Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 125 (2007) 396–407
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Modeling carbon black/polymer composite sensors

Hua Lei [a], William G. Pitt [a,*], Lucas K. McGrath [b], Clifford K. Ho [b]

[a] *Department of Chemical Engineering, Brigham Young University, 350 Clyde Building, Provo, UT 84602, USA*
[b] *Sandia National Laboratories, Albuquerque, NM 87185, USA*

Received 30 November 2006; received in revised form 16 February 2007; accepted 19 February 2007
Available online 2 March 2007

Abstract

Conductive polymer composite sensors have shown great potential in identifying gaseous analytes. To more thoroughly understand the physical and chemical mechanisms of this type of sensor, a mathematical model was developed by combining two sub-models: a conductivity model and a thermodynamic model, which gives a relationship between the vapor concentration of analyte(s) and the change of the sensor signals. In this work, 64 chemiresistors representing eight different carbon concentrations (8–60 vol% carbon) were constructed by depositing thin films of a carbon black/polyisobutylene composite onto concentric spiral platinum electrodes on a silicon chip. The responses of the sensors were measured in dry air and at various vapor pressures of toluene and trichloroethylene. Three parameters in the conductivity model were determined by fitting the experimental data. It was shown that by applying this model, the sensor responses can be adequately predicted for given vapor pressures; furthermore, the analyte vapor concentrations can be estimated based on the sensor responses. This model will guide the improvement of the design and fabrication of conductive polymer composite sensors for detecting and identifying mixtures of organic vapors.

Keywords: Chemiresistor; Sensor array; Carbon black–polymer composite; Model; General effective media equation

1. Introduction

Chemical sensor arrays have been studied extensively for application in an "electronic nose" which simulates the mammalian olfactory system. Unlike the traditional chemical sensors that use a "lock-and-key" approach, wherein a specific receptor is synthesized to bind an analyte strongly and selectively, an array of chemical sensors, with each sensor chosen to respond differently to given analytes, allows a detector to respond to and distinguish a large number of analytes [1]. In such a system, identification of an analyte cannot be accomplished from the response of a single chemical sensor; but a distinct pattern of responses in the array of sensors can provide a fingerprint from which the analyte can be classified and identified. Once the sensor array is calibrated, it can provide both quantitative and qualitative information regarding the composition of a mixture.

Conductive polymer composite sensor arrays made from carbon black dispersed in various insulating polymers have been explored actively by Lewis and co-workers [1–3], Ho et al. [4–6] and others [7–12]. Since the response of this type of device is the change of resistance of the sensor, it is called a "chemiresistor". Upon exposure to an analyte, the analyte diffuses into the polymer composite and the polymer swells, which causes the dispersed conductive carbon particles to move further apart from each other. As the result, the resistance of the sensor increases. The diversity of the responses of sensors is achieved by selecting polymers with various thermodynamic properties. For example, poly(*N*-vinyl-pyrrolidone) is hydrophilic, so it swells substantially (and increases the sensor resistance) in water vapor, but not in toluene vapor; whereas polyisobutylene is hydrophobic, so it swells (and increases the sensor resistance) in toluene vapor, but not water vapor. Given the various responses of a sensor array to various analyte vapors, samples can be classified, identified and quantified by using statistical methods, such as linear discriminate analysis (LDA), principle component analysis (PCA), partial least squares (PLS), neural networks, and more [13].

The response mechanism of the individual carbon black/polymer composite sensors is qualitatively explained by percolation theory, which describes the relationship between the resistivity of the composite and carbon black content [1,3,14,15]. When the concentration of carbon black is very high, the carbon black particles pack very close in the composite and form

* Corresponding author. Tel.: +1 801 422 2589; fax: +1 801 422 0151.
E-mail address: pitt@byu.edu (W.G. Pitt).

