

Development and environmental application of a nitrate selective microsensor based on doped polypyrrole films

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Abstract

This work describes the development and testing of a sensitive and selective potentiometric nitrate microsensor based on doped polypyrrole films. Utilizing 6–7 μm carbon fibers as a substrate for pyrrole electropolymerization allowed fabrication of flexible, miniature and inexpensive sensors for in situ monitoring of nitrate. The sensors have a rapid response (several seconds) and in their characteristics are competitive with expensive commercial nitrate ion selective electrodes (ISE), exhibiting Nernstian behavior (slopes 54 ± 1 mV per log cycle of nitrate concentration ($n = 8$), at $T = 22^\circ\text{C}$), a linear response to nitrate concentrations spanning three orders of magnitude ($0.1\text{--}10^{-4}$ M or 6200–6.2 ppm of NO_3^-), and a detection limit of $(3 \pm 1) \times 10^{-5}$ M (1.25–2.5 ppm). After a 2-month-period, the response was unchanged, and after 4.5 months, one version of the electrode continued to exhibit significant sensitivity to nitrate. Several polypyrrole nitrate microsensors were embedded sequentially downstream from a point source of nitrate solution in an intermediate scale physical groundwater model as a test of their performance under simulated environmental conditions. The microsensors responded appropriately to the approaching nitrate solution front, demonstrating dispersion and attenuation of the nitrate concentrations that increased with distance from the source.

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1. Introduction

Sensitive, non-toxic and inexpensive sensors for reliable in situ nitrate (NO_3^-) monitoring would be desirable for a variety of applications in different fields, including environmental engineering, precision agriculture, biology, medicine, and others. For example, nitrate fertilizers are used extensively in agriculture, and can negatively impact the quality of rivers, groundwater and other water resources by stimulating the occurrence of eutrophication-causing algal blooms [1]. Potential impacts on human health [2,3] give cause for regulation and monitoring of nitrate levels in drinking water, particularly from groundwater wells in agricultural regions where livestock waste releases are a problem. The maximum

allowable contamination level for nitrate in drinking water stipulated by US Environmental Protection Agency (EPA) is 44 ppm as NO_3^- (10 ppm as nitrogen) [4]. In the near future, even lower regulatory limits may be applied to address concerns about the role of nitrate in ecosystem dynamics.

Commercial nitrate ion selective electrodes (ISE) are available for deployment in water. They typically respond to ions according to Hofmeister selectivity series [5]: large lipophilic anions $> \text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{PO}_4^-$. This series implies that commercial nitrate ISEs are in few orders of magnitude more selective to, say, perchlorate and iodide than for nitrate [6]. In addition to their potential selectivity problems, these sensors are less suitable for soil measurements because they are relatively large (diameter 1–2 cm, length 10–15 cm), and structurally rigid. The cost per lifetime is also an important consideration (for commercial sensors it is more than \$100 per several months of

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laboratory measurements), especially when numerous sensors are required for investigating spatial and temporal patterns, and when retrieving the embedded sensors is time or labor intensive.

Doped polypyrrole (PPy) films can be used as highly selective membranes in ISE fabrication [7–10]. These ISEs exhibit high selectivity toward the dopant ion which is not related to its lipophilicity. Electrodes prepared in this manner may result in a few orders of magnitude higher selectivity toward the target ion than commercial analogs, with the same sensitivity [6,10]. The form factor (size and shape) envisioned for several applications may be quite different from the common laboratory electrodes mentioned above. For example, specific environmental or agricultural applications may require large networks of miniature sensors embedded in natural porous media (soils, sediments and rocks) or within the plant rhizosphere.

