Title
Development and Environmental Applications of a Nitrate Microsensor Based on Doped Polypyrrole Films

Authors
Bendikov, Tatyana
Kim, Juyoul
Harmon, T C

Publication Date
2003-10-10

Center for Embedded Networked Sensing

Development and Environmental Applications of a Nitrate Microsensor Based on Doped Polypyrrole Films

Tatyana A. Bendikov, Juyoul Kim and Thomas C. Harmon
UCLA Civil & Environmental Engineering Department

Introduction and Problem Description:

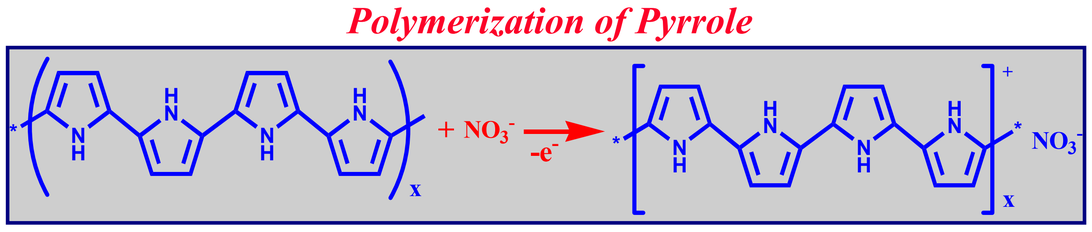
The *nitrate anion (NO_3^-)* is an important environmental and human health analyte and thus its detection and quantification is considered essential. A large number of strategies have been employed in the study of nitrate determination including spectroscopic, chromatographic and electrochemical techniques. However, these methods often require the use of toxic reagents, have a nonlinear response to nitrate, or are not sufficiently selective and sensitive.

The Idea is: Using chemical recognition principles, incorporate highly selective interactions between the electrode sensitive layer and target ion (NO_3^-) to fabricate a nitrate selective chemical sensor. This can be achieved by using conductive polypyrrole films doped with nitrate as a sensitive layer.

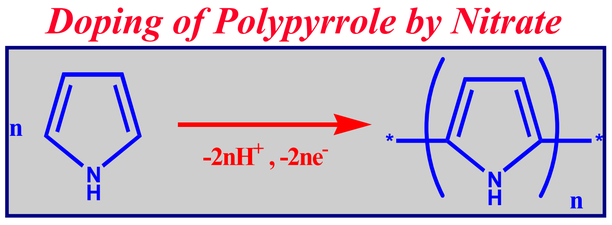
Polypyrrole in its oxydized state exists as a polyradical cation, and at the oxidation stage anions are attracted electrostatically into the polymerized films as counter ions (dopants). This particular structure, involving an exchangeable counter ion, has led to application of polypyrrole as a membrane component for ion selective electrodes (ISE). These ISE show highly selectivity towards dopant ions which is not related to their lipophylicity.

There are many studies addressing polymerization processes, polypyrrole (PPy) doping with various ions and applications of this doped polypyrrole films for ion selective electrodes (ISE). This work extends these studies in two directions: *1)* miniaturization of the nitrate ISE based on doped PPy films using 7 μm carbon fibers and *2)* application of these PPy(NO_3^-) electrodes to nitrate transport experiments in an intermediate scale physical aquifer model, which is a prototype for environmental (*in situ*) measurements of nitrate in soils.

Polymerization of Pyrrole



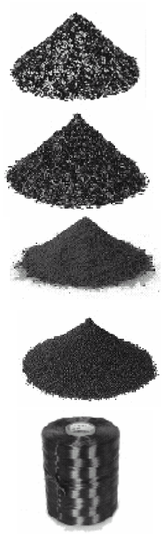
Doping of Polypyrrole by Nitrate



Carbon Fibers: Mini-Scale Potentiometric Approach

Alternative conductive materials were investigated as a possible candidates for electrochemical polymerization of pyrrole, including various graphite and carbon substrates. Carbon fibers (7 μm diam., carbon content > 95%) were found to be an excellent substitute for the glassy carbon substrate.

