated into the polymer matrix of a given thickness. The amount of iodine is, of course, dependent on result of the KI concentration and the doping period. It is also obvious that as the film thicknesses are increased, the amount of dopant required for an optimum elec-

TABLE 2

Reproducibility of electrode preparation ^a

Concentration (M)	Mean potential (mV)	Standard deviation (mV)
1×10^{-1}	211	3.56
1×10^{-2}	276	3.70
1×10^{-3}	337	3.77
1×10^{-4}	397	4.27
1×10^{-5}	454	5.89
1×10^{-6}	493	8.17

^a Sample size = 9. Other conditions: film thickness, 30 s; dopant, 1×10^{-2} M KI (in 0.1 M NaNO_3); doping for 60 s at +0.70 V.

trode must also be increased, as is shown in Fig. 5, where the need for higher dopant levels for relatively thicker films is clearly demonstrated.

Performance of the electrode

Reproducibility of electrode preparation. During the course of this experiment a large number of electrodes had been prepared to test the effect of various electroactivation parameters. In order to determine the reproducibility of electrode preparation, the previously collected data were examined for a set of electrodes that had been prepared under the same conditions. Table 2 shows the reproducibility of electrode measurements for

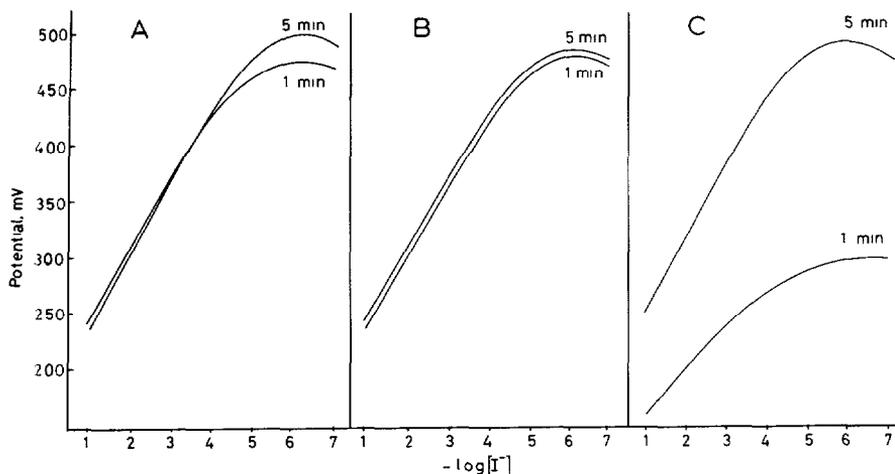


Fig. 5 Doping period as a function of film thickness. Film thickness (A) 30 s; (B) 60 s; (C) 120 s. Doping periods are given on respective curves. Dopant: 1×10^{-2} M KI^- (in 0.1 M NaNO_3).

the electrodes having 30-s film thicknesses and doped with 1×10^{-2} M KI for 60 s at 0.70 V. The data in Table 2, which were extracted from a large collection of data obtained over a period of 4 months, confirm a reasonable degree of precision in electrode preparation, as demonstrated by the standard deviation of the recorded potential values for a given analyte concentration.

Stability of potential measurements. The effect of subsequent runs on the measured potential of a given electrode for identical analyte concentrations was also examined. For a given electrode, a 2-h period or more, in which the electrode was left standing in air, was allowed between subsequent runs. The electrode was then equilibrated in gently stirred pure water for 15 min prior to the next set of measurements. It was observed that the calibration graph as a whole was shifted in a parallel manner to less positive potentials on subsequent measurements. This phenomenon, however, did not result in any change in slope, especially in the 1×10^{-1} – 1×10^{-5} M range. For lower concentrations ($< 1 \times 10^{-5}$ M) the shift was slightly more pronounced. As illustrated in Fig. 6, it was also observed that the magnitude of potential shifts decreased with each new set of measurements.

On the other hand, if the subsequent measurements were made immediately after the first set, then the potential shift for the next randomly chosen solutions was negligible. For example, the data in Table 3 show the potential differences observed for various concentration levels after the first set of measurements.

