Textile Chemiresistors for Gas Detection – New Materials of Sensitive Layers

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***Abstract*—The contribution presents novel research of textile chemiresistors prepared on textile substrates (Evolon and Polyester) equipped with graphite electrodes and sensitive layers based on polymer ionic liquid. The polymer ionic liquid, i.e. poly(tributylhexylphosphonium 3-sulfopropylacrylate) was in-situ polymerized on the textile substrates. The responses of such sensors to toxic gases (10 ppm of methanol, nitrogen dioxide, 4-bromoacetophenone and diethylmalonate) were then investigated in dc-mode of measurement – the reference was "pure" synthetic air. It was shown that sensor dynamics depends mainly on molecular weight of the analytes.**

Keywords-chemiresistor; textile substrate; polymer ionic liquids; detection of toxic gases.

I. INTRODUCTION

Application of functional elements and nanostructures on flexible substrates is a promising trend in electronics. Also for fabrication of chemiresistors, there are intensively studied substrates, such as plastic foil, paper and fabric; they seem to be a suitable alternative for conventional "hard" alumina substrates equipped with metal electrodes. Textiles are materials with great potential, whose mechanical properties (high strength, large surface area, lightness, flexibility, effortless integration into clothing) make it unique even in comparison with other flexible substrates [1]. There are several ways to add new functionalities to textiles when used in sensor applications. The textile substrate can be covered with gas sensitive layer by "wet" and "vacuum" coating techniques, e.g., ink-jet printing or magnetron sputtering technology. A common feature of textile sensors is that they operate at either laboratory or at a slightly higher temperature. Therefore, organic conductors are preferred to be their sensitive layers.

Polymerized ionic liquids (PILs) have been reported for the first time in 1998, and a brief overview of their properties can be found, e.g. in [2]. Their electrotransport properties are unique (when compared with other organic substances), as they are purely ionic conductors. Moreover, majority of them can be considered as single-ion conductors. PILs are characterized by large capacity to absorb analytes with small molecules – especially CO_2 and water. After such absorption, the internal volume of polymer is modified, hence the mobility of ions changes. Such a phenomenon could work as a prospective transducer mechanism in chemiresistors. This property of PILs is very valuable, because namely CO_2 and numerous other analytes (whose molecule has neither redox properties, nor dipole moments) cannot be detected on chemiresistors by any other mechanism.

II. EXPERIMENTAL

This contribution details the development of a gas sensing chemiresistor using a non-conductive textile (dimensions 10 x 15 mm) as the substrate. The architecture of the sensor can be seen in Figure 1. Two kinds of textiles of different composition and method of production were used: Evolon - non-woven textile (70% polyester/30% polyamide) and Polyester. These textiles were first continuously cleaned in methanol using Soxhlet extraction (10 cycles) then washed with deionized water and finally dried at room temperature. In order to improve the mechanical flexibility of the sensor, the thermal adhesive film (Sealon Co., Ltd.) was laminated on the back side of the textile. The film was applied via a Heated Roll Laminator (model Titan-110) under the following conditions: adhesive bonding temperature of 80°C for 10 s, at a pressure between 70-140 kPa.

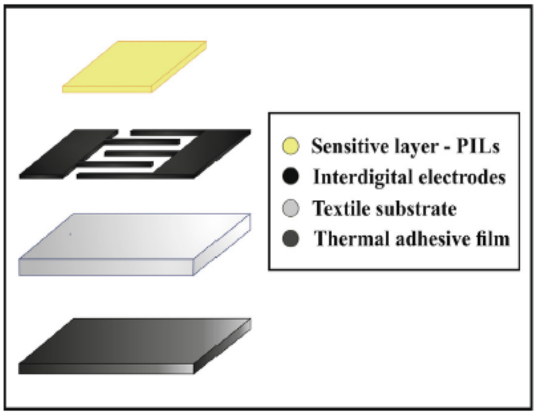

Figure 1. Vertical architecture of the textile-based sensor (left) and its real appearance indicating variable distances between electrodes (right).

