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Wireless smart tag with on-board conductometric chemical sensor

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ABSTRACT

A contactless smart card with integral wireless power and data link and on-board chemical sensor is described. The chemical sensor part of the smart card comprises a planar conductometric interface onto which a chemically or biologically sensitive thin film may be cast using microfabrication techniques. The thin film sensor and conductometric interface form an integral part of a radio-frequency smart card that has been designed for use in distributed chemical and biological detection systems, and which is based upon the International Standards Organisation high-frequency (HF) ISO 15693 radio-frequency identification (RFID) protocol. Conductometric measurements are controlled, sampled and stored by the smart card electronics. Measurement results achieved with an organic semiconductor, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT-PSS, as a model thin film conductometric sensor material cast on planar gold electrodes are reported. The standardisation of short-range wireless radio protocols such as Bluetooth, RuBee, ZigBee, WiFi and RFID is opening new markets for distributed sensors and sensor networks, and the fusion of chemical and biosensor technologies with short-range, low-cost, wireless technologies will create new opportunities for chemical and biological sensor systems in healthcare, environmental monitoring, process and quality control, and chemical and biological threat detection. The chemical sensor smart card described here could in future be suitable for use in various distributed short range wireless data applications and sensor networks as part of the emerging sensor Internet of Things.

1. Introduction

The integration of chemical and biosensor technologies with wireless devices has application in healthcare, personal care, environmental monitoring, process and quality control, and chemical and biological threat detection [1–6]. Contactless physical, chemical and biosensors based on the radio-frequency identification (RFID) protocol have been reported previously in the scientific literature. These include RFID sensors for the analysis of DNA [7], tracking the temperature of perishable foods [8], simultaneous detection of different vapour-phase analytes [9], gas detection in food products [10,11], surface wetness [12], light, temperature and humidity tracking of fresh fish through the food supply chain [13], pH measurement [14], and disinfection control in hospitals [15].

Other short-range wireless chemical and biological sensors that are not based on the RFID protocol have also been described in the literature, and this growing body of work demonstrates the awareness of the advantages of non-contact biosensing. Different short-range contactless technologies have included, for example, surface acoustic wave (SAW) sensors [16–19], magnetoelastic sensors [20–23], tuned inductor-capacitor (LC) sensors [24,25], and fuel cell based biosensors [26,27]. Such devices are generally low cost, and do not require batteries or in some cases even active electronic circuitry in order to function, which makes their deployment extremely attractive in certain chemical sensing applications. However, the majority of such non-contact sensing devices are not network compatible, and do not support anti-collision protocols—the ability of multiple devices to be interrogated simultaneously. Both these attributes require active electronics, and therefore, in order to support these functions, the additional overhead in electronic complexity and cost must be incurred. By comparison, RFID-based devices can be batteryless, otherwise known as *passive*, yet do contain active electronics and are thus network compatible, scalable, and the relevant international RFID standards support anti-collision protocols without being either overly complex or expensive to implement.

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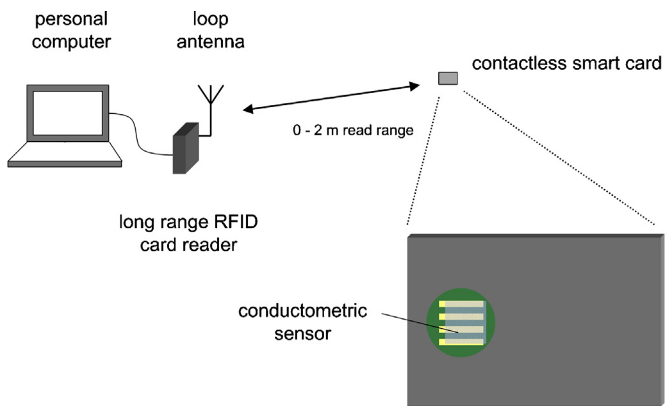

Fig. 1. Schematic diagram of the contactless conductometric smart card with a long range RFID card reader, and PC-based data acquisition system. The smart card is batteryless and is simultaneously powered and interrogated from the loop antenna of the card reader over distances of up to 40 cm.

Analytical devices based on the International Standards Organisation high-frequency (HF) ISO 15693 radio-frequency identification specification [28] are therefore currently in development in our laboratory with which to address this emerging need for non-contact chemical sensors with standardised machine-readable outputs.

The first optical absorbance-based pH chemical sensor to use this standard was reported by us [14], whereas more recently we have reported a classical potentiometric type pH tag [29], as well as a detailed evaluation of a potentiometric tag with solid contact ion selective electrodes (SC-ISEs) for water quality monitoring [30], and a microenvironment resistivity sensor [31].

