

Application of polypyrrole-based selective electrodes in electrochemical impedance spectroscopy to determine nitrate concentration

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Abstract—Nitrate is a commonly found nitrogen species in the environment, especially in agricultural regions. Since excessive nitrate accumulation has negative impacts on the environment, the quantitative monitoring of nitrate levels in the field is a critical component of precision agriculture. Electrochemical impedance spectroscopy (EIS) has been shown to be a versatile tool for the characterization of ionic solutions. Researchers recently showed the application of plasticized polyvinyl chloride electrodes in conjunction with this method to monitor nitrate levels. In this paper, we show that nitrate doped polypyrrole PPy(NO₃⁻) electrodes (which have a simpler fabrication) also have the potential of serving as nitrate sensors in EIS applications. To the knowledge of the authors, PPy(NO₃⁻) electrodes have not been used before to monitor nitrate levels using EIS. We also show that the low-frequency EIS behavior of PPy(NO₃⁻) electrodes can result in a nitrate sensor whose output response spans ~100X for an input dosage range of 30 ppm–6200 ppm. This, in turn, may lead to the future development of low-power nitrate sensors for large-scale field deployment wireless sensor networks.

Keywords—Electrochemical impedance spectroscopy, Polypyrrole-based ion selective electrode, Nitrate sensor

I. INTRODUCTION

Nitrate (NO₃⁻) can accumulate in groundwater and other water resources due to their excessive use in fertilizers. Due to the negative impacts this has on both the environment and human health [1-3], the nitrate levels in water (particularly from groundwater wells in agricultural regions) are regulated and monitored. Inexpensive and sensitive sensors for the accurate quantitative monitoring of nitrate levels in the field thus have application in precision agriculture and environmental engineering.

Electrochemical impedance spectroscopy (EIS) is becoming a powerful tool in precision agriculture because it involves simple electrical measurements that can be correlated with complex material variables such as mass transport of fertilizers and local ion concentrations [4]. Indeed, the use of ion-selective electrodes (ISEs) in conjunction with EIS measurements (which can be automated and implemented using conventional microelectronics) has the potential of

enabling portable sensors for monitoring nitrate levels in the environment [5].

In this paper, we describe an EIS-based nitrate sensor that uses ISEs fabricated with doped polypyrrole (PPy) films. Our work differs from that in [5] by using nitrate-doped polypyrrole (PPy(NO₃⁻)) ISEs, instead of plasticized polyvinyl chloride ISEs. Due to its facile fabrication, PPy(NO₃⁻) ISEs are less expensive to make into sensors [6,7]. They also exhibit highly selectivity and appreciable selectivity to NO₃⁻ in comparison to several common anions [8]. While PPy(NO₃⁻) ISEs have been used in the context of voltammetric methods to determine nitrate concentration [6,7], they have not been used before to monitor nitrate levels by means of EIS (to the knowledge of the authors). Using our PPy(NO₃⁻) ISEs, we also show that a trend-line with a high coefficient of determination appears to exist between the charge transfer resistance extracted from our low-frequency EIS measurements and nitrate concentration. This spanned an input dosage range of 300 ppm–6200 ppm for nitrate, and resulted in an output response that spanned ~100X. The potential to have such responsive sensors operating at low frequencies (coupled with the simple fabrication process of PPy(NO₃⁻) ISEs) may enable the future realization of low-power nitrate sensors for large-scale field deployment wireless sensor networks.