Selectivity coefficients. Selectivity coefficients of the polymer-based iodide-selective electrode for the commonly encountered anions were de-

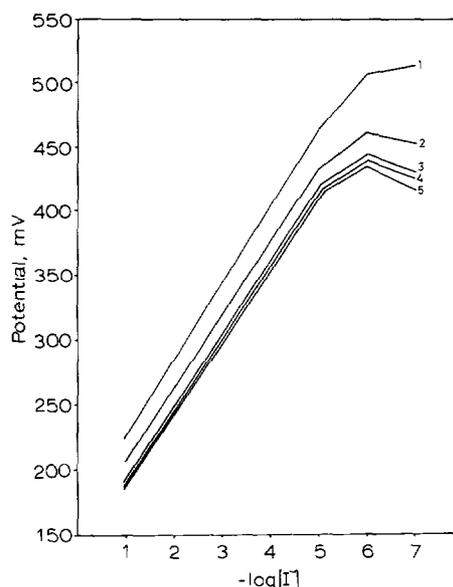


Fig. 6 Effect of consecutive runs on the potential of the polymer electrode. Film thickness: 60 s. Doped with 1×10^{-2} M KI (in 0.1 M NaNO_3) for 60 s. Run numbers are given on each curve.

termined by the mixed solution technique [14] at a constant interferent concentration of 1×10^{-2} M.

The results summarized in Table 4 show that for the large majority of anions the selectivity coefficients are of the order of 1×10^{-3} or smaller. The poorer selectivity coefficients observed with CN^- and OH^- will be discussed later.

Effect of pH. The effect of pH on the potential response of the electrode was investigated at two different concentrations of iodide (1×10^{-2} and 1×10^{-4} M). The desired pH was obtained by addition of HNO_3 or NaOH solution. It can be seen from Fig. 7 that the useful pH range for the

TABLE 3

Short-term drift of electrode potential ^a

Concentration (M)	Measurement sequence				
	1	2	3	4	5
1×10^{-5}	415		413(2)		
1×10^{-4}	366				364(2)
1×10^{-3}	314	314(0)			
1×10^{-2}	263			263(0)	

^a The numbers in parentheses refer to the potential difference for the respective concentration level from the value obtained in the first set of measurements.

TABLE 4

 Selectivity coefficients of the polymer-based iodide-selective electrode^a

Anion (x)	Selectivity coefficient, $k_{I,x}$	Anion (x)	Selectivity coefficient, $k_{I,x}$
Chloride	1.37×10^{-3}	Cyanide	0.45
Bromide	3.81×10^{-3}	Hydroxide	0.08
Nitrate	3.22×10^{-3}	Carbonate	3.69×10^{-3}
Perchlorate	3.20×10^{-3}	Sulfate	3.67×10^{-4}
Acetate	3.94×10^{-3}	Thiosulfate	3.82×10^{-3}
Formate	1.11×10^{-3}	Tartrate	6.35×10^{-5}
Thiocyanide	2.67×10^{-3}	Citrate	5.61×10^{-4}
Dihydrogenphosphate	3.86×10^{-4}		

^a 60-s film; 90-s doping at +0.70 V with 1×10^{-2} M KI.

electrode is about 3.5–10.0 at the 1×10^{-4} M and 2.0–10.0 at the 1×10^{-2} M iodide level.

Response time of the electrode. The response time of the electrode was examined by injecting a small amount of concentrated iodide solution bringing the solution to a concentration of 1×10^{-6} M in iodide, into a gently stirred 1×10^{-3} M HNO₃ solution in which the electrodes had been previously conditioned; The potential change on injection was recorded on a strip-chart recorder.

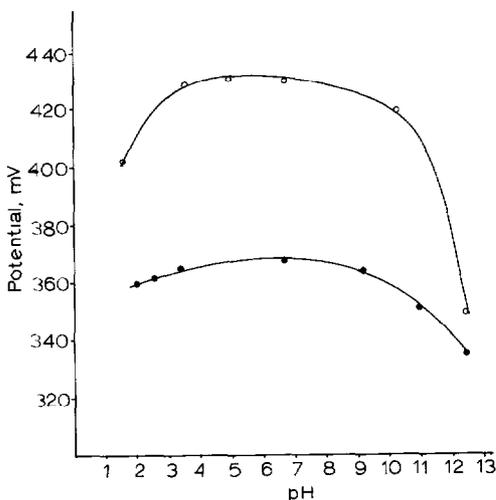


Fig. 7 Effect of pH on the potential response of the polymer electrode at two different iodide levels. Film thickness: 60 s. Doped with 1×10^{-2} M KI (in 0.1 M NaNO₃) for 90 s. (●) 1×10^{-2} M I⁻; (○) 1×10^{-4} M I⁻

