

## Polypyrrole Modified Electrode as a Nitrate Sensor

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The potentiometric response behavior of a polypyrrole(PPy) coated Pt electrode to nitrate ion has been studied. The electrode shows a nernstian behavior with a slope of 59 mV over 0.50 M to  $1.0 \times 10^{-3}$  M  $\text{NO}_3^-$  and a detection limit of  $1.0 \times 10^{-4}$  M  $\text{NO}_3^-$ . The response of the electrode is fast and the selectivities for  $\text{I}^-$ ,  $\text{ClO}_4^-$ , and  $\text{IO}_4^-$  are found to be improved. The effect of pH on the potential response to  $\text{NO}_3^-$  is compared with the existing nitrate ion selective electrodes.

### Introduction

The studies on polypyrrole(PPy) as an organic conducting polymer have been focused on understanding the structure and properties of PPy film<sup>1-8</sup> and on enhancing the stability of photoelectrodes used in converting solar energy to electrical or chemical energy.<sup>9</sup> However, only a few applications have employed PPy modified electrodes as ion-sensing electrodes.<sup>10-13</sup> Although the PPy modified electrodes are not considered to be ion-selective electrodes,<sup>12</sup> it appears to be possible to make the electrodes to be selective to anions by changing the conditions used in the electropolymerization. Recently, it has been demonstrated<sup>10</sup> that the chloride-doped PPy film shows a stable and selective potential response towards  $\text{Cl}^-$  ions in solution.

This paper reports the first attempt of a PPy electrochemically modified Pt electrode as a potentiometric sensor for nitrate ion, although there are some reports concerning the application to nitrate ion employing wire electrodes coated with different polymers such as poly (vinyl chloride)<sup>14</sup>, poly (methyl methacrylate)<sup>15</sup>, epoxy resin<sup>16</sup>, or carbon paste<sup>17</sup>. The potential response as functions of pH and possible interfering anions are also included.

### Experimental

**Chemicals.** Pyrrole(Fluka) was purified by vacuum distillation before use. All chemicals were reagent grade, and used without further purification. All solutions were deoxygenated with a stream of nitrogen gas within electrochemical cell before measurements. The pH of the solution was adjusted with phosphate buffer solutions. For the measurement of selectivity coefficients, ionic strength was adjusted to 0.1M with  $\text{Na}_2\text{SO}_4$ , which showed a very small selectivity coefficient.<sup>10</sup>

**Preparation of Electrode.** Polypyrrole(PPy) coated Pt electrodes were prepared on a platinum electrode from an aqueous solution containing 50 mM pyrrole and 1.0M  $\text{HNO}_3$  using cyclic voltammetry as described previously.<sup>18</sup> Film thickness was controlled by the number of scans and the optimum performance the PPy coated Pt electrode from 3.0M  $\text{KNO}_3$  over the potential range of 0.05V to 0.40V for about 12 hours at the scan speed of 50 mV/sec. All the potentials given here are referred to Ag/AgCl electrode. The electrode doped with  $\text{NO}_3^-$  was stored in a saturated  $\text{KNO}_3$  solution when not in use.

**Electrochemical Measurements.** The electrochemical measurement was carried out with a PPy coated Pt working

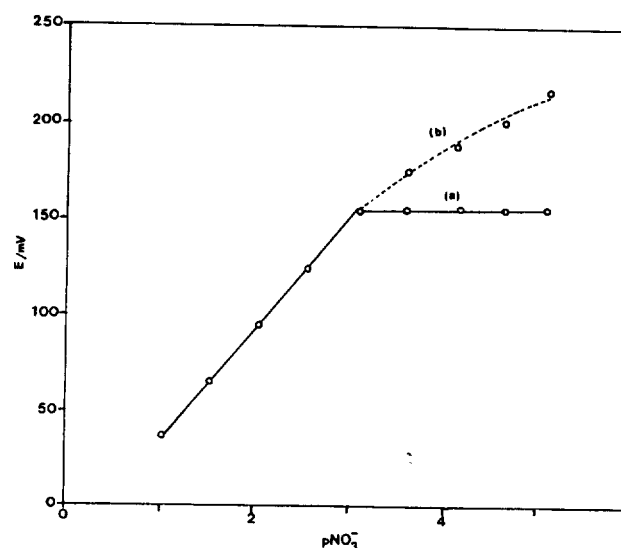


Figure 1. Nitrate ion responses of the PPy coated Pt electrode at ionic strength  $\mu = 0.1\text{M}$  (a) and  $\mu$  is not adjusted (b).

electrode and a platinum coil counter electrode separated by a Vycor frit and a Ag/AgCl reference electrode connected to the analyzing compartment through a Vycor frit. A Princeton Applied Research Model 273 potentiostat/galvanostat and RE 0091 X-Y recorder were used for electrochemical polymerization. All potential responses were measured on a Horiba Model F-7 ssII pH meter.

