Phenomena Based Dynamic Model of Carbon Black-Polymer Composite Sensors

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Abstract

A novel physically based mathematical model of carbon black-polymer sensor-analyte uptake and response is proposed. The advantage of this modelling approach is that the environmental dependencies of sensor responses may be investigated. It also permits the chemical kinetics of the sensors to be separated from the physical aspects of the sensors. Data were collected under varying ambient environmental conditions. Three different polymers were tested. A total of 336 such experiments were performed over a 2-week period. The model was validated with respect to these data, and was fitted to two vapour responses in parallel, showing its applicability to 'real world systems'. Evident temperature dependence of the parameters were judged to be most important outcome of this study.

Keywords

Dynamic modelling, Sensor Modelling, Parameter Estimation, Environmental Conditions

INTRODUCTION

It is evident that, for many applications, the dynamic responses of chemoresistor sensors hold a great deal of information. Previously, researchers have attempted to harvest this information using black box modelling, or shape analysis, by convolution with standard functions such as exponentials [1]. However, these are data-driven techniques and the resulting models provide little or no interpretation as far as the internal processes of the sensor are concerned. It would be beneficial for practical applications to separate out the physical aspects of the sensor response from the chemical aspects. This would help to enable pattern recognition algorithms to correct for changes in sensor response due to environmental and other interferences. It is apparent that a greater understanding of such effects would help us to design more robust electronic nose systems.

Composite polymer sensors take advantage of the change of polymer chain confirmation when a polymer dissolves into a solvent [2]. The polymer is blended with fine carbon nanospheres, which make the composite an electrical conductor if the carbon content is above a threshold value ρ_c. During absorption the distances between nanospheres is modified and so a change in resistance is observed. These sensors undergo three interesting effects: diffusion of the solvent through the polymer, polymer chain conformation

changes and the resulting conductivity changes. It is evident that such sensors are greatly affected by temperature and humidity.

THE MODEL

The mathematical model developed predicts the current (at a constant voltage) flowing through a sensor as a function of time. The sensor response breaks down into two stages: solvent uptake and the resulting conductivity change. The model is reduced to one dimension because it is assumed that the concentration of the solvent is constant across the surface of the sensor and the electric field (see Section on Conduction) is constant in the direction parallel to the sensor electrodes at its bisection point. These assumptions greatly simplify the electro-magnetic calculations.

The model described below will assume the following:

Assumption I The composite material is homogeneous. This means that diffusion will progress in the same manner throughout the polymer.

Assumption II The carbon content is above the threshold volume. The content is assumed initially to be sufficiently high so that the absorption effect never takes it below ρ_c, the threshold value.

Assumption III Only one chemical species is present in the solvent.

Evidence, including a sharp diffusion front followed by a constant concentration [3], suggests that diffusion is not fully driven by the concentration gradient, it is more likely that there is a concentration dependent diffusion rate.

The boundary problem is thus specified:

$$\frac{\partial c}{\partial t} = D(c)\frac{\partial^2 c}{dx^2}, \qquad (1)$$

where

$$D(c) = \begin{cases} 0 & \text{if } c(x,t) < C_X, \\ D & \text{if } c(x,t) \geq C_X. \end{cases} \qquad (2)$$

where a C_X is the diffusion rate threshold value, below which no diffusion occurs. This model implicitly requires a sharp diffusion front for its solution.

The boundary conditions are set as

$$
\begin{aligned}
c(X_1, t) &= c_0 Q \qquad (3)\\
c(-y_0, t) &= 0 \\
c(X_p, t) &= C_X.
\end{aligned}
$$

where c_0 is the atmospheric concentration of the solvent vapour and Q is the partition coefficient. Here X_p repre-

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Figure 1. Plot of steady state solution to finite media problem. Here $c_0Q = 1$, $C_X = 0.5$, $\alpha = 0.1$ **and** $\beta = -0.1$. **The axes are nondimensional as the simulation is performed for random parameter values.**
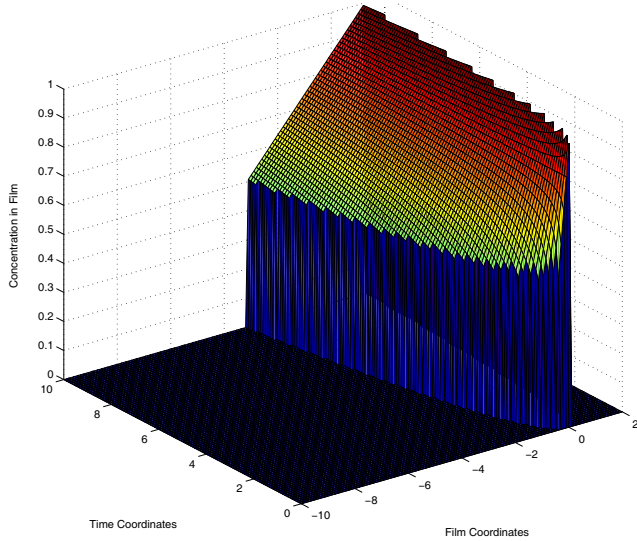
sents the position of the diffusion front within the polymer, X_1 represents the position of the sensor surface, which will expand due to the swelling effect. This form of diffusion is well studied and a comprehensive review may be found in [4].

Steady state solutions in the swollen polymer

A simplification that proves beneficial when calculating the current between the electrodes of the sensor (discussed in Section on conduction) is that of the assumption of quasi-steady state in the swollen region of the polymer.