II. ION-SELECTIVE ELECTRODE FABRICATION AND EXPERIMENTAL SETUP

A. Polypyrrole-based Nitrate Sensor

The fabrication of the PPy(NO₃⁻) ISEs followed a process similar to that described in [6]. Electrodes were prepared from pencil lead (2B, 0.7 mm diameter, 6 cm length, Promarx) connected to copper wire (Fig. 1). It has been previously shown that the potentiometric response of pencil lead-based electrodes to NO₃⁻ are comparable to that of carbon fiber and commercial nitrate ISEs [7]. To ensure electrical contact between the pencil lead and copper wire, solder was applied to the connection. The pencil lead was then immersed in the electropolymerization solution (1 M pyrrole solution and 0.1 M NaNO₃) for polypyrrole deposition. Before deposition, this solution was purged with nitrogen for 5 minutes to remove oxygen. In order to conduct electropolymerization of the

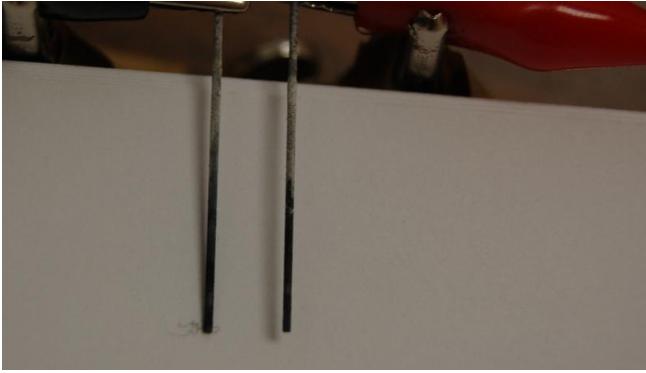


Figure 1. Picture of a pair of PPy(NO_3^-) ISEs fabricated and used in this study. A white backdrop has been placed behind the electrodes in order to highlight the doped polypyrrole deposited onto the pencil lead.

pyrrole doped with nitrate, two AA batteries were used to supply constant voltage for 4 minutes. Once the doped polypyrrole was deposited onto the pencil lead (working electrode), we used a platinum wire as the reference electrode and a paper clip as the counter electrode. After polymerization, electrodes were stored in 0.01 M NaNO_3 solution for 24 hours for conditioning.

B. Electrochemical Impedance Spectroscopy

Laboratory measurements were performed by immersing the PPy(NO_3^-) ISEs in different nitrate-containing (KNO_3 , NH_4NO_3 , or NaNO_3) deionized water solutions at room temperature. Prior to data collection, the sensors were left immersed in the solution for 5 minutes (which was observed to be enough time to allow for measurement stability and equilibrium with the ions). Impedance measurements and data collection for the PPy(NO_3^-) ISEs were performed by following a setup similar to that described in [9]. The source of the input sine wave was a Tektronix AFG3021B function generator, and the sampling was performed with a multiplexed 12 bit A/D converter on the EK-TM4C123GXL LaunchPad (Texas Instruments). PPy(NO_3^-) ISEs immersed in the different nitrate solutions served as the unknown impedance (Z_U). In order to determine Z_U , the sampled function generator and voltage drop across the reference resistor R_m signals ($V_{TOT[n]}$ and $V_R[n]$, respectively, where n is an integer multiple of the sampling period T_S) [9], were first fitted by using a Fourier fit operation in Matlab's curve fitting toolbox (Mathworks). This then allowed the phase θ and the amplitude A of $V_{TOT[n]}$ (A_{TOT} and θ_{TOT}) and $V_R[n]$ (A_R and θ_R) to be determined. Subsequently, Z_U was calculated using the following equation [9]:

$$Z_U = R_m \cdot ((A_{TOT} \angle \theta_{TOT}) / (A_R \angle \theta_R) - 1) \quad (1)$$

The value of the reference resistor R_m [9] was changed for the different nitrate-containing solutions such that the AC amplitude value across the PPy(NO_3^-) ISEs remained 100mV (all other experimental parameters were identical for the different samples). A Randle's circuit (Fig. 2) was used as the equivalent circuit to model the electrochemical impedance data obtained.