### Results and Discussion

**Response Behavior.** Figure 1 shows a typical potentiometric response of the PPy coated Pt electrode to nitrate ion in natural pH solution. The response showed a nernstian behavior with a slope of 59.0 mV over 0.50 M to  $1.0 \times 10^{-3}$  M  $\text{NO}_3^-$  and a linear correlation coefficient of 0.999. This characteristics of the electrode to  $\text{NO}_3^-$  can be attributed to the formation of a kind of interfacial potential between the PPy phase and the aqueous solution. At the applied potential of 0.6V the PPy is in an oxidized state where every three to four Py units is known to share a positive charge.<sup>12</sup> To neutralize the polycations, nitrate ions as counter ions should be present in the PPy phase. When the electrode is brought into contact with an aqueous  $\text{KNO}_3$  solution, nitrate ions in the PPy phase are free to exchange with those in an aqueous solution. In a short time after the phase contact, nitrate ions in the PPy phase are gained or lost to the aqueous phase to

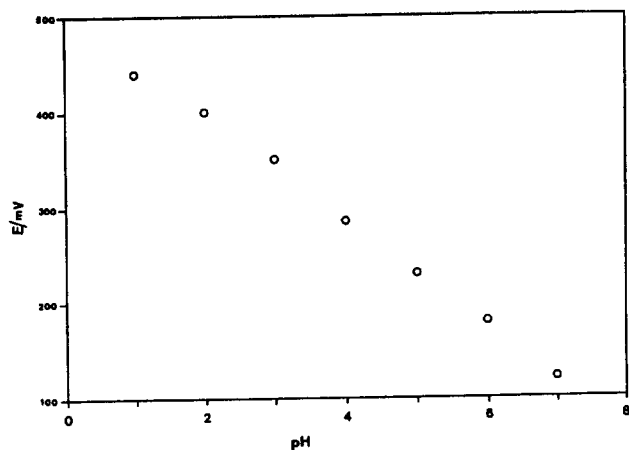


Figure 2. Effect of pH on the potential response of the PPy coated electrode in  $10^{-3}\text{M KNO}_3$ .

create space charge and an interfacial potential appears to be developed. The potential increases positively with decreasing aqueous solution activities of nitrate ion.

Below  $10^{-3}\text{M NO}_3^-$  the figure deviates from the linearity. When the ionic strength of the solution was adjusted to 0.1M with  $\text{Na}_2\text{SO}_4$  as the solutions above  $10^{-3}\text{M NO}_3^-$ , nitrate ions do not show essentially any potentiometric response (curve a) to nitrate ions. This is possibly because high concentrations of other ions, especially sulfate ions, interfere severely with the potentiometric response by the relatively dilute concentration of  $\text{NO}_3^-$ . However, when the ionic strength was not adjusted assuming the solutions below  $10^{-3}\text{M NO}_3^-$  are dilute enough to neglect the variation of activity coefficients, the response shows a convex curvature (curve b). Under the latter condition a smaller concentration of  $\text{NO}_3^-$  than  $10^{-3}\text{M}$  could be measured.

A detection limit<sup>19</sup> was down to  $1.0 \times 10^{-4}\text{M NO}_3^-$ . The detection limit is not particularly low, but comparable to those of the most other nitrate ion-selective electrodes. The response was fast and the potential reading could be taken in two to three minutes. The more concentrated the nitrate solutions were to be measured, the longer it took for the potential to become stabilized.

**Effect of pH.** Figure 2 shows the effect of pH on the potential response of the PPy coated Pt electrode over the pH range of 1.0 to 7.0 in  $1.0 \times 10^{-3}\text{M KNO}_3$ . The potential response of the PPy film to hydronium ion agrees well with the previous result.<sup>11</sup> Contrary to  $\text{NO}_3^-$  ion, the cause of the potential response to hydronium ion appears to involve a protonation-deprotonation equilibrium<sup>11</sup> of a proton in the oxidized PPy.

However, the pH dependence is in disagreement with a recent report<sup>10</sup> by Dong *et al.*, where the response potential remained almost constant over the pH range 2.5 to approximately 7.0 in  $10^{-3}\text{M LiCl}$  solution. Although the doping and sensing anions are different between two studies, the discrepancy in the pH dependence seems to be significant. From the experimental point of view nearly constant potential response over the pH range will be quite advantageous to monitor the doping anion. This discrepancy may be caused by the different condition used in the electropolymerization. However, it has been verified that the nature of cation does

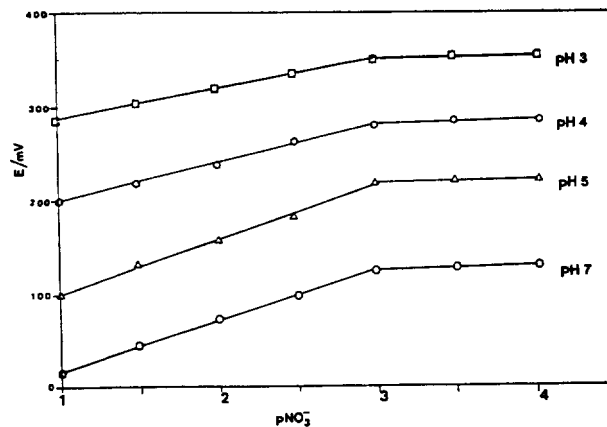


Figure 3. Potential response of the PPy coated Pt electrode at various pH.

