Available online at www.sciencedirect.com

ScienceDirect

Sensors and Actuators B 133 (2008) 5–14

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Ion chromatography-potentiometric detection of inorganic anions and cations using polypyrrole and overoxidized polypyrrole electrode

Mutlu Şahin, Yücel Şahin*, Adnan Özcan

Anadolu University, Faculty of Science, Department of Chemistry, 26470 Eskişehir, Turkey

Received 16 June 2007; received in revised form 31 December 2007; accepted 7 January 2008
Available online 12 January 2008

Abstract

Polypyrrole (PPy) and overoxidized polypyrrole (OPPy) films were used as a potentiometric detector in ion chromatography, in order to determine some anions and cations in water samples. Electrodeposition of PPy film was performed by constant potential at +0.80 V (vs. Ag/AgCl) in an aqueous solution containing 0.1 M pyrrole and 0.2 M sodium nitrate. The overoxidation of PPy film was carried out in 0.1 M NaOH solution by cycling the potential between +0.80 and +1.20 V at 50 mV s^{-1}. The PPy film exhibited good sensitivity toward, especially, fluoride and chloride ions. The lowest detection limit (3σ) observed was 10^{-8} M for fluoride with PPy detector. This is the first study using OPPy electrode for the potentiometric detection of both monovalent and divalent cations in literature. The correlation coefficients obtained from the calibration curves were 0.947–0.991 for anions and 0.998–0.999 for cations. The response of ions at the PPy and OPPy electrodes maintained over 90–94% of the original value for 45 and 30 days, respectively. It can be concluded from the observed data that these electrodes can be used as an alternative detector materials to analyse anions and cations in the water samples by ion chromatography.

Keywords: Polypyrrole; Overoxidized polypyrrole; Potentiometric detection; Ion chromatography; Water analysis

1. Introduction

Ion chromatography (IC) has become a powerful, widely used analytical method enabling simple, selective and fast determination of a variety of inorganic and organic anions and cations [1–4]. While conductivity is the primary detection method for most IC systems, there are still continuing research efforts to develop alternative detection methods. Ion-selective electrodes (ISEs) are nowadays routine analytical tools, with important applications in clinical diagnostics, process monitoring and environmental analysis [5]. Over 60 inorganic and organic ions can be assessed directly with ion-selective electrodes, and novel selective ionophores are continuously synthesized to enlarge this number [6]. In recent years, there have been many works about the potentiometric sensor with nanomolar or subnanomolar detection limits in the literature. Bakker and Pretsch reported a review which summarizes recent progress in the development and application of potentiometric sensors with limits of detection in the range 10^{-8} to 10^{-11} M [7]. Rubinova et al. used a potentiometric sensor based on polymer membranes which shows a detection limit in the nanomolar concentration range [8]. Szigeti et al. reported a novel potentiometric and optical sensors for silver ion with subnanomolar detection limits (3×10^{-11} M) [9].

Potentiometric ion-selective electrode (ISE) detectors have been tested for such purposes, utilizing their advantages in a flow-through system; namely, rapid and reproducible response, low detection limits, low cost, and ease of fabrication and miniaturization [10]. These are particularly attractive advantages in case that a very small sample volume is available for detection, such as in open-tubular micro capillary liquid chromatography [11,12]. However, common ISEs are devised to exhibit highly selective response to specific ions [13], while a general type IC detector must be able to monitor many different ions with similar sensitivity [14]. Thus, their applications have been directed mainly to enhanced detection of particular ionic species in single-column IC or for general detection of sample ions in the form of replacement ions in suppressed-column IC [15,16].

---

* Corresponding author. Tel.: +90 222 3350580; fax: +90 222 3204910.
E-mail address: ysahin@anadolu.edu.tr (Y. Şahin).

0925-4005/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.01.004

Potentiometric detection systems are not yet routinely applied in IC. A limited number of papers have appeared on this subject. Manz and Simon [12] and Trojanowicz and Meyerhoff [17,18] used potentiometric detection for the LC determination of anions. Poels et al. [19] employed a conducting oligomer electrode prepared from a mixture of phenylene vinylene trimer with a polycarbonate host polymer and iodine; it was applied to the detection of organic acids. Isıldak and Asan [20] used poly(vinyl chloride) (PVC) membrane electrodes for anion or/and cation separations. The active component of the membrane was a hydrophobic quaternary ammonium salt for the detection of anions or a crown ether for detection of cations. In recent years, the field of polymer-modified electrodes (PMEs) has received rather extensive interest from analytical chemists. The main reasons to modify electrodes are to improve selectivity and sensitivity of electrodes with modifiers. These electrodes generally consist of a polymer layer attached to an electrode surface. Intrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials. Among those conducting polymers, PPy is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. PPy can easily be prepared from aqueous and organic solvents by either chemical or electrochemical oxidative polymerization of pyrrole. The electrochemical polymerization is simple and rapid. Electropolymerized PPy films have been widely used in recent years as a means to modify electrode surfaces for potentiometric sensors and ion-selective electrodes [21–24].