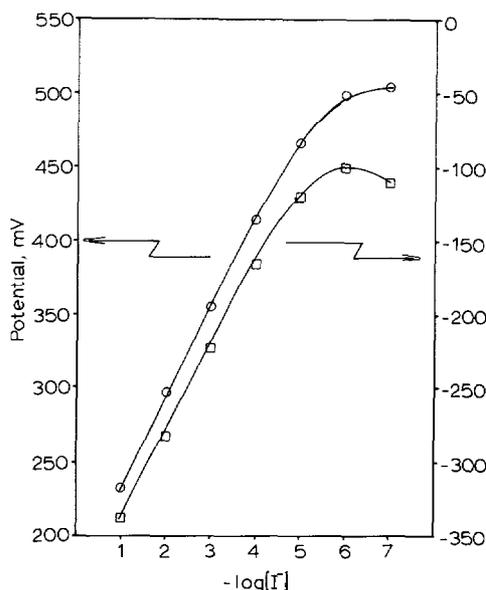


Fig. 8 Calibration graphs for (○) polymer-based and (□) Orion (94-53) iodide-selective electrodes. Millivolt scale for Orion electrode is given on the right.

The time between the points of injection and a new potential plateau reached was taken as the response time. For concentrations above 1×10^{-4} M, the response time was less than 20 s. It was ca. 40 s for an analyte concentration of 1×10^{-6} M.

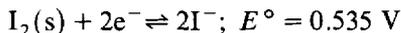
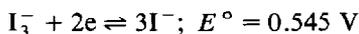
Comparison with a commercial iodide-selective electrode. The final performance test was a direct comparison of its response with a commercial Orion 94-53 iodide electrode. For this purpose, an electrode having a 60-s film thickness and doped with 1×10^{-2} M KI for 120 s was prepared. Both the polymer-based and the Orion electrodes were dipped in the same test solutions and measurements were taken at the same time with respect to the same reference electrode. Typical calibration graphs obtained with the two electrodes are given in Fig. 8. Both electrodes produced a linear response in the 1×10^{-1} – 1×10^{-5} M concentration range and displayed practical working ranges down to the 1×10^{-6} M level. The slope of the polymer-based electrode was 58 mV per decade in the mentioned concentration range, whereas a slope of 54.3 mV per decade was obtained with the Orion electrode. Further, as shown in Fig. 8,

the response of the Orion electrode showed a greater deviation from linearity at low concentration levels and the response time of the Orion electrode was longer than that of the polymer based electrode.

Response characteristics of iodide-selective electrode

The oxidation of iodide in aqueous solutions on solid electrodes has been widely investigated. For instance, iodide gives two voltammetric anodic waves on a platinum electrode, the first of which corresponds to the oxidation of iodide to iodine and the second to the oxidation of iodine to iodate [15]. On the pyrolytic graphite electrode three waves are found, which have been attributed to the successive oxidation of iodide to iodine, I^+ and iodate [16].

I^- may be oxidized to either I_2 or I_3^- in the same potential region [12]:



Therefore, on oxidation I_2 may be formed initially; then, with subsequent reaction with I^- , I_3^- formation may take place in relatively concentrated ($> 2.5 \times 10^{-3} \text{ M}$) I^- solutions [17].

We do not have direct evidence as to what type or in what ratio the oxidation products exist inside the polymer matrix. However, in analogy with work concerning the oxidation of iodide at an electrodeposited polycarbazole film electrode [18], it may be suggested that iodine is fixed on the polymeric electrode and at the same time I_3^- is formed in the diffusion layer. The formation of I_3^- seems essential for electroneutrality of the oxidized film. On the other hand, it may be further suggested that a substantial fraction of I_3^- leaches out during the equilibration of the electrode in water prior to the potential measurements. Assuming that iodine predominantly prevails on the polymer, the potential of the electrode can then be expressed by

$$E = E^\circ + (RT/2F) \ln(a_{I_2})_f / (a_{I^-})_w^2 \quad (1)$$

where $(a_{I_2})_f$ denotes activity in the polymer film and $(a_{I^-})_w$ denotes the activity in the aqueous

phase. For dilute solutions activity terms can be replaced by concentration terms, so that

$$E = E^\circ + 0.0296 \log[I_2]_f - 0.0592 \log[I^-]_w \text{ (at } 25^\circ \text{C)} \quad (2)$$

From Eqn. 2, it follows that the potential of this electrode depends on the concentration of iodine in the polymer film and on the concentration of iodide in aqueous sample. If, however, $[I_2]_f$ can be kept constant, Eqn. 2 converts to

$$E = \text{constant} - 0.0592 \log[I^-] \text{ (at } 25^\circ \text{C)} \quad (3)$$

A liquid-state iodide selective electrode based on a carbon rod impregnated with iodine from an organic phase was described many years ago, when the electrode behavior was interpreted in a similar way [19].