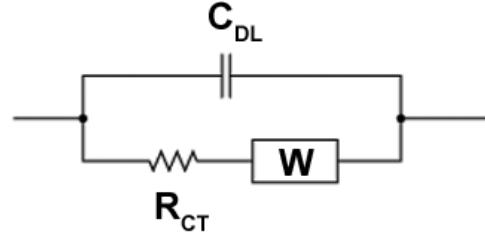


Figure 2. Randle's equivalent circuit, a circuit analogy of the electrochemical behavior of ionic solutions. C_{DL} is the double layer capacitance, R_{CT} is the charge transfer resistance, and W is the Warburg diffusion impedance.

III. RESULTS AND DISCUSSION

Plotting $-Z_{Im}$ vs. $\omega^{-1/2}$ (or Z_{Re} vs. $\omega^{-1/2}$) for low frequencies (where Z_{Im} and Z_{Re} are the imaginary and real parts of Z_U , respectively, and ω is the frequency of operation) allows the analysis of the Warburg-type diffusion impedance of the system [10]. For our PPy(NO_3^-) ISEs immersed in nitrate-containing solutions, this is shown in Fig. 3 for a couple of representative samples. The frequency range selected was 0.05 Hz–2 Hz. For a given nitrate-containing solution, note that the linear regressions for $-Z_{Im}$ vs. $\omega^{-1/2}$ and Z_{Re} vs. $\omega^{-1/2}$ have comparable slopes to one another (as is to be expected of the Warburg-type diffusion impedance, which gives rise to a 45° line in the Nyquist complex plane representation of impedance). The y-intercept of the Z_{Re} vs. $\omega^{-1/2}$ plot corresponds to the charge transfer resistance R_{CT} of the Randle's equivalent circuit [11]. In the representative plots depicted in Fig. 3, the observed R_{CT} is ~50kΩ and ~1300Ω for the 60 ppm and 6200 ppm KNO_3 -containing solutions, respectively.

We next determined R_{CT} (extracted from electrochemical impedance data in the low-frequency range, Fig. 3) for 15 different samples (each done in duplicate) that spanned a nitrogen concentration range of 30 ppm–6200 ppm. Fig. 4 shows the cumulative results. Note that the use of R_{CT} as the sensor output metric appears to result in a trend-line with a high coefficient of determination ($R^2 = 0.9793$). Our results also suggest that the polypyrrole-based sensor is quite responsive, with the R_{CT} output metric varying by a factor of ~100X for the tested nitrate input dosage range of 30 ppm–6200 ppm.

Our results suggest that PPy(NO_3^-) ISEs may be well suited to serve as sensors for determining nitrate concentration by means of EIS. Not only does the sensor appear to exhibit responsive behavior with a high coefficient of determination, the simplicity and inexpensive nature of the PPy(NO_3^-) ISE fabrication process may make polypyrrole-based sensors an attractive option for the development of low-cost portable sensors for environmental monitoring. Since the dynamic power dissipation of microelectronics is directly proportional to the frequency of operation, the ability to have responsive sensor behavior at low frequencies (Fig. 4) may also enable the realization of large-scale field deployment of wireless nitrate sensor networks.