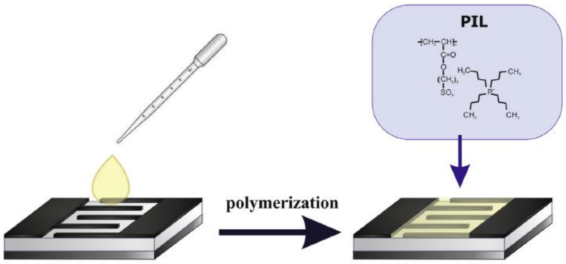

Figure 2. The deposition of sensitive layer on textile substrate.

The gas sensitive layer is composed of the following polymer ionic liquid: poly(tributylhexylphosphonium 3-sulfopropylacrylate) abbreviated as $P_{4,4,4,6}SPA$.

In the next step, the polymerization mixture was prepared, having the following composition: $P_{4,4,4,6}SPA$ monomer, photoinitiator (phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide) and crosslinker (trimethylolpropane ethoxylate triacrylate) dissolved in the solvent mixture (deionized water with acetonitrile). This mixture was photo-polymerized directly onto the surface of the textile substrate. Firstly, the mixture was drop-cast onto the surface of the textile using a micropipette and subsequently it was polymerized using a LMI-6000 Fiber-Lite white light source (~200 kLux) for 30 min to create compact sensitive film on textile substrate. The process is schematically depicted in Figure 2.

The dc-responses of the prepared sensors were evaluated according to (1):

$$S_{\mathrm{dc}} = R_{\mathrm{air}} / R_{\mathrm{gas}}. \tag{1}$$

The symbol S_{dc} denotes dc-response, R_{air} steady-state resistance value of the sensor in synthetic air and R_{gas} steady-state resistance value of the sensor in detected analyte.

III. RESULTS AND CONCLUSIONS

Just a few examples: As for dependence of sensor response on concentration of the analyte, an example is given on Figure 3, which illustrates detection of methanol (MeOH) on sensor based on $P_{4,4,4,6}$SPA. The grey areas correspond to reference atmosphere – synthetic air, the white areas to synthetic air with MeOH vapor. What is apparent: (i) the sensor baseline (R_{air}) slightly drifts to lower values; (ii) an average value of S_{dc} achieves 1.05 for 100 ppb, 1.25 for 1 ppm, 1.29 for 10 ppm and 1.39 for 100 ppm of MeOH, respectively; (iii) the sensor output signal exhibits a very low level of noise, hence as low concentration as 100 ppb of MeOH is above the detection limit.

Figure 4 presents dynamic response of $P_{4,4,4,6}$SPA sensor to 10 ppm of yperite. The meaning of grey/white areas is the same as in the previous figure.

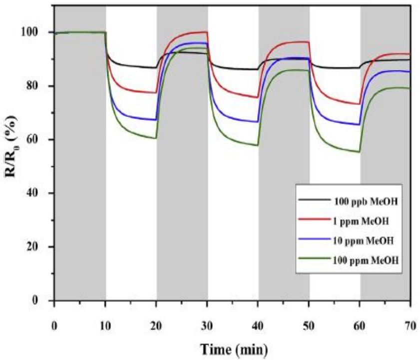

Figure 3. Response of sensor with $P_{4,4,4,6}$SPA to

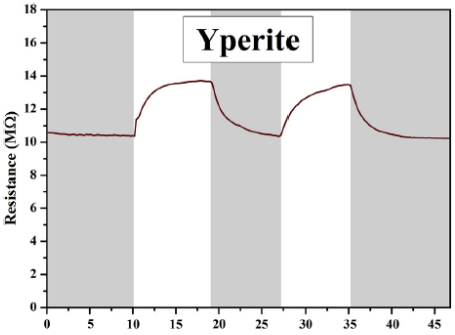

Figure 4. Response of sensor with $P_{4,4,4,6}$SPA to 10 ppm of yperite.

As for response dynamics: It is apparent that both the response- and recovery- time is approximately 5 min when detecting yperite and the response dynamics for yperite is (in general) slower than that for MeOH.

The only chemiresistor based on PILs was reported in [3]. It has $R_{\mathrm{air}} \approx 1.7$ GΩ, i.e. 2-3 orders higher than our samples. Such high baseline brings troubles in practical operation.

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