Table 1. Selectivity Coefficients ( $K_{\text{NO}_3^-, X^-}$ ) of PPy Coated Pt Electrode.

$X^-$	$K_{\text{NO}_3^-, X^-}$	Mobility ( $\text{m}^2/\text{s}\cdot\text{V}$ )	Ionic radius ( $\text{\AA}$ )
$\text{F}^-$	$3.17 \times 10^{-1}$	$5.70 \times 10^{-8}$	119
$\text{Cl}^-$	1.01	$7.91 \times 10^{-8}$	167
$\text{Br}^-$	$1.38 \times 10^{-1}$	$8.13 \times 10^{-8}$	182
$\text{I}^-$	$3.06 \times 10^{-1}$	$7.96 \times 10^{-8}$	206
$\text{BF}_4^-$	$1.49 \times 10^{-1}$		228
$\text{ClO}_4^-$	$4.56 \times 10^{-2}$	$7.05 \times 10^{-8}$	236
$\text{IO}_4^-$	$3.08 \times 10^{-2}$		249
$\text{NO}_2^-$	2.48		

not seem to change the potential response to pH. The replacement of  $\text{K}^+$  ion used in this work by  $\text{Li}^+$  ion did not alter the linear potential response to pH.

Similar effect of pH on the potential response of various  $\text{NO}_3^-$  ion concentrations are compared in Figure 3. The responses are nearly Nernstian with a slope of 59 mV at pH 5 and 7 up to  $1.0 \times 10^{-3}\text{M NO}_3^-$ , but the slope becomes somewhat smaller as pH is reduced. The deterioration of the slopes at acidic media could be explained in terms of simultaneous response of the electrode to  $\text{H}_3\text{O}^+$  and  $\text{NO}_3^-$ . At pH 3, for example, hydronium ion concentration is comparable with that of nitrate ion, and the potential response is caused by both ions, since the potential measurements were not taken under the condition of complete equilibrium. Because two ions are oppositely charged, the contribution of  $\text{H}_3\text{O}^+$  to the observed potential is apparently acting in the direction of reducing the contribution by  $\text{NO}_3^-$ . Therefore, the best performance of nitrate ion-sensing electrode based on a PPy polymer film may be achieved in buffer solutions at near neutral pH. In alkaline solutions,  $\text{OH}^-$  ions will compete with  $\text{NO}_3^-$  ions for PPy polycations.

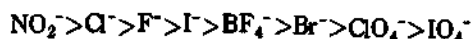
**Ion Selectivity.** Since every three to four Py units in PPy is known to share a positive charge, large conjugated PPy polycations may develop an interfacial potential due to ion-exchange process to a varying degree with different anions. Thus, in addition to  $\text{NO}_3^-$  a PPy coated Pt electrode may respond to a variety of monovalent anions. The extent of this response should lead to an order of an ionic selectivity.

**Table 2.** Comparison of  $K_{NO_3, X^-}$  of PPy Coated Pt Electrode with Coated Wire Electrodes

X <sup>-</sup>	Carbon paste <sup>a</sup>	PMMA <sup>b</sup>	Epoxy <sup>c</sup>	PVC <sup>d</sup>	Orion-ISE <sup>d</sup>	PPy
Cl <sup>-</sup>	0.035	0.040	0.097	0.063	0.006	1.01
I <sup>-</sup>	2.331		3.1	7.7	20	0.306
NO <sub>2</sub> <sup>-</sup>	0.195	0.158	0.290	0.150	0.06	2.48
ClO <sub>4</sub> <sup>-</sup>	1.628		2.3	10	1000	0.046

<sup>a</sup>from ref. 17. <sup>b</sup>from ref. 15. <sup>c</sup>from ref. 16. <sup>d</sup>from ref. 14.

The selectivity coefficients of some possible interfering anions were measured over a range of concentration ratio of [anion]/[NO<sub>3</sub><sup>-</sup>] from about 0.1 to 10<sup>-4</sup> and the results are listed in Table 1. From the selectivity coefficients given in Table 1, the order of selectivity found is as follows:



The selectivity order generally agrees with the literature values as compared in Table 2. However, the PPy coated electrode shows better selectivity for I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and IO<sub>4</sub><sup>-</sup>. As can be seen in Table 1, the selectivity order appears to be independent of mobility of ions in water, but may be roughly related to the ionic radius. Probably the ion associate between PPy polycations and anion may be governed by the ratio of charge to radius. That is, the larger charge density the anion has, the greater becomes the selectivity coefficient. Nitrite ion, in particular, exhibits unusually high selectivity.

In conclusion, a nitrate ion-sensing PPy coated Pt electrode is easy to prepare and shows a fast response compared with the nitrate ion-selective electrodes using liquid membrane or PVC membrane. Moreover, the nitrate ion chemical sensor using PPy polymer is almost comparable with typical coated wire nitrate ion-selective or membrane electrodes in potentiometric response and has better selectivity coefficients for I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and IO<sub>4</sub><sup>-</sup>. Studies to obtain a lower detection limit are under way.

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