In this work, to solve the problems of sensor form factor and cost, we propose using polyacrylonitrile (PAN)-based carbon fibers as a substrate for a doped polypyrrole layer. Polymerization of pyrrole onto carbon fibers has been previously studied [11–14], but it has not been considered as a possible material for microsensor applications. Using small diameter (6–7 μm) carbon fibers as a substrate for pyrrole polymerization, flexible and inexpensive nitrate microsensors with characteristics competitive with commercial analogs were prepared. A physical aquifer model was used as a test bed for the in situ deployment of prototypical sensors for the purpose of monitoring dynamic nitrate transport in a natural porous medium.

2. Experimental

2.1. Reagents

All chemical reagents were analytically pure grade and used as purchased from Aldrich or Fisher Scientific. Pyrrole was refrigerated in the dark and purified before use by distillation (b.p. = 129–131 $^{\circ}\text{C}$ at atmospheric pressure) or by passing pure pyrrole through an alumina (Al_2O_3) column. Sodium nitrate (hygroscopic grade reagent) was dried in an oven at 80–100 $^{\circ}\text{C}$ before use. All aqueous solutions were prepared using deionized water with a resistivity of $\sim 18 \text{ M}\Omega\text{-cm}$ (Ultrapure Water System, Nanopure Infinity, Inc.).

2.2. Preparation of nitrate-doped polypyrrole (PPy(NO_3^-)) microelectrodes

Sigrafil C30 T045 EPY (SGL Technic, Inc.) or PLS 003 (Fortafil Fibers, Inc.) carbon fibers were used. Bundles of 20–30 fibers or single filaments (6–7 μm diameter) were connected to copper wire using silver paint (Structure Probe, Inc.). Polymerization of pyrrole doped with nitrate onto carbon fiber substrate was performed electrochemically. A potentiostat/galvanostat (CH Instruments, Model 660B) was

used as a constant current source for electropolymerization. The initial polymerization solution consisted of 1 M pyrrole and 0.1 M NaNO_3 in aqueous media. The solution was deoxygenated by purging it with nitrogen for 5–10 min before polymerization and by bathing the system headspace with nitrogen gas during the experiment. A one compartment cell was employed including a 1.5 cm length of carbon fiber (bundled or single filament) working electrode, a Ag disk/wire reference electrode and a Pt disk/wire counter electrode. Polymerization was performed under constant current conditions (current densities 1.5–2.1 mA/cm^2) for 20 min. The freshly prepared nitrate-doped polypyrrole (PPy(NO_3^-)) microelectrodes were rinsed with water and conditioned for at least 24 h in a 0.01 M NaNO_3 solution at room temperature in the dark.

2.3. Potentiometric measurements

Potentiometric measurements were performed with a pH/ISE Meter (Orion Research, Inc., Model 720). Potential differences were measured between the prepared carbon fiber-based polypyrrole-coated microelectrodes and a Ag/AgCl double junction reference electrode (Bioanalytical System, Inc.). A 0.01 M $(\text{NH}_4)_2\text{SO}_4$ solution was used as an ionic strength adjuster (ISA). Between measurements, the electrodes were stored in the dark in the conditioning solution at room temperature.

2.4. SEM analysis and film thickness measurements

The surface of carbon fibers and polypyrrole films was observed using a cold field emission scanning electron microscope (SEM, Hitachi S4700). The thickness of the polymer was evaluated from the SEM images by comparing uncoated and polypyrrole-coated fibers.

2.5. Set-up for nitrate transport measurements in the physical aquifer model

A 150 cm (length) \times 50 cm (width) \times 35 cm (height) glass container packed with homogeneous, clean sand (nominal grain diameter 0.33 mm) was used as an in situ sensing test bed. Details about this system are described elsewhere [15]. The primary capability of the system is to convey steady, unidirectional flow in a manner approximating groundwater behavior. In this work, a continuous source of nitrate was introduced through tubing at a fixed location in the sandy medium via a peristaltic pump (Cole-Parmer, Masterflex, Model 7519-10). An array of nitrate microsensors was embedded in the medium at various positions downstream of the nitrate injection point. Microsensor responses were monitored automatically using a data acquisition (DAQ) system controlled by LabView software (National Instruments, version 6.1).