0925-4005/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2007.02.041

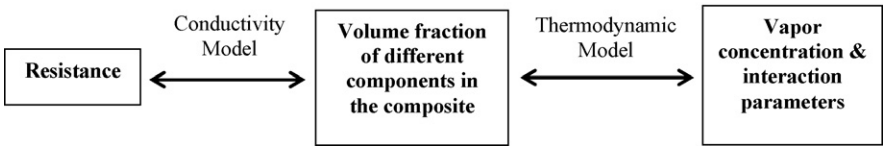

Fig. 1. Modeling the chemiresistor by combining the conductivity model and the thermodynamic model.

conductive pathways, which imparts a low resistance response of the sensor. As the concentration of carbon black decreases (e.g., in a swollen polymer), the distances between carbon black particles increase, and the resistance of the composite increases gradually. When the concentration of carbon black decreases to a point at which the conductive pathways are disrupted, the resistance of the composite increases sharply (by many orders of magnitude). This point is called the percolation threshold. In carbon black/polymer composite sensors, the carbon black concentration is usually only slightly higher than the percolation threshold. Therefore, a small amount of swelling may cause a dramatic change in the sensor resistance. Lewis and coworkers demonstrated the correlation of their sensor responses with percolation theory [3]. However, percolation theory cannot describe the complete sensor performance. The relationships among composite resistance, resistivity, carbon black concentration, polymer swelling, and vapor concentration are not well known. Thus, it is difficult to design sensors and to optimize polymer selection for an anticipated sample or set of samples.

In our previous work, we proposed that an individual carbon black/polymer composite sensor can be modeled by combining two sub-models: a conductivity model and a thermodynamic model [16]. The conductivity model was well described; the geometry of the sensor was modeled and analyzed. In this work, we combine that previous conductivity model with a thermodynamic model and demonstrate that the responses of sensor arrays can be estimated from the analyte vapor pressures; conversely, and more importantly, the vapor pressure of analytes can be predicted from the resistance of sensors in the array. In the conductivity model, three key parameters of the polyisobutylene (PIB)–carbon black composite model were optimized by fitting the experimental data. These same model parameters were then used to successfully estimate the responses of chemiresistors in various vapor pressures of trichloroethylene (TCE). Finally, we discuss how to improve the fabrication of this type of sensor.

2. Theory

To date, little work has been done to model the carbon black/polymer composite sensor theoretically. Two sub-models are used to describe such sensors: a conductivity model and a thermodynamic model (Fig. 1).

The conductivity model establishes the relationship between the concentration of carbon black in the composite and the resistance of the composite in the sensor. The thermodynamic model relates the sum of volume fractions of the polymer and analytes in the composite to the vapor pressure of analytes. By combining these two models, we can estimate the vapor pressure (and thus the concentration) of analytes based on the change of resistance of sensors in the array, or predict responses (resistance) of sensors as a function of the vapor pressures or concentrations of analytes.

2.1. Conductivity model

In the conductivity model, the resistance of the composite is related to the sum of volume fraction of polymer and analytes by two steps as shown in Fig. 2. The resistivity was calculated from experimental measurements of resistance by modeling the circuit and applying the definition of resistivity. The general effective media (GEM) equation further related the resistivity to the volume fraction of the high resistivity phase.

In the first step, the responses (the change of the sensor resistance) must be converted to resistivity. This can be done by using the definition of resistivity, as shown in Eq. (1):

$$\rho = \frac{RA}{L} \tag{1}$$

where R is the resistance, A the cross-section of the material perpendicular to the current flow, and L is the length between source electrodes. Eq. (1) shows that resistivity of the composite can be obtained if the geometry of the composite and electrodes are available.

In this research, actual chemiresistors made at Sandia National Laboratories were used. In these chemiresistors, both electrodes are adjacent two-turn spirals (Fig. 3A). This design makes it complicated to define the cross-section A in Eq. (1). A symmetrical model was made by simplifying the adjacent spiral electrodes into a model of two adjacent straightened electrodes (Fig. 3B–D). We previously showed, using finite element software, that the estimated error generated by this simplification

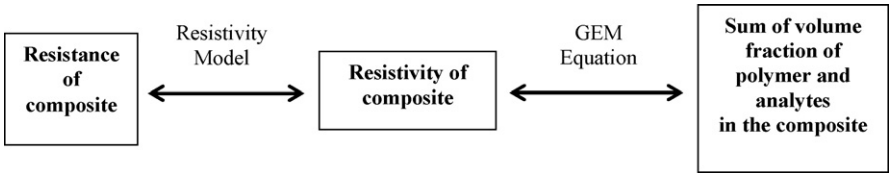

Fig. 2. The conductivity model.