Carbon Fibers



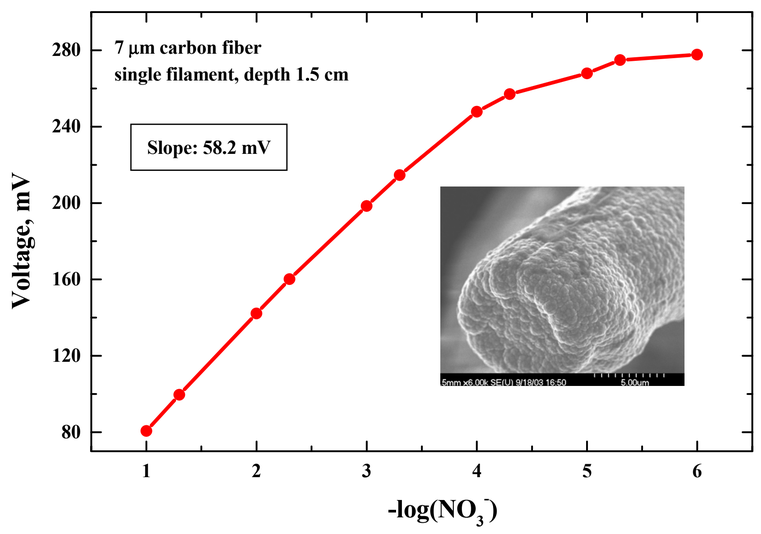


Figure 1. Potentiometric response of PPy(NO_3^-) electrode to nitrate. Substrate: single carbon filament 7μm diameter (SGL Technic Ltd).

The typical potentiometric response of PPy(NO_3^-) electrodes electrochemically prepared on carbon fiber`s substrate is shown in Figure 1. These electrodes show an improvement in the lifetime and linear range relative to the macro-scale prototype. The slopes are 53-54 mV for 20-30 filaments electrode and 58 mV for single filament (Figure 1).

SEM images of a single 7 μm carbon fiber and the same fiber coated with the doped polypyrrole are shown in Figure 2. This SEM image polypyrrole indicates a layer thickness of approximately 4 μm.

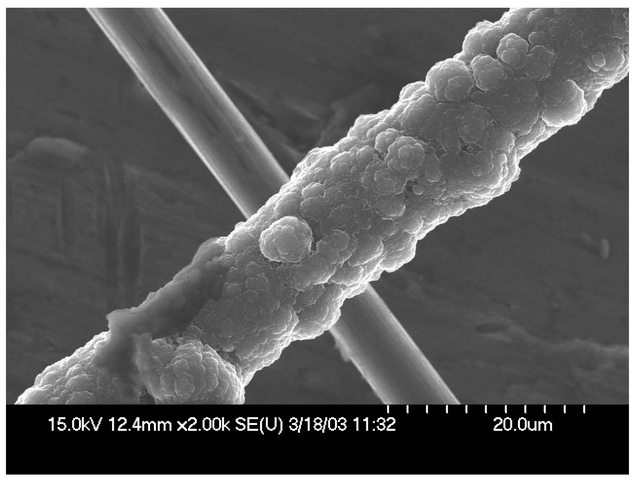


Figure 2. SEM images of noncoated (back) and coated with doped polypyrrole (front) carbon fibers.

Nitrate Transport Measurements: Test Box Experiments

After successful testing of the PPy(NO_3^-) electrodes under batch laboratory conditions, the electrode's behavior was investigated under realistic, but controlled, transport conditions. For this purpose, a glass container (150 cm x 50 cm x 35 cm) packed with homogeneous, clean sand and saturated with water was used. A schematic illustration of the system is given in Figure 3 and preliminary experimental results from this system with fifteen nitrate sensor are shown in Figure 4.

