Array of Chemosensitive Resistors with Composites of Gas Chromatography (GC) Materials and Carbon Black for Detection and Recognition of VOCs: An Optimization Study

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***Abstract*—In our previous work, we developed the concept and tested the viability of fabricating a 16-element chemosensitive resistor array for detection and recognition of volatile organic compounds. The sensing elements were fabricated using blends of Carbon Black (CB) and Gas Chromatography (GC) stationary-phase materials by coating over chemosensitive resistor devices. In this work, we extend our basic study with an ongoing attempt at optimizing the performance of our developed 16-element array versus vapors of pyrrole, benzenal, nonanal, and 2-phenethylamine. Our main concern here was studying the percolation threshold and aging of the sensing devices. The results indicate that the best performance of the fabricated sensing devices can be expected for sensing films with CB to GC-material ratio of 1.5:1 to 2:1. Sensing devices coated with blends of such composition performed in a relatively similar manner right after fabrication and after around 5-month long aging at room temperature.**

Keywords- odor sensor; chemical sensor; artificial olfaction; chemoresistance; sensor array; GC material; carbon black.

I. INTRODUCTION

Biological olfaction can be regarded as a powerful tool, acquiring and analyzing airborne chemical information [1]. The sense of smell has been widely applied in numerous fields for either expert or non-expert evaluations, using techniques of sensory analysis [2]. In certain cases, the sensory analysis has been supported by instrumental analytical methods such as spectroscopy or chromatography [3]. However, the use of both sensory and instrumental analyses is seriously limited by their cost, time and lack of mobility. A still relatively novel field of instrumental analysis called artificial olfaction has emerged as a promising and attractive alternative to the above analytical techniques [4][5].

The biological sense of smell can be generally represented as consisting of two general stages: (i) receptive - olfactory receptors, and (ii) processing - olfactory bulb and the subsequent stages of olfactory cortex. Mimicking that general configuration, the electronic noses consist of a sensing stage (chemical, gas/vapor sensors) and a signal preprocessing/processing stage (various pattern recognition and classification techniques).

The gas/vapor sensors used in the artificial olfaction applications need to be non-specific, i.e., respond to groups of odorants rather than a particular one. Responses of such non-specific sensors' arrays are then processed using various pattern recognition techniques – from quite simple principal component or linear discriminant analyses to neural networks [6]-[10].

Electronic nose systems and their components are intensively studied with a number of successful attempts at their application ranging from food and beverage industries to environmental monitoring to medical diagnostics [11]-[17].

The chemical sensors used in the electronic nose systems can be classified in the following manner: Metal Oxide Semiconductor (MOS), Metal Oxide Semiconductor Field-Effect Transistor (MOSFET), calorimetric, optical, Quartz Crystal Microbalance (QCM), Surface Acoustic Wave (SAW), conducting polymer, and carbon material composites (carbon nanotubes or carbon black particles) [14][18]-[20].

The carbon material composites sensors, often called volumetric sensors, have a number of features that make them great candidates for the artificial olfaction applications. Among them, one can list a relatively simple structure, ease of fabrication and customization, as well as potential miniaturization that seems perfect for creation of large sensor arrays [21]-[24]. Such sensors are typically composed of two electrodes and an analyte-interactive film capable of changing its volume upon sorption of analytes. The film has to be electrically conductive, which is usually realized by application of either intrinsically conductive materials or composites/blends of conductive particles (e.g., carbon black or zinc oxide) with sorptive, insulating materials [25]-[28]

In our previous work, we presented our basic study on selection and application of GC stationary phase materials as the sorptive (non-conductive) part in odor-sensing

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composites used in chemosensitive resistor-based odor sensors [29]. An important issue concerning performance of the chemosensitive resistors is a relation between the carbon black content in carbon black–organic polymer composites and resistivity of such composite described by percolation theory [27]. Briefly, the composite is effectively an insulator at low carbon black content. Increasing the amount of carbon black results in decreasing resistivity of the composite, which is gradual until a sharp transition occurs in which the resistivity of the composite can fall dramatically (by up to 10 orders of magnitude) with a small variation in the carbon black concentration. At this transition point, designated as the percolation threshold, a connected pathway of carbon black particles is formed.

