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Potentiometric sensors using cotton yarns, carbon nanotubes and polymeric membranes†

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A simple and generalized approach to build electrochemical sensors for wearable devices is presented. Commercial cotton yarns are first turned into electrical conductors through a simple dyeing process using a carbon nanotube ink. These conductive yarns are then partially coated with a suitable polymeric membrane to build ion-selective electrodes. Potentiometric measurements using these yarn-potentiometric sensors are demonstrated. Examples of yarns that can sense pH, K^+ and NH_4^+ are presented. In all cases, these sensing yarns show limits of detection and linear ranges that are similar to those obtained with lab-made solid-state ion-selective electrodes. Through the immobilization of these sensors in a band-aid, it is shown that this approach could be easily implemented in a wearable device. Factors affecting the performance of the sensors and future potential applications are discussed.

Introduction

Embedding sensors into garments to build body sensing networks (BSN) that are seamlessly integrated into daily routines is becoming a major area of research.[1] BSN may allow remote monitoring of patients – a crucial need in telemedicine – checking the vital signs of military personnel in the field or following in real-time physical conditions of athletes, among many other applications. It has been shown, for example, that sweat composition is an indicator of an athlete's physical state.[2] The levels of chloride in sweat are the gold standard to detect cystic fibrosis.[3] Also, several studies have suggested a strong relationship between the pH of a wound and the process of healing.[4] In this and many other examples, sensors embedded into textiles to generate chemical information could be an invaluable tool. Conceptually, the idea of garments with enhanced functionality has been around for decades but there were many technological barriers limiting their actual implementation. However, with the recent progress in flexible electronics, many of those obstacles have been overcome.[5–7] Today, wearable electronic devices that are able to process and wirelessly transmit data are becoming more and more common and are quickly reaching the mass market.[8] The growth and consolidation of these platforms is increasingly demanding the incorporation of sensors, the ultimate link between the physical world and the global network of information.

Wearable devices for healthcare applications are quickly gaining terrain.[9] A smart shirt that can monitor vital signs[10] (heart rate, body temperature, *etc.*) has been recently proposed. Patches to monitor blood pressure and several physiological parameters have also been developed.[11] A plethora of composite materials with sensing capabilities[6,12] aimed at monitoring body position, stretching and movements promise a revolution in areas such as sports, medicine, rehabilitation, ergonomics, *etc.* Contrasting with this proliferation of approaches to sense "physical" parameters, significantly less progress has been achieved in the area of wearable chemical sensors.[13,14] Diamond *et al.* have partially described the inherently higher degree of complexity involved in the construction and operation of wearable chemical sensors as the "chemical sensor paradox".[13] As a matter of fact, the problem of building wearable devices to generate chemical information involves aspects related to the analytical performance as well as more practical issues such as usability and cost. In the first case, baseline drifts, changes in sensitivity and the specificity of the sensors have to be considered. Regarding the most practical aspects, it must be borne in mind that wearable devices are subject to mechanical stress and, due to the need to adapt to the end user's needs, they must be designed paying particular attention to the portability, safety and simplicity of operation. Last but not least, a truly vast network of sensors requires technologies that can be developed at the mass market level. All in all, the need to combine performance, portability, safety, simplicity and cost turns the task of making wearable chemical sensors into an extremely intricate problem. However, as the need to incorporate sensors into garments is growing steadily, the involvement of the

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