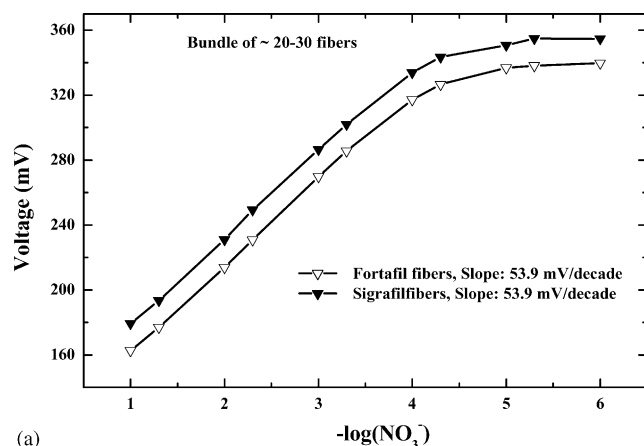
3. Results and discussion

3.1. Potentiometric response of PPy(NO₃⁻) microelectrodes to NO₃⁻ ion

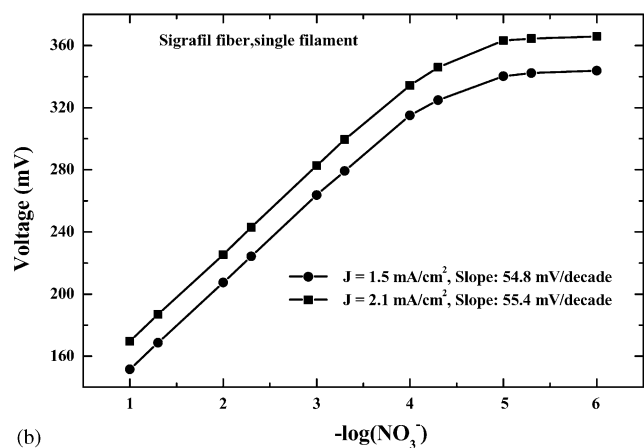
PPy(NO₃⁻) microelectrodes, were tested for their potentiometric response to NO₃⁻ several days after deposition. The response time of the electrodes was on the order of a few seconds. Typical calibration curves obtained for the bundle of fibers and single filaments are shown in Fig. 1.

The electrodes exhibited Nernstian behavior (slopes 54 ± 1 mV per log cycle of nitrate concentration ($n = 8$), at $T = 22$ °C), with a linear response spanning three orders of magnitude (0.1 – 10^{-4} M or 6200 – 6.2 ppm of NO₃⁻) and a detection limit $(3 \pm 1) \times 10^{-5}$ M (1.25 – 2.5 ppm) of nitrate. This detection limit is more than order of magnitude lower than safe levels of nitrate in drinking water as regulated by U.S. EPA [4].

SEM images of a single $6 \mu\text{m}$ carbon fiber and second fiber coated with the doped polypyrrole are shown in Fig. 2. The surface of the polymer coating is rough and its thickness varies spatially along the sensor. According to this SEM



(a)



(b)

Fig. 1. Potentiometric response of PPy(NO₃⁻) electrodes to NO₃⁻ ion ($T = 22$ °C). (a) substrate is a bundle of 20–30 carbon fibers; (b) substrate is a single carbon fiber. Deposition of PPy(NO₃⁻) layer at constant current densities of 1.5 – 2.1 mA/cm² for 20 min.