A new class of cation permselective films overoxidized polypyrrole (OPPy) films can be made quite permeable, and have ionic conductivity, although the electrical conductivity of PPy is lost after overoxidation. It has been reported that, during overoxidation, polypyrrole loses its electroactivity due to ejection of dopant, and oxygen containing groups such as carbonyl and carboxylate are introduced to the pyrrole unit [25–27]. The high electron density of the carbonyl group acts as a barrier to hinder the diffusion of anions in the film. In our previous investigations the overoxidized sulfonatedpolypyrrole (OSPPy) films have been shown to have excellent cation permselectivity [28–30]. Overoxidation in the pyrrole ring lead to effective rejection of the anionic species and preferential collection of the cationic species.

Although much work has been performed on PPy based ion-selective electrode, limited information is available about the use of PPy as a potentiometric detector in ion chromatography. However, to the best of our knowledge this is the first time that the OPPy potentiometric detector in ion chromatography for monovalent and divalent cations has been reported. The polymer films were deposited electrochemically, directly onto platinum electrode. This makes this kind of a material very suitable for constructing miniaturized electrodes. The analysis conditions were optimized to obtain both efficient separations and sensitive potentiometric responses. The PPy electrode showed more stable and the OPPy electrode exhibited more reproducible response without any influence of interferents commonly existing in water samples.

2. Experimental

2.1. Chemicals and reagents

Pyrrole (Aldrich) was distilled repeatedly under vacuum until a colorless liquid was obtained, and kept under nitrogen in darkness at 4 °C prior to use. All the other chemicals used were of analytical reagent grade and used without further purification. Sodium salts of inorganic anions, hydrochloric acid, and lithium perchlorate were purchased from Aldrich. Nitrate salts of inorganic cations were obtained from Fluka. All solutions were prepared daily by appropriate dilution from stock solutions using ultra-pure deionized water (Sartorius).

2.2. Instrumentation

Chromatographic measurements were carried out using a Dionex DX100 ion chromatography with 25 μl sample loop and a cation-separation column (Dionex IonPac CS12) and an anion-separation column (Dionex IonPac AS9-SC). The IonPac CS12 column (4 mm × 250 mm) is a 8.0 μm poly(ethylvinylbenzene/divinylbenzene) macroporous substrate resin that is functionalized with a relatively weak carboxylic acid. The eluent used was 20 mM HCl for cation separations. IonPac AS9-SC column is a 13-μm microporous resin bead, consisting of ethylvinylbenzene cross-linked with 55% divinylbenzene. The anion exchange layer is functionalized with quarternery ammonium groups. The eluent used was a buffer solution of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ for anion separation. The eluents were filtered through a 0.45 μm syringe-type filter (Millipore) and then degassed for 15 min. Eluent pH was measured using the IONcheck45 model (Radiometer, France) pH-ion meter. The optimum flow-rate of the eluent was 1 mL min^{-1} for both cation and anion separations. The polypyrrole and overoxidized-polypyrrole electrodes were used as a potentiometric detector for anions and cations, respectively. The potentiometric response of the detectors was logged with a ChromaSimple software program (Dizge Analitik, Turkey) and AC converter to obtain a full chromatogram. The indicator electrode was Pt/PPy for anions and Pt/OPPy for cations. Ag/AgCl electrode was used as a reference electrode. The indicator and reference electrodes were coupled with ion-exchange chromatographic system for potentiometric detection of the ions.

The electrochemical instrumentation consisted of an Autolab PGSTAT-100 Potentiostat/Galvanostat with GPES software (EcoChemie, The Netherlands). Electrochemical measurements were carried out under nitrogen atmosphere in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl) and the counter electrode (Pt spiral). Prior to each electrochemical measurement, the indicator electrode (Pt wire ring electrode with 1 mm diameter, 99.99%, Aldrich) was polished with an aqueous suspension of 0.05 μm Gamma Alumina Powder (CH Instruments, Inc.), washed with deionizied water and acetone to eliminate the alumina after that dried.