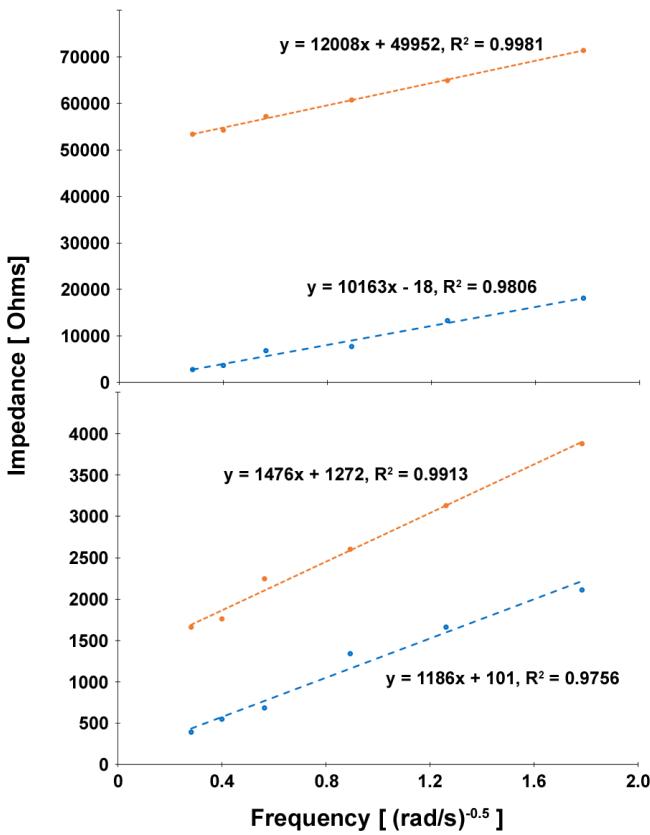


Figure 3. Representative Warburg impedance plots for PPy(NO_3^-) ISEs immersed in different nitrate-containing solutions. Top panel corresponds to a 60ppm KNO_3 -containing solution, while the bottom panel corresponds to a 6200ppm KNO_3 -containing solution. Orange represents Z_{Re} vs. $\omega^{-1/2}$ while blue represents $-Z_{\text{Im}}$ vs. $\omega^{-1/2}$.

The data in Fig. 4 appear to suggest that the R_{CT} measured by PPy(NO_3^-) ISEs is not appreciably affected by the presence of different cations alongside of nitrate. When polyvinyl chloride-based ISEs were used in [5], the authors observed that their sensor output metric was affected by the presence of Cl^- anions. As future work, we will be investigating whether our PPy(NO_3^-) ISEs exhibit better selectivity towards Cl^- and other anions. As the US Environmental Protection Agency (EPA) recently reduced the maximum allowable contamination level for nitrate in drinking water to 10ppm [12], we will also be characterizing our sensor response to nitrate concentrations in the 1–10ppm range.

IV. CONCLUSION

In this paper, we have shown that PPy(NO_3^-) ISEs have the potential of being used in EIS to determine nitrate concentration. The simpler fabrication process needed for PPy(NO_3^-) ISEs make them a viable alternative to plasticized polyvinyl chloride-based ISEs in EIS studies. Furthermore, the potential to operate the system at low frequencies may enable the future realization of low-power nitrate sensors for large-scale field deployment wireless sensor networks. We believe that the implementation of such sensor networks are an important component of enabling “smart farming” in the future.

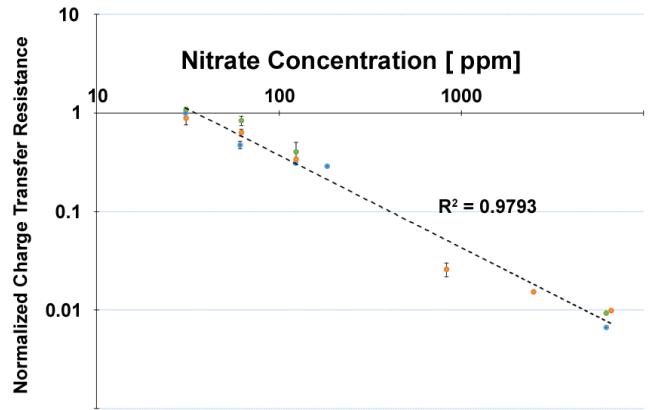


Figure 4. Relation between the charge transfer resistance R_{CT} and the nitrate concentration in solution. Blue, orange, and green correspond to KNO_3^- , NH_4NO_3^- , and NaNO_3 -containing solutions, respectively. R_{CT} values have been normalized to that obtained for the 30ppm KNO_3 -containing solution. Each sample was tested in duplicate. Mean values have been displayed, with the error bars denoting standard error.

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