In the present work, we focused on two topics important from the standpoint of the ongoing optimization of the composites of GC-material with carbon black particles, namely: (i) evaluation of aging of the fabricated sensitive devices, and (ii) evaluation of the percolation threshold conditions for 16 composite materials described in our basic study.

II. MATERIALS AND METHODS

The chemosensitive resistors used in this work were 16-channel microdevices fabricated on a p-type Si monocrystalline substrates (8 × 8 mm2). Two platinum electrodes were formed as concentric circles using a photo lithography process. The distance between the electrodes was 50 µm to 280 µm. Schematic representation of the 16-channel device is shown in Figure 1. All devices were fabricated by Panasonic.

The carbon black particles were mixed with the GC materials dissolved in DMSO (Dimethylsulfoxide) or DMSO/MeCN. Concentration of the GC materials in each composite was 10 mg/mL. Concentration of carbon black was 5, 10, 15, 20, 30 and 40 mg/mL.

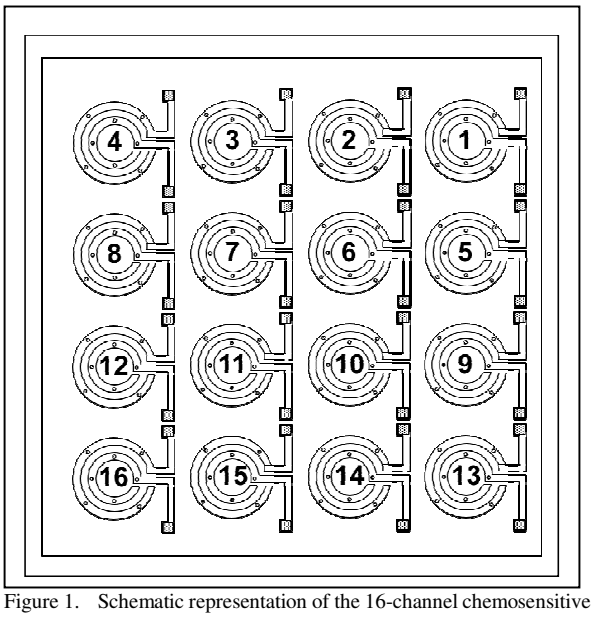

Figure 1. Schematic representation of the 16-channel chemosensitive resistor device used in this study. The numbers refer to Table I.

The GC materials used in this study are listed in Table I. Materials 1, 3 and 11 were obtained from GL Sciences Japan. Materials 2 and 10 were obtained from Tokyo Kasei. Materials 4, 5 7, 8, 9, 12 and 16 were purchased from Sigma Aldrich. Lastly, materials 6, 13, 14 and 15 were obtained from Shimadzu. All materials were used as obtained. Conductive carbon black particles (graphite carbon black) were obtained from Sigma-Aldrich.

The composites were coated as a circle mark using a customized automatic spotting machine with a microsyringe. The volume of the ejected solvents was 25 nL. The ejections were carried out 4 times for each mark. The diameter of a spotted mark was 950 µm while the thickness of the deposited film was typically 700–800 nm.

The fabricated sensors were evaluated in exposure experiments using nonanal, benzaldehyde, 2-phenethylamine, and pyrrole. The samples were purchased from Tokyo Kasei Co. and Sigma-Aldrich and were used as obtained.

The exposure experiments consisted of 60 s exposure to carrier gas, followed by alternating 60 s exposures to analyte vapor and carrier gas (recovery phase). Each sensor was exposed thrice to analytes presented at 4 concentration levels (i.e., total of 12 exposures = 4 concentration levels × 3 exposures at each level).

TABLE I. GC MATERIALS USED IN THE STUDY

Spot number	GC material	Abbreviation
1	Tetrahydrohyethylenediamine	THEED
2	N,N-Bis(2-cyanoethyl)formamide	BCEF
3	LAC-3-R-728 (12% DEGS)	LAC-3
4	Diethylene Glycol Succinate	DEGS
5	Poly(ethylene succinate)	PES
6	UCON 75-H-90000	UCON
7	1,2,3-Tris(2-cyanoethoxy)propane	TCEP
8	SP-2330	SP-3
9	SP-2340	SP-4
10	Diglycerol	DI
11	Reoplex 400	Re-400
12	Poly[di(ethylene glycol)adipate]	PDEGA
13	Poly(ethylene glycol) 4000	PEG4k
14	Poly(ethylene glycol) 20000	PEG20k
15	Poly(ethylene glycol) 20M	PEG20M
16	Free Fatty Acid Phase	FFAP

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III. RESULTS AND DISCUSSION

The chemosensitive resistor sensors were initially evaluated in the exposure experiments carried out within 48h after fabrication. Prior to the evaluation, each fabricated sensing device was first conditioned in the atmosphere of dry nitrogen for 24h. After that, each device was exposed to the odorant samples.

