Analytica Chimica Acta 687 (2011) 105–113

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Chemiresistors based on conducting polymers: A review on measurement techniques

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ARTICLE INFO

Article history:
Received 19 September 2010
Received in revised form
11 November 2010
Accepted 12 November 2010
Available online 19 November 2010

Keywords:
Chemiresistor
Chemotransistor
Conducting polymer
Chemosensor
Contact resistance
s24-Technique

ABSTRACT

This review covers the development of measurement configurations for chemiresistors based on conducting polymers. The simplest chemiresistors are based on application of a two-electrode technique. Artifacts caused by contact resistance can be overcome by application of a four-electrode technique. Simultaneous application of the two- and four-electrode measurement configurations provides an internal control of sensor integrity. An incorporation of two additional electrodes controlling the redox state of chemosensitive polymers and connecting to the measurement electrodes through liquid or (quasi)solid electrolyte results in a six-electrode technique; an electrically driven regeneration of such sensors allows one to perform fast and completely reversible measurements.

Ulrich Lange studied chemistry at the University of Regensburg from 2002–2007. His master thesis was focused on in-situ resistance measurements of thin conducting polymer films. The work was awarded with the Siemens VDO Award. His Ph.D. work which he did in the same university under the supervision of Prof. V.M. Mirsky and finished in 2010 was focused on new measurement techniques and new composite nanomaterials in chemiresistors and electrochemical transistors based sensors.

Vladimir M. Mirsky is a professor at Lausitz University of Applied Sciences, Germany. He graduated from Moscow Medical University in biophysics and went on to study physical chemistry and electrochemistry at the Frumkin Institute of Electrochemistry, obtaining his Ph.D. in 1986. He subsequently held an AvHumboldt Research Fellowship and a research position at CNRS prior to joining the Institute of Analytical Chemistry, Chemical Sensors and Biosensors at Regensburg University in 1995. After habilitation he became a professor of nanobiotechnology and moved to Lausitz. He is an editor of three books. His work has led to about 20 patents and patent applications as well as to about 120 peer-reviewed scientific papers.

1. Introduction

The most fascinating property of conducting polymers is their intrinsic conductivity and the ability to switch this conductivity over 10 orders of magnitude. The conductivity is not present in their neutral (uncharged) state, but results from the formation of charge carriers upon oxidizing (p-doping) or reducing (n-doping) their conjugated backbone. Such a formation of charge carriers is accompanied by changes in optical and electrical properties and by changes of the dopant (counterions) concentration in the polymer. These changes are used in chemo- and biosensors [1–5].

There are several reasons to apply conducting polymers in chemo- and biosensors. All of them possess an intrinsic affinity towards redox active species and many to acidic or basic gases and

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doi:10.1016/j.aca.2010.11.030