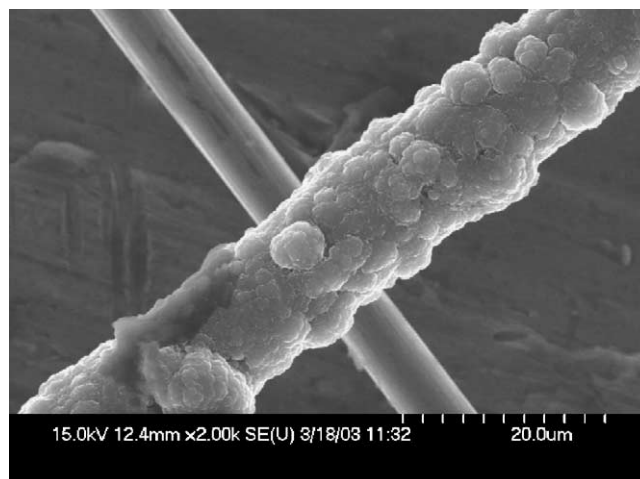


Fig. 2. SEM images of uncoated (back) and coated with doped polypyrrole (front) carbon fibers.

image, a polypyrrole layer of $3.7 \pm 0.6 \mu\text{m}$ was obtained (polymerization conditions as in Fig. 1b, $J = 1.5$ mA/cm²).

With respect to deployment in the environment, an important aspect of a sensor is its lifetime. We studied the potentiometric response of PPy(NO₃⁻) sensors plated on two kinds of carbon fibers substrate as a function of time after polymerization. These results are summarized in Table 1. These data illustrate that in both cases (Sigrafil and Fortafil fibers) there is almost no change in the response of the sensors after 2 months (very slight decrease in slopes). After 4.5 months, the Fortafil fibers substrate sensor calibration curve exhibited 77% of its initial slope value, while the Sigrafil-based sensor no longer responded to nitrate.

Recently we have also proposed the use of everyday pencil leads as a substrate for polymerization of pyrrole [16]. PPy(NO₃⁻) sensors, prepared on a pencil lead, substrate greatly facilitated handling and use. These electrodes may be good alternatives to carbon fiber-based electrodes for *in situ* nitrate measurements in cases in which microsensing and flexibility are not required.

In Fig. 3, the potentiometric response of some commercial nitrate ISEs is compared to that for the fabricated carbon fiber and pencil lead-based PPy(NO₃⁻) electrodes. These results demonstrate that carbon fiber and pencil lead-based electrodes exhibit a similar linear response range between 0.1 M and 10^{-4} M with more ideal (Nernstian) slope values than the commercial probes.

Table 1
Longevity of PPy(NO₃⁻) microelectrodes

Time after deposition	Slope, mV/decade of concentration	
	Substrate–Sigrafil fibers	Substrate–Fortafil fibers
7 days	53.9	53.9
1 month	52.2	53.2
2 months	50.9	52.6
4.5 months	No response	41.4

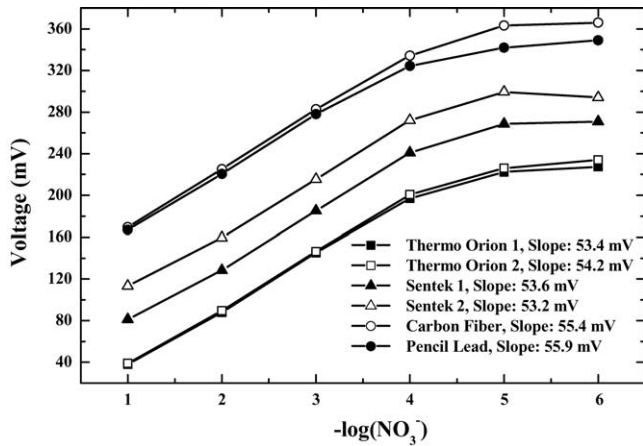


Fig. 3. Potentiometric response to NO_3^- ion for some commercial and laboratory-fabricated mini- and microelectrodes.

3.2. Nitrate transport measurements in an intermediate scale aquifer

After successful testing of the $\text{PPy}(\text{NO}_3^-)$ electrodes under laboratory conditions the electrode's behavior was investigated under realistic, but controlled, transport conditions in an intermediate scale physical aquifer model [15,17]. A schematic illustration of the system is given in Fig. 4 and preliminary experimental results from this system with one nitrate sensor are shown in Fig. 5.