The data regarding the stability of electrode response which are presented in Fig. 6 indicate that electrode potential drifts to lower values and the rate of drift decreases with each new set of successive measurements. The drift of the potential to lower values can be interpreted as the leaching out of I_2 from the polymer body. As indicated by Fig. 6, this process apparently continues until a stable value for $[I_2]_f$ is reached or, alternatively it slows down to the extent that Eqn. 3 holds for all practical purposes.

Electrochemically produced iodine can adsorb on graphite electrodes [20]. It may be suggested that an iodide-treated plain graphite electrode can function in the same way as a polymer coated-iodine doped electrode and the need for a polymer coating can be questioned. Indeed, non-coated graphite electrodes that were activated with the same procedure as described for coated electrodes showed a response with non-Nernstian slopes up to the $1 \times 10^{-4} \text{ M}$ level and then the response leveled off. However, when this iodide doped graphite electrode was subjected to further runs, unlike polymer-coated electrodes, it completely lost its response, as illustrated in Fig. 9. In fact, the electrode base need not be graphite at all. A platinum electrode, made of a circular platinum foil affixed to the end of a glass tube, when coated and doped with I_2 behaves in exactly the same way as do the coated and doped graphite electrodes.

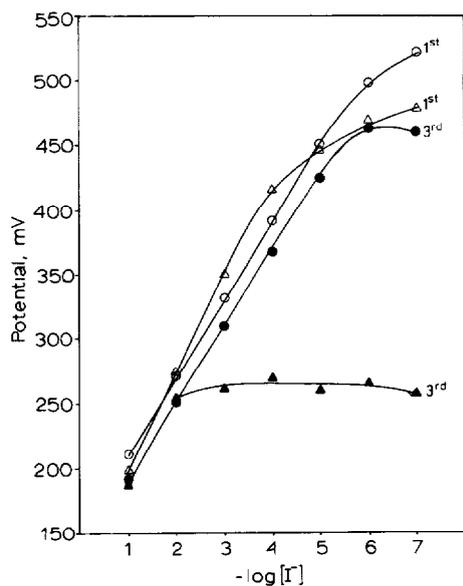
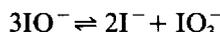


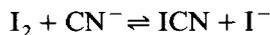
Fig. 9. Effect of multiple runs on the polymer coated and plain graphite electrodes (both doped with I_2). (○, ●) Polymer-coated electrodes, (△, ▲) graphite electrode. Film thickness: 60 s. Doped with 1×10^{-2} M K for 90 s. Run numbers are given on each curve

Instead of electrochemical incorporation of iodine, the procedure involving only dipping of the coated electrodes in iodide solutions was also examined. Dipping was the procedure employed by Dong and co-workers [4,5] with polypyrrole-based chloride and perchlorate selective electrodes. The potentials to which the polymer-coated electrodes were subjected prior to dipping were found to be very crucial. Five electrodes were coated with PMeT for 60 s and then placed in monomer-free electrolyte solution at various voltages for 10 min: -0.20 , $+1.50$ and the last three $+0.70$ V. They were then dipped into 0.1 M KI solution for 10 min. The first two electrodes (at -0.20 and $+1.50$ V) displayed a virtually flat response with varying iodine concentration the range 1×10^{-7} – 1×10^{-1} M. Those which were treated at $+0.70$ V exhibited a noticeable change in potential. The precision of the potential readings with these electrodes was so poor, however, that the dipping procedure was considered inadequate for the preparation of polymer based electrodes.

The relatively poor selectivity coefficients obtained for OH^- and CN^- anions can be explained by the following reactions [19]:



Hence the concentration of iodine in the film will decrease with a concomitant increase of iodide in the aqueous phase. From Eqn. 2 it follows that electrode potential will shift to lower values as a result of above occurrence, and this will be reflected as an interference. Similarly, the cyanide effect can be accounted for by the following reaction [21]:



Regarding the selectivity coefficients, it can also be expected that any redox system which can reduce iodine or oxidize iodide would interfere with the measurements.