A. *Aging Effect*

Evaluation of the aging effect was carried out on the basis of the exposure experiments using pyrrole in dry nitrogen, right after fabrication and after 5-month aging. Two characteristics of each sensing element were compared: S/N ratios and responses at 1.8 ppm. The Signal level (S) was calculated as a response to pyrrole at 1 ppm while the Noise level (N) was the response recorded for the carrier gas only. The results are shown in Figure 2.

As can be seen, responses of nearly all sensing elements decreased to some extent after 5-month aging period (exception being the PEG4k composite at channel 13). Interestingly, however, evolution of the S/N ratio values formed quite a different pattern, with a number of materials exhibiting higher values after aging – most apparent in case of UCON, PEG and FFAP materials (channels 6, 13, 14, 15 and 16, respectively).

This ostensible discrepancy is associated with a large decrease of the noise level for those sensing elements and indicates enhanced stability of the coated composite materials after aging. Obviously, such a development would be of a great benefit for the potential application of the studied sensing devices, although further work is required to accurately model the actual evolution of the evaluated characteristics.

B. *Percolation Threshold*

Evaluation of the percolation threshold was carried out using the sensing devices with the composites composed of GC materials at a constant 10 mg/mL concentration and varying content of the carbon black particles. According to theory, increasing the content of the conducting constituent (carbon black) should result in decreasing resistivity – initially gradual, and very sharp when the percolation threshold is reached. Figure 3 shows the results of the resistance measurements for each sensing composite material with varying content of the carbon black particles. With the exception of PES, all the composites exhibited a dramatic increase of resistivity for the carbon black concentrations in the range of 15-20 mg/mL. Again, theoretically, that dramatic increase indicates formation of the connected pathway of carbon black within the GC material matrix.

In order to validate that claim we measured responses of the sensing devices with carbon black content within 5-20 mg/mL concentration range to odorant samples at ca. 1.8 ppm. The results of those experiments are shown in Figure 4. As can be seen, the highest magnitude of responses was recorded for the composite with the carbon black concentration of 15 mg/mL. That content level has been tentatively assumed as optimal and is being verified in the ongoing experiments.

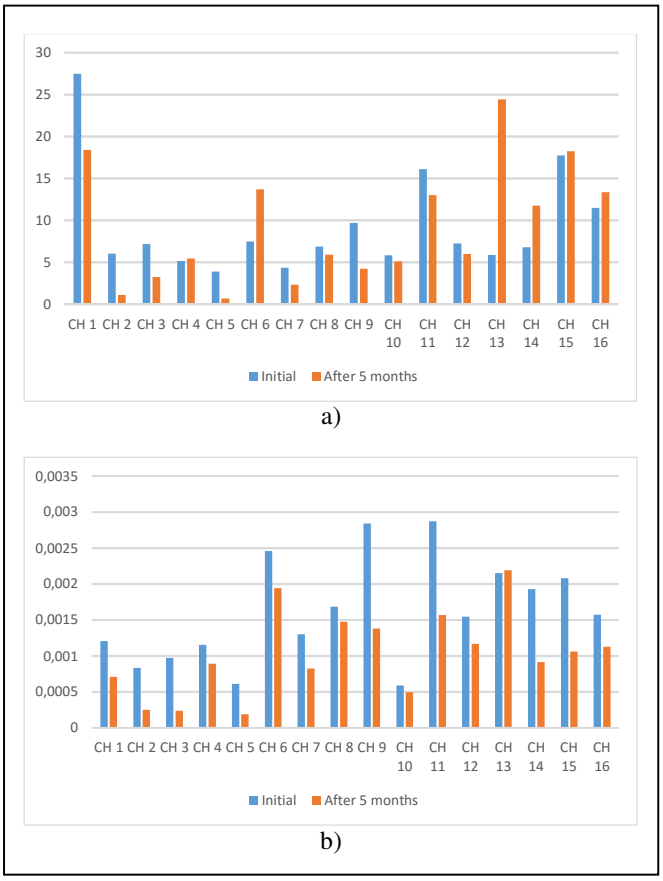

Figure 2. Sensing elements characteristics measured right after fabrication ("initial") and after 5 months of aging at room temperature: (a) S/N Ratio, (b) responses to Pyrrole at ca. 1.8 ppm.