The purpose of the preliminary experiment was to test the dynamic response of the sensor in sandy media. One nitrate sensor and one reference electrode (Ag/AgCl) were embedded 0.5 cm from the continuous source of nitrate/water with constant flow rate of 1.7 mL/min. As illustrated on Fig. 5, when water was provided from the source, a constant voltage of about 320 mV was monitored. When the source was changed to a 0.1 M NO_3^- solution, a clearly defined and sig-

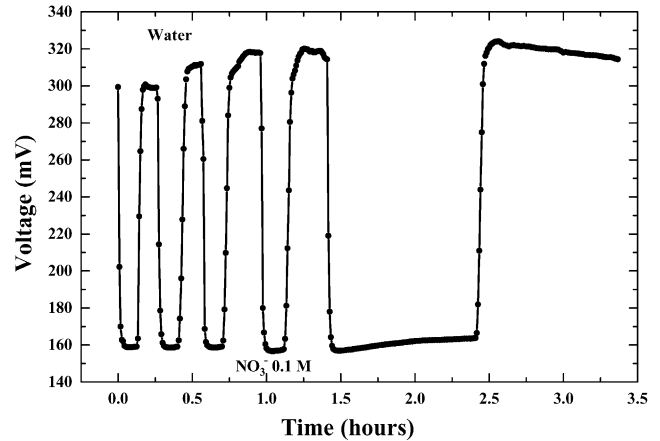


Fig. 5. Preliminary experiment for a $\text{PPy}(\text{NO}_3^-)$ nitrate mini-sensor embedded in the intermediate scale aquifer (sensor size: pencil lead 0.5 mm diameter, 2 mm length; sensor distance from source: 0.5 cm; continuous alternating source: $\text{H}_2\text{O}/0.1 \text{ M } \text{NO}_3^-$ solution; injection rate: 1.7 mL/min; uniform water flow velocity: 7.1 cm/h).

nificant voltage drop to approximately 160 mV was observed. Nitrate was exchanged with water a few times, and these observations were found to be repeatable. The close proximity of the sensor to the source in this preliminary study precluded significant transport effects.

In situ nitrate observation may require embedding multiple nitrate sensors in the ground to monitor the three-dimensional nitrate propagation and attenuation due to transport processes. Thus, a final experiment was undertaken to observe the response of multiple microsensors embedded at increasing distances from the nitrate source. Three nitrate sensors were deployed in the experimental test box directly downstream and 2, 5 and 8 cm from the source. A step change from clean water to a 0.1 M NO_3^- solution was executed 30 min after the start of the experiment (Fig. 6). ΔE (y-axis in Fig. 6) is the difference between the starting potential

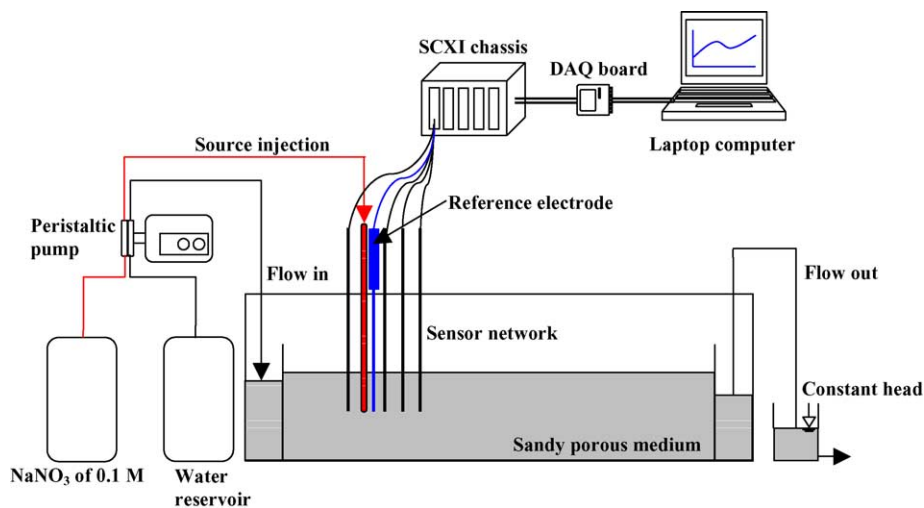


Fig. 4. Schematic cross-sectional diagram of the experimental and data acquisition (DAQ) systems for nitrate transport monitoring using $\text{PPy}(\text{NO}_3^-)$ mini- and microsensors.

