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A textile based polypyrrole chloride sensor for agricultural use

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Abstract:

This paper describes the feasibility of developing a novel polypyrrole (PPy) potentiometric sensor. Conductive PPy-based polymers has been grown through a textile scaffold to create a flexible and robust sensing structure that can survive environments such as soil, with the choice of the scaffold materials offering control of the environmental impact. Further work has demonstrated that doped PPy has an electrochemical response that is sensitive to different measurands' concentration and in this case, we look at chloride response. Various chloride sensors were evaluated in varying concentrations of the potassium chloride test solutions in terms of their chloride ion sensitivity, hydration times and usable lifetime. The best performing sensor has shown a near-Nernstian response between 45-48 mV/decade to chloride ions and at least 2 weeks initial lifetime.

Keywords: Chloride sensor; potentiometric sensor; conducting polymer; polypyrrole, environment

1. Introduction

Chloride is an essential mineral for many plant functions. Greater than natural chloride concentrations can influence growth, reproduction and survival of species. Therefore, it is important to monitor the impact of chloride on the environmental conditions and detect any fluctuation caused by this pollutant. To detect the contamination of natural water sources and soil a network of early warning systems consisting of in-situ miniaturised electrochemical sensors are required as a simple alternative to the current methods of detection of pollution [1]. This approach enables the localization of pollution sources and better control of the environment but requires larger numbers of miniaturised, rugged and biodegradable devices suitable for field deployment [2, 3].

The rapid progress in information technology and microelectronics opens the way for development of new and low cost sensors for continuous environmental monitoring measurements [4]. In 1990s, organic conjugated polymers (conducting polymers) have emerged as potential candidates for electrochemical sensors [5]. It has been known for some time [6] that doped PPy films have an electrochemical response to ions concentration and therefore they might be used as potentiometric sensors.

This paper investigates the feasibility of developing a potentiometric sensor based on conducting polymers around single or multiple fibres integrated into an electronic system [7-8]. The mechanism for this will be to utilize the sensing capabilities of PPy initially to investigate its performance as a chloride ion sensor. The proposed sensor differs from more traditional sensors in that it does not have a separate conduction electrode layer, such as in the silver/silver chloride sensor [9-11]. Instead, the sensing layer is the electrode which does not to be isolated from the solution to be measured.

2. Sensor fabrication and testing

A 65%/35% polyester-cotton fabric was chosen as a substrate for the chloride sensor. A 13.8 x 2.9 cm^2 strip of the fabric was supported by a graphite plate measuring 4.0 x 2.5 x 0.3 cm^3 to allow a thin and homogeneous film growth on the fabric with the electro polymerization technique in 0.4M Py 1MKCl solution. This was followed by the printing an insulating barrier layer of FabInk UV-IF 1039, to prevent the solution from wicking up the fabric. The PPy was grown under different conditions, as detailed in Table 1 and Table 2 shows the dimensions of the sensors.

Table 1. PPy(Cl$^-$) *s*ensors' growing conditions.

Sensor	Potential (V)	Pyrrole (M)	KCl (M)	Volume (mL)	Duration (h)
1	0.85	0.4	1.0	100	1
2	0.85				2
3	0.75				1
4	0.75				2

Table 2. PPy(Cl$^-$) electrodes' sensing area.

Sensor	Electrode sides length (mm)				Total area (mm^2)	Barrier area (mm^2)	Sensing area (mm^2)	
	a	b	c	d	b x c	b x d	a x b	b x c
1	28	8	36	10	288	80	224	-
2	30	7	38	10	266	70	210	-
3	28	13	38	5	494	65	364	-
4	-	11	29	-	319	-	-	319

The three-electrode setup used in the electrolytic cell consisted of a reference electrode (RE), counter electrode (CE) and working electrode (WE). For the reference electrode a VWR 662-1806 Ag/AgCl reference electrode was selected. For the counter electrode two graphite rods measured 10cm x 0.5cm^3 each were used. A graphite plate operated as a working electrode. The probes connected to each of the three electrodes were attached to a potentiostat (Autolab PGSTAT302N). The software used to set up the potentiostat was NOVA 1.5. Sensor evaluations were undertaken through a series of experiments: Sensitivity (before drift), Drift, and Repeatability (Sensitivity after drift). Four sensors (1, 2, 3 and 4) were immersed into various test solutions and measured with respect to a commercial reference electrode (VWR 662-1806) located centrally within a beaker containing the constantly stirred test solutions. The test solutions were designed to produce decade step changes of chloride ion concentrations. Each sensors electro-potential difference was measured using a Keighley 2000 multimeter and recorded using a RealTerm Serial Capture Program 3.0.0.30.

4. Results and Discussion

Some interesting initial results have been obtained in laboratory trials of the sensor and typical example sensitivity and drift response patterns are shown below. Sensitivity response for each $PPy(Cl^-)$ sensor with barrier was obtained every 1 minute for 1 hour. Figure 2 shows a simple graphical representation of the voltages against time of Sensor 2.