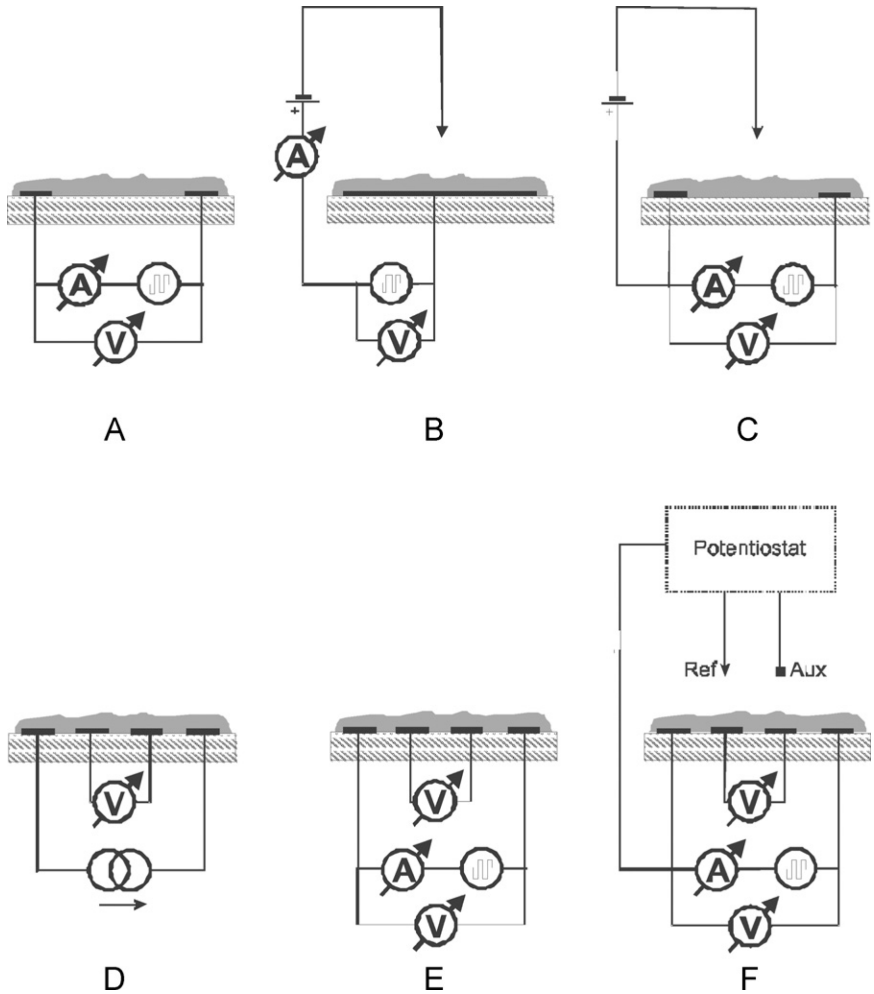

Fig. 1. Main configurations used for the analysis of the resistance of conducting polymers. (A) Two point configuration without fixation of polymer potential. (B) Typical configuration used in electrochemical experiments. (C) Two point configuration with fixation of polymer potential. (D) "Classical" four-point technique with a current source. (E) s24-configuration providing simultaneous two- and four-point measurements without fixation of polymer potential. (F) s24-configuration with fixation of the electrode potential.

solvent vapours. They can be modified with receptors to obtain a specific interaction with the analyte. Being immobilized on conducting polymers, such receptors provide an important advantage in comparison to monomer based receptors: the CP-wire provides a collective system response leading to high signal amplification in comparison to single molecular receptors [6]. Zhou and Swager demonstrated that a conjugated polymeric receptor for methylviologen shows a 65 times signal amplification in comparison to the monomer based receptor [7,8]. The amplification depends on the molecular weight.

The application of conducting polymers in chemo- and biosensors can be realized with a number of different transducing techniques, allowing one to choose the most appropriate one for a particular sensor design. A detailed discussion of these aspects is given in [1].

Conductometric transducing of the sensor response is probably the most common method in chemo- and biosensors based on conducting polymers. There are several advantages of this transducing technique in chemosensors based on conducting polymer (such devices are named chemiresistors). (i) Small perturbations anywhere along the polymer chain can alter the conductance of the whole chain. Therefore, this approach provides a higher sensitivity than other techniques based on the modification of integral volume properties of the polymer, as, for example, electrochemical or colorimetric techniques [9]. (ii) Conductometric sensors can be realized with a simple setup which nevertheless allows high precision measurements. (iii) Conductometric chemosensitive measurements can be realized even on nanowires of CP [10], therefore this technique is perfectly compatible with the actual trend for miniaturisation of analytical devices. (iv) Single chemiresistors can be easy combined into sensor arrays. (v) Using RFID technology, such sensors can also be adapted for non-contact measurements [11].

There are several devices for measuring the conductometric response of such sensors. The simplest and most often used is a chemiresistor (Fig. 1A, D and E). In the more common two point technique (Fig. 1A) the conducting polymer is deposited between two (typically interdigitated) electrodes separated by a narrow gap. The conductivity is measured by applying a constant current or voltage (dc or ac) between these electrodes and measuring the resulting voltage or current. The less used four-point measurement technique measures the conductance of the bulk polymer layer without the influence of the potential drop on the polymer–metal contacts (Fig. 1D). This technique was modified recently by combining the two- and four-point techniques for simultaneous measurements (Fig. 1E) [12,13] and was named as s24. Another possibility is the use of organic field effect transistors as sensors [4,14,15]. Here the current between the source and drain electrodes is controlled by the gate voltage. However these devices are out of the scope of this review. Based on the similarity