IV. CONCLUSION

The present work describes our ongoing study aiming at optimization of the 16-channel chemosensitive resistor devices with composites of GC materials and carbon black particles toward sensing of odorant vapors. We focused on two important factors pertaining to optimization – the percolation threshold and aging. The results obtained so far indicate that in case of composite materials selected in our work, the percolation threshold can be expected for the ratios of carbon black to GC material within the 1.5:1 to 2:1 range. The initial validation of those values by means of exposure to the odorant samples indicated that the best sensing characteristics can be expected for the ratio of ca. 1.5:1. The results of the exposure experiments performed within 48h and 5 months after fabrication of the sensing devices indicate that the aging effect can be of two-fold nature – the decrease of the sensor response magnitude accompanied by a slight to significant enhancement of the S/N ratio, most likely associated with the enhanced stability of the composites. The studies are being continued and their results will be presented in the future.

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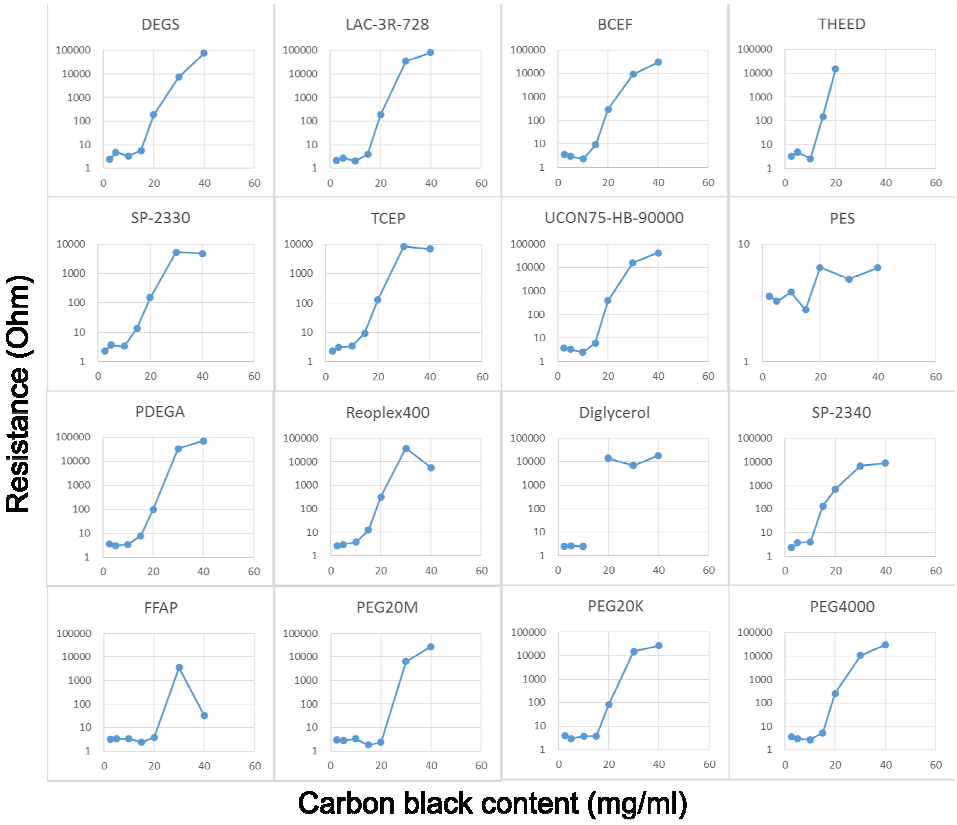

Figure 3. Resistance of the 16 composite materials versus their carbon black content. Evaluation of percolation threshold.

Figure 4. Responses of the sensing elements with various carbon black contents to odorant samples at ca. 1.8 ppm (carrier gas: dry nitrogen).

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