In this present work, a prototype radio-frequency smart card has been developed that includes an on-board conductometric sensor (Fig. 1). Conductometric sensors are employed widely in different types of chemical sensors and biosensors, particularly in electronic noses, and therefore constitute an important class of transduction device. The conductometric interface on the smart card makes use of a constant current 4-point measurement method in order to accurately determine changes in sheet resistivity of a sensitive conducting polymer layer [32]. The conductometric sensor interface has been calibrated against a laboratory 4-point probe with measurement data made on thin films of the organic semiconducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT-PSS, cast on planar gold electrodes as a model conductometric system. PEDOT-PSS is an attractive material for organic conductometric and thin film transistor chemical sensors, and has been widely used in such devices because of its many favourable material and electronic properties [33]. The smart card described here might in future be suitable for adoption in different chemical and biosensor applications where mobile, wireless or non-contact networked conductometric transduction is required.

2. Materials & methods

2.1. Radio-frequency smart card

A prototype contactless (wireless) smart card based on the high-frequency (HF) ISO 15693 RFID vicinity card standard has been developed around an ultra-low power microcontroller (PIC12F683, Microchip Technology Inc., Chandler AZ, USA). The smart card has length and width dimensions of a standard credit card, measuring 80 mm × 50 mm (Fig. 2(I)). Electronic circuits for the card were designed using a schematic capture design and printed circuit board (PCB) layout suite (EASY-PC Professional v11.0, Number One Systems Ltd., Gloucester, UK), and printed circuit boards were fabricated from standard FR4 materials (RAK Printed Circuits Ltd., Saffron Walden, UK). Code for the PIC12F683 microprocessor was developed and programmed into flash-memory devices using an integrated software design environment and device programmer (MPLAB v8.0 with PICStart plus, Microchip Technology Inc., Chandler AZ, USA). Smart card circuit boards were populated with through-hole (leaded) components and dual-in-line packaged integrated circuits to simplify testing in the laboratory.

2.2. Model thin film conductometric interface

Planar electrode structures were designed using the printed circuit layout software, and four different electrode types were subsequently fabricated by an electroless gold plating process on standard FR4 printed circuit substrates (RAK Printed Circuits Ltd., Saffron Walden, UK). The electrode substrates were coated with a resist layer to leave only the active electrode areas exposed (Fig. 2(II)). Commercial PEDOT-PSS was obtained dispersed in an aqueous solution (1.3 wt% dispersion in H_2O, conductive grade, Sigma-Aldrich). A cocktail optimised for spin coating and containing the PEDOT-PSS dispersion was prepared by mixing ethylene glycol, ethanol, and dodecylbenzenesulfonic acid (DBSA) with the polymer solution, as described in detail elsewhere [34]. In brief, the cocktail contains 3.0 ml of PEDOT-PSS solution, 0.30 ml of ethylene glycol, 1.5 ml of ethanol and 15 mg of DBSA, homogenised for 10 min in an ultrasonic bath. This particular cocktail is suitable for preparation of thin films of PEDOT-PSS on FR4 substrates by spin coating, where the substrate is coated with a hydrophobic solder-resist layer. Substrates were first rinsed with ethanol and then with distilled water, and oven dried at 100 °C for 10 min before coating. Films were processed by dispensing 100 μL of the prepared cocktail and spinning at 1600 rpm for 30 s (KW-4A precision spin-coater, Chemat Technology Inc., Northridge CA, USA), followed by an oven bake at 115 °C for 20 min. Processed substrates were stored in the laboratory at room temperature and pressure in glass containers under ambient light conditions.

2.3. Measurement methods

The resistance of the PEDOT-PSS thin films was determined from the underlying gold planar electrodes by three alternative measurement methods in the laboratory; 2-point resistance measurements were made with a digital multimeter (IDM 19 Multimeter, IsoTech, France), current–voltage (*I*–*V*) curves were determined with a precision laboratory 4-point probe system (Yokogawa 7651 DC current source, and Agilent 34420A nanovoltmeter) and finally the resistance of the films was measured with the custom 4-point probe implemented in hardware and software on the contactless smart card, described in more detail below. The smart card was energised in the laboratory with a high-frequency 13.56 MHz long-range RFID reader (Ridel 5001, TAGnology GmbH, Graz, Austria) and digital measurement data captured on a digital storage oscilloscope (DSO6052A, Agilent Technologies Inc., Santa Clara CA, USA).

2.4. Smart card 4-point probe

The smart card scavenges energy from the 13.56 MHz RF vicinity field generated in the loop antenna of the long range RFID card reader (Fig. 1). The field induces an alternating voltage in the smart card antenna, and is rectified to produce a stable power supply for the on-card electronics (Fig. 3). Once activated by the vicinity field, the smart card enables its 4-point probe interface for a period of 40 ms, makes a measurement, processes the data, and transmits it in frames delimited with the appropriate start, stop and cyclic redundancy check (CRC) code required by the ISO 15693 protocol