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Rubber-based substrates modified with carbon nanotubes inks to build flexible electrochemical sensors

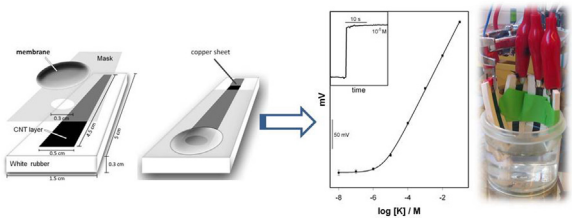
María Cuartero [a], Jonathan Sabaté del Río [b], Pascal Blondeau [b], Joaquín A. Ortuño [a], F. Xavier Rius [b], Francisco J. Andrade [b,*]

[a] Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, Murcia E-30100, Spain
[b] Department of Analytical and Organic Chemistry, Universitat Rovira i Virgil, Campus Sescelades, Marcel·lí Domingo s/n, Tarragona 43007, Spain

HIGHLIGHTS

- A new platform for electrochemical sensors based on carbon nanotubes and commodity substrates.
- Uses rubber as a flexible, low-cost and rugged substrate for the sensor.
- A full potentiometric cell incorporated in a daily object.
- Potassium monitoring in sweat.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of a solid-contact potentiometric sensor based on conducting rubbers using a carbon nanotubes ink is described here. Commercial rubbers are turned into conductive ones by a simple and versatile method, i.e. painting an aqueous dispersion of single-walled carbon nanotubes on the polymer surface. On this substrate, both the working ion-selective electrode and the reference electrode are built in order to form an integrated potentiometric cell. As a proof-of-principle, selective potassium electrodes are fully characterized giving comparable performances to conventional electrodes (sensitivity, selectivity, stability, linear range, limit of detection and reproducibility). As an application of the rubber-based electrodes, a bracelet was constructed to measure potassium levels in artificial sweat. Since rubbers are ubiquitous in our quotidian life, this approach offers great promise for the generation of chemical information through daily objects.

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1. Introduction

Collecting information remotely using chemical sensing networks (CSN) or body sensing networks (BSN) [1,2] is becoming increasingly important, since it may have significant impact in healthcare, environmental monitoring, sport performance, military applications, etc. Remote monitoring of physiological parameters is sought to be used in telehealth [3] to improve a patient's quality of life or to improve an athletés performance [4]. In order to deploy this CSN in an unobtrusive way, sensors must be embedded into conventional objects, such as wearable items or any other device (sport equipment, tools, packaging, buildings, etc.) to turn them into "smart objects". In short, remote data-streaming from the physical world [5] using highly pervasive network of embedded sensors is part of a major technological trend that is helping to reshape many social systems.

Traditional barriers for instrumentation and connectivity have been debunked through the progress in printable and bendable

* Corresponding author at: Universitat Rovira i Virgili, Analytical Chemistry, Marcel·li Domingo s/n, Campus Sescelades – Quimica Analitica, 43007 Tarragona, Tarragona, Spain. Tel.: +34 661267756; fax: +34 977 55 84 46.
E-mail address: franciscojavier.andrade@urv.cat (F.J. Andrade).

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electronics, which now allows that whole electronic components can be knitted into textiles or embedded into any type of materials [6,7]. The major challenge today is the development of suitable sensing platforms, a problem that has to face both, analytical and practical issues. From the analytical side, it is necessary to develop and optimize robust sensors, instrumental techniques and operational procedures. From the practical perspective, the challenge is to seamless embed the sensing platform into objects. Truly effective solutions that can be used beyond the lab walls must address both challenges simultaneously, in order to develop platforms that show adequate performance, low-cost, simplicity of operation and can be produced in mass scale. Without technology to produce large numbers of sensors at affordable cost, truly distributed CSN are hardly achievable. Platforms to monitor physical parameters are successfully achieving this goal [8].

Today, smart garments that can monitor heart rate, temperature, breathing patterns, body movements, etc., and a plethora of embedded sensors in sport equipment, packaging, smartphones, etc. are becoming available in the mass market [9–13]. Chemical sensors, however, are still lagging behind, although the situation is currently changing. Chemical sensors embedded into wearable devices have been developed by Diamond et al., who reported wearable patches to monitor pH [14] and other ions [15] using spectroscopic as well as electrochemical devices.

Electrochemical methods are ideally suited to build embedded systems because of their easy miniaturization and low power consumption. Wang et al. developed a smart watch to monitor blood glucose levels [16], and also screen printed electrodes in underwear [17] and on a neoprene suit [18] to build wearable amperometric sensors. More recently, temporary tattoo sensors that can be directly placed on the skin have been reported [19–21].