Conclusion

The described polymer-based iodide-selective electrode is very easy to prepare and provides a relatively large linear analytical range, with a slope close to the expected Nernstian slope. The working range of the electrode extends down to 10^{-6} M levels. It displays a good short-term and a reasonable long-term stability.

So far as the electroactivation parameters are concerned, each parameter displays a relatively large range of values within which an electrode with an optimized response can be obtained. In other words, an exact set value for a given parameter does not seem to be critically important in the optimization of the electrode response.

The selectivity of the electrode for iodide with most of the anions tested compares favorably with commercial iodide electrodes. Reducing species such as CN^- , which deplete the electrode of iodine, unfavorably affect the electrode response. For the same reason, the electrode sensitivity is adversely affected in alkaline solutions. The last two drawbacks can be overcome by suitable buffering of the samples.

Although not exhaustively examined, the electrode material onto which the polymer is coated appears not to be a critical factor. So far, only one

type of graphite and platinum have been used in these experiments, but different kinds of graphite and carbon-based materials might also be used for producing these electrodes.

Finally, it may be suggested that polymer-based miniature iodide electrodes can be prepared by using carbon microfiber or very thin platinum wires as coating surfaces. This approach may produce useful electrodes especially for biological studies, provided that a suitable means for a built-in reference electrode can be improvised.

This work was partially supported by Edison Sensor Technology Center funds.

REFERENCES

- 1 T.A. Skotheim (Ed.), *Handbook of Conducting Polymers*, Vols. 1 and 2, Dekker, New York, 1986.
- 2 K. Takemoto, Y. Inaki and R.M. Ottenbrite (Eds.), *Functional Monomers and Polymers*, Dekker, New York, 1987.
- 3 R.W. Murray, in A.J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 13, Dekker, New York, 1983, pp. 191–368.
- 4 S. Dong, Z. Sun and Z. Lu, *Analyst*, 113 (1988) 1525.
- 5 Z. Lu, Z. Sun and S. Dong, *Electroanalysis*, 1 (1989) 271
- 6 L. Camperella, T. Ferni, M. Majone, T. Mihuc, M.V. Russo and A.M. Salvi, in P.A. Williams and M.J. Hudson (Eds.), *Recent Developments in Ion Exchange*, Elsevier, Amsterdam, 1987, pp. 315–321.
- 7 J. Yano and T. Tanaka, *Chem. Lett*, (1988) 1943.
- 8 L. Laguren-Davidson, C.V. Pham, H. Zimmer and H.B. Mark, Jr., *J. Electrochem Soc.*, 135 (1988) 1406
- 9 D.D. Cunningham, A. Galal, C.V. Pham, E.T. Lewis, A. Burkhardt, L. Laguren-Davidson, A. Nkansah, O.Y. Ataman, H. Zimmer and H.B. Mark, Jr., *J. Electrochem Soc.*, 135 (1988) 2750
- 10 G.C. Russell, Z.-L. Xue, A. Galal, A.E. Karagozler, O.Y. Ataman, H. Zimmer and H.B. Mark, Jr., paper presented at the 197th ACS National Meeting, 9–14 April 1989, Dallas, TX.
- 11 N.F. Atta, A. Galal, A.E. Karagozler, G.C. Russell, H. Zimmer and H.B. Mark, Jr., *Biosensors Bioelectron*, (1991) in press.
- 12 J.A. Dean (Ed.), *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 13th edn., 1985, p. 6–10
- 13 D.C. Harris, *Quantitative Chemical Analysis*, Freeman, New York, 2nd edn., 1987, p. 343
- 14 E. Pungor and K. Toth, *Anal. Chim. Acta*, 47 (1969) 191.
- 15 G. Raspi, F. Pergola and D. Cozzi, *J. Electroanal. Chem.*, 15 (1967) 35
- 16 G. Dryhurst and P.J. Elving, *Anal. Chem.*, 39 (1967) 607
- 17 E.C. Toren, Jr., and C.P. Driscoll, *Anal. Chem.*, 38 (1966) 872.
- 18 R.N. O'Brien and K.S.V. Santhanam, *Electrochim. Acta*, 34 (1989) 493
- 19 J. Ruzicka and K. Rald, *Anal. Chim. Acta*, 53 (1972) 1.
- 20 K. Kinoshita, *Carbon Electrochemical and Physicochemical Properties*, Wiley, New York, 1988, p. 41.
- 21 I.M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. II, Interscience, New York, 1957, p. 302