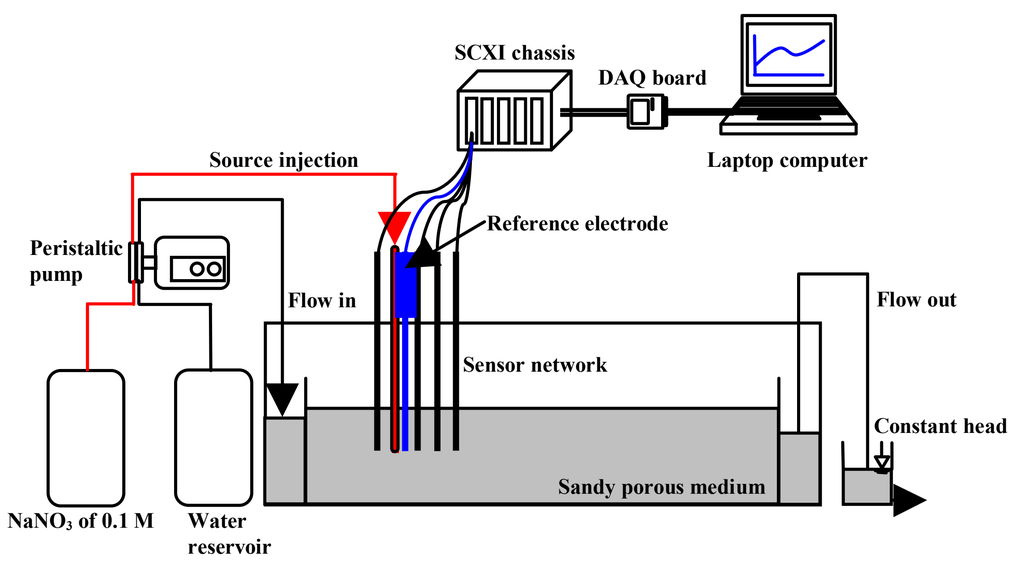


Figure 3. Schematic diagram of the experimental and data acquisition (DAQ) systems for nitrate transfer monitoring.

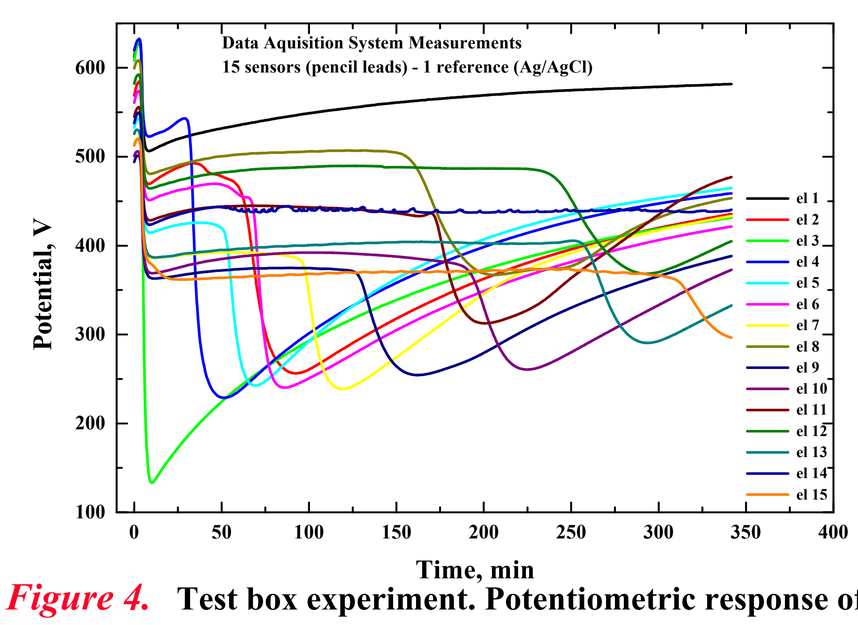


Figure 4. Test box experiment. Potentiometric response of 15 PPy(NO_3^-) electrodes to nitrate (the electrodes are at the different distances from the point nitrate source).