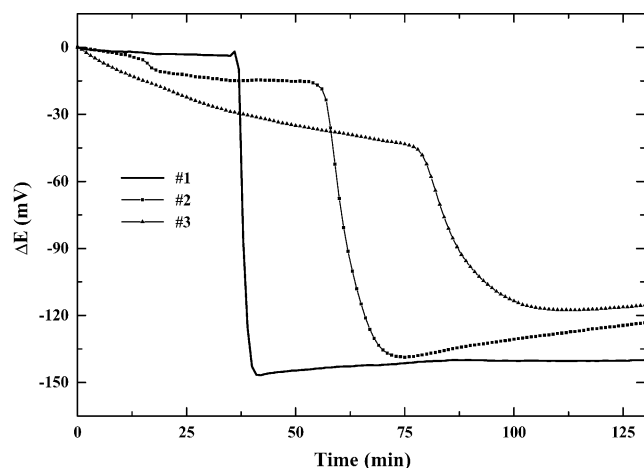


Fig. 6. Test box experiment. Potentiometric response of three $\text{PPy}(\text{NO}_3^-)$ microsensors to nitrate (sensor size: bundle of 100–150 carbon fibers, 2 mm length; sensors #1, #2, #3 deployed directly downstream and 2, 5 and 8 cm, respectively, from the source, a step change from clean water to a 0.1 M NO_3^- solution at $t = 30$ min; injection rate: 1.4 mL/min; uniform water flow velocity: 8.2 cm/h).

(response to DI water) and steady-state potential measured during the experiment. As expected, the voltage value for each sensor decreased when the nitrate concentration front arrived at each sensor location. As a result of the hydrodynamic dispersion that occurs during transport in porous media, the nitrate concentrations decrease with propagation distance in the sand. While the microsensor responses capture the dynamics of the experimental system qualitatively, aspects of their responses exhibit non-classical transport behavior. First, the arrival times at the three locations suggest local flow velocities significantly greater than the bulk value (8.2 cm/h) at locations #1 and #2. This behavior was most likely caused by the source flow that increases the local hydraulic gradient. Thus, the flow field was non-uniform in the vicinity of the source. Second, and more difficult to explain, are the microsensor responses at locations #2 and #3 relative to that at #1. Both microsensors appear to identify an increasing nitrate presence even before it has arrived at microsensor #1. This type of behavior can only be explained by flow anomalies, such as that caused by the source injection. In addition, density-driven transport of nitrate in a manner that caused small quantities to bypass microsensor #1 may have contributed to this problem. The main objective of the present work was to obtain qualitative confirmation of the microsensor responses *in situ*. The issues discussed here point to the need to further test these microsensors under simulated environmental conditions.

4. Conclusions

Flexible, miniature and inexpensive nitrate sensors were fabricated by electropolymerizing pyrrole onto carbon fiber substrates, using nitrate as a dopant. 6–7 μm carbon fibers

were found to be an excellent substitute to expensive conductive materials such as glassy carbon or platinum for electropolymerization of pyrrole. The electrodes with a 3–5 μm layer of polypyrrole doped with NO_3^- ion exhibited fast response times (seconds), sensitivity competitive to commercial nitrate ISE, and a lifetime of at least 2 month without changes in sensitivity and linear response. Preliminary tests of these polypyrrole-based electrodes as microsensors for distributed, in situ monitoring of nitrate transport were performed in an aquifer model and yielded qualitatively accurate results.

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