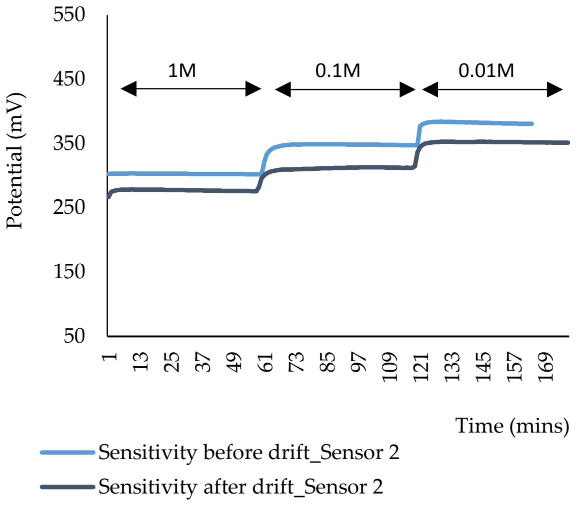

Figure 2. Sensitivity and repeatability tests of Sensor 2.

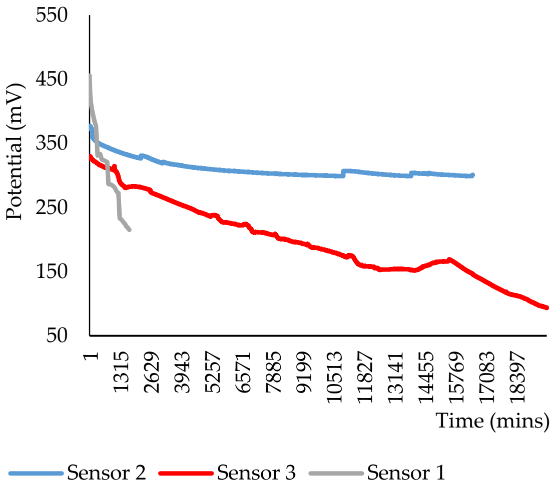

Figure 3. Drift test of Sensors 1, 2, 3 with layer barrier.

The traces on Figure 3 show the drift of Sensors 1-3 which were recorded every 1 minute in 0.1MKCl solution. Sensitivity, repeatability and drift results are summarised in tables below. Sensor 4 failed very early on and so is not reported here.

Table 3. Sensitivity and repeatability tests' results.

		$PPy(Cl^-)$ Sensor					
		1		**2**		**3**	
Sensitivity tests		Solution Conc.		Solution Conc.		Solution Conc.	
		0.1M – 0.01M	0.01M – 1M	1M – 0.1M	0.1M – 0.01M	1M –0.1M	0.1M – 0.01M
Before drift (mv/decade)	Test 1	47.3	107.5	45.0	38.1	23.2	271.7
	Test 2	27.9	80.4	47.6	45.2	not recorded	
After drift (mv/decade)	Test 3	25.4	18.1	33.1	41.3	38.2	30.3

The Nernst equation predicts a change of -59mV/decade of chloride ion concentration. The best performing $PPy(Cl^-)$ Sensor 2 showed a sensitivity between 45 and 48 mV/decade of $[Cl^-]$ with the most stable drift potentials over 13 days (Table 4).

Table 4. Drift test results.

$PPy(Cl^-)$ Sensor	**Drift duration**	**Barrier layer**	**Initial potential**	**Final potential**	**Difference**
1	8 days	Yes	455.7	147.5	308.2
2	13 days		326.7	299.7	27.0
3	15 days		326.6	93.6	232.4
4	25 minutes	No	439.3	179.2	260.1

There was no direct control of the temperature of the test solutions. The ambient temperature within the laboratory varied by ±3°C from the set temperature of 21°C. The temperature changes governed the level of solution in the beaker. Through the course of investigation, the solution was top up with de-ionised water when necessary to leave the sensors immersed at a constant depth, as shown by the graph traces on Figure 3.

5. Conclusion and future plan

In this study, a novel substrate was employed for the potentiometric chloride sensor based on doped PPy. It was shown that PPy can be electrochemically grown on/through an insulating substrate by means of a tight contact between the working electrode and the substrate. Normally the conducting surface becomes an integral part of the structure, but in this case the material can be separated from the conducting surface, bringing the PPy with it, leaving the PPy layer combined with the scaffold material. The construction is advantageous because it is grown around the fibres (rather than printed on the top). It uses the fibres as a support matrix and in principle could make individual fibres into sensing elements. The results show that this process is repeatable. The dynamic potentiometric response of sensor showed reproducibility and near-Nernstian behavior. So far, measurements have been performed in chloride solutions, but we intend to start growing the sensor in nitrate solutions to emphasise its nitrate response.

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