An approach that is becoming increasingly attractive to build sensors for CSN is the use of nanotechnology in combination with commodity substrates. Nanotechnology provides a way to build electrically conductive and chemically versatile surfaces, while the use of commodity materials reduces the cost and helps with the seamless integration of the sensor. Carbon nanotubes (CNT), for example, are well known for their outstanding electrical and chemical properties [22,23]. Suspensions of CNT in aqueous solutions using suitable surfactants (i.e. CNT inks) have been also used to transform commodity substrates, such as paper [24,25] or cotton [26], into electrical conductors with outstanding performance. Very recently, our group demonstrated that ion-selective potentiometric sensors could be produced using conventional filter paper [27] or cotton yarns [28] modified with carbon nanotubes and polymeric membranes. These sensors showed similar performance than the conventional lab-made counterparts. The approach is attractive because is extremely simple, so low-cost and robust sensors could be produced using mass manufacturing approaches (direct printing) and commodity substrates, opening the way to mass-scale production of sensors. Furthermore, solid-contact potentiometry is an instrumental approach that shows robustness and unbeatable simplicity of operation. Paper and cotton show good performance in many applications, but they are limited in terms of chemical and mechanical resistance. Thus, to fully exploit this approach, a range of materials that can be adapted to different circumstances could open new horizons and applications.

In this work, an approach to build ion-selective potentiometric sensors using conventional rubber as a substrate is presented. Rubbers are commodity materials widely used in the industry, with a huge range of applications in packaging seals, garments, machinery, buildings, etc. Therefore, finding ways to embed sensors in this material could unleash a huge potential to build sensing networks. The method presented here is based on the generation of a conductive surface on a commercial rubber using CNT. This substrate is then used to build ion-selective potentiometric sensors by drop casting a suitable polymeric membrane. The platform, demonstrated here by using a rubber-based potentiometric cell for sensing K^+, is extremely simple to build and to operate, and can produce sensors at low cost and at mass-scale. Analytical performance of the device and potential future applications are discussed.

2. Experimental

2.1. Chemicals and materials

Single-walled carbon nanotubes (SWCNTs) were purchased in bulk form from HeJi (Zengcheng, China) with >90% purity, 150 μm average length and 1.4–1.5 nm average diameter. Tetrahydrofuran (THF), sodium dodecylbenzensulfonate (SDBS), valinomycin (potassium ionophore I), bis(2-ethylhexyl) sebacate (DOS) with >97% purity, polyvinylbutyral (BUTVAR polymer B98) 10% weight in methanol, potassium tetrakis(4-chlorophenyl) borate (KTPB) with >98% purity and polyvinyl chloride high molecular weight (PVC), were purchased from Sigma–Aldrich.

Analytical grade chloride salts of potassium, sodium, lithium, ammonium, calcium and magnesium; sodium salts of acetate, bicarbonate, nitrate, sulphate and pyruvate; sodium hydroxide, glucose, urea and albumin were all also purchased from Sigma–Aldrich.

Commercial rubber, PVC film mask, copper sheets and a small paintbrush (1-Bowen paintbrush) were bought from local suppliers.

Concentrations of components of artificial sweat were 4×10^{-2} mol L^{-1} NaCl, $(2.48–2.68) \times 10^{-3}$ mol L^{-1} KCl, 5.4×10^{-5} mol L^{-1} $MgCl_2$, 6×10^{-3} mol L^{-1} urea and 2×10^{-2} mol L^{-1} lactic acid. The pH was adjusted to about 5 with NH_4OH.

Milli-Q water (18.2 MΩ s^{-1}) was used throughout.

2.2. Apparatus and electrodes

Potentiometric measurements were carried out at room temperature (22 ± 3 °C) in stirred solutions (500 rpm) using a high input impedance (10^{15} Ω) EMF 16 multichannel data acquisition device (Lawson Laboratorios, Inc. Malvern, USA). A double junction Ag/AgCl/KCl 3 M reference electrode (type 6.0726.100, Methrom AG) containing a 1 M LiAcO electrode bridge was used.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a potentiostat/galvanostat AutolabPGSTAT128N with a frequency response analyzer electrochemical impedance module (FRA2) (Autolab, Eco Chemie, B.V., Utrecht, the Netherlands). A three-electrode configuration was used in a cell containing an unstirred 10^{-2} mol L^{-1} KCl solution at room temperature. The target rubber-based electrodes were connected as the working electrodes. A Ag/AgCl single-junction electrode (model 6.0733.100, Metrohm) was used for reference, and a glassy carbon rod (3 mm Ø) was used as auxiliary electrode. The impedance spectra were recorded at open circuit using an excitation amplitude of 10 mV and a frequency range of 100 KHz–10 mHz.

Environmental scanning electron microscopy (ESEM) images were taken using a JSM-6400 scanning electron microscope (JEOL Ltd., Tokyo, Japan). The tested samples were coated with a thin layer of gold by using an argon sputtering (time = 2 min, pressure = 9×10^{-2} mbar and applied current 30 mA) in an EMITECH K575X Peltier cooled sputter coater (Quorum Technologies Ltd., Ashford, England). Raman spectra were recorded with an Invia Renishaw Raman microspectrometer (50 × objective) using a 514 nm laser line from an Ar laser.

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