Taking the initial and boundary conditions (3) as before, an approximate solution in the swollen region of the polymer is proposed to be [4]

$$c(x,t) = [c_0Q - C_X]\left[\frac{X_p - x}{X_p - X_1}\right] + c_X. \qquad (4)$$

It is immediately obvious that this expression satisfies the initial conditions (3). It has been shown [4] that the form for X_1 and X_p that satisfy the conditions of this boundary value problem are:

$$X_1 = k_1 t^{\frac{1}{2}} \quad , \quad X_p = k_p t^{\frac{1}{2}}. \qquad (5)$$

Where k_1, k_p are constants to be determined from the experimental data. In Figure 1 a plot of the time evolution of the steady state solution is shown.

The linear expression (in x) in (4) is only an approximation: it does not satisfy the diffusion equation itself. However the quasi-steady state approximation has been used in a number of studies to great effect [5][6]. In [7] the error incurred was investigated. The errors were calculated using numerical methods and an error of no more than 5% was estimated

compared with an analytical solution to the boundary value problem specified above. Its effect will be seen when fitting the model to real data below.

CONDUCTION WITHIN THE COMPOSITE MATERIAL

Here an electron hopping type model is considered for the relationship between local concentration and conductivity. Electron hopping is a quantum mechanical effect which can take place in the absence of physical contact between the granules. Here an electrical potential difference exists between the nanospheres. This model can be extended to a macroscopic level by appealing to Effective Medium Theory. The conduction model considered is of the form [8]:

$$\sigma = \sigma_0 \exp\left(-\chi_s\right) \qquad (6)$$

where σ is the conductivity of the polymer, σ_0 is the conductivity of the virgin polymer and χ_s is a function of the local swelling factor. By assuming small changes in resistance ($\chi_s \approx 0$), (6) may be linearised to obtain

$$\sigma \approx \sigma_0(1 - \chi_s). \qquad (7)$$

In this model it is assumed that χ_s is proportional to the volume change, ΔV_p, which is proportional to the local solvent concentration, c.

$$\chi_s = Nc, \qquad (8)$$

for some constant N.

To calculate the current flowing between the two electrodes of the sensor, it is easiest to integrate the conductivity against the electric field over the surface bisecting the electrodes. The expression for the component of the electric field, E, parallel to the direction between two semi-infinite coplanar electrodes at a depth y_0 in some film, over the plane $x = 0$ is given by [9]

$$E(0,y) = \frac{V}{\pi}\left[(y + y_0)^2 - \frac{w^2}{4}\right]^{-\frac{1}{2}}. \qquad (9)$$

Thus, assuming quasi-steady state, as in Equation (4) the time dependent expression for the current through the sensor is given by:

$$i = \frac{\sigma_0}{\pi}\left[N\left(c_0Q - C_X\right)\frac{1}{(k_1 - k_p)t^{\frac{1}{2}}}\left[k_p t^{\frac{1}{2}}\left[\cosh^{-1}(k_1 t^{\frac{1}{2}} + y_0)\right.\right.\right.$$
$$- \cosh^{-1}(k_p t^{\frac{1}{2}} + y_0)\right] - \left[\exp(\cosh^{-1}(k_1 t^{\frac{1}{2}} + y_0))\right.$$
$$- \exp(\cosh^{-1}(k_p t^{\frac{1}{2}} + y_0)) - y_0\left[\cosh^{-1}(k_1 t^{\frac{1}{2}} + y_0)\right.$$
$$\left.\left.\left.\left.- \cosh^{-1}(k_p t^{\frac{1}{2}} + y_0)\right]\right]\right] - \log 2y_0 - NC_X\cosh^{-1}(k_p t^{\frac{1}{2}} + y_0) + 1\right].$$
$$(10)$$

For parameter estimation C_X was set to $\frac{1}{2}Qc_0$. This was found to give the best fit by trial and error.

EXPERIMENT

The test bed used is a simple electronic nose rig and its basic design has been tested a number of times with success [10].

The main aim of the test bed is to measure the response of gas sensors and in order to do this it imitates the basic function of a mammalian nose. Conceptually this process includes the production of some odour external to the nose and transport to the sensor where the odour is detected.

For the mounting of the sensors it was decided to use a new 'smart nose' design. This sensor chamber uses a narrow channel with the sensor surface set to be flush with one side of the channel. The resulting flow, for velocities in the range used in the experiments described in this section, is laminar with a parabolic profile across the channel.

The rig, as designed, is capable of housing and performing measurements on six resistive sensors at a time. Three polymers were used in sets of two sensors: poly(caprolactone), poly(styrene-co-butadine) and poly(vinyl acetate).

Temperature and humidity sensors (SHT 71, Sensiron. 2% accuracy) were mounted near the sensor chamber in order to measure environmental conditions. This enabled an investigation into the effect of these conditions on the parameters within the sensor response model.

An 'experiment' consisted of two solvent exposures: one to acetone and one to ethanol vapour in ambient air. This allows for a more rigorous validation of the model by fitting the two responses simultaneously. Thus an experiment involves firstly a fresh air 'purge' then an acetone exposure, this is followed by a second fresh air 'purge' and an ethanol exposure. In each experiment an 1800 second fresh air purge was followed by a 4 second sample phase. Acetone and ethanol responses were stored together so that the model could be fitted simultaneously to both.

COMPUTER IMPLEMENTATION OF PARAMETER ESTIMATION

Model optimisation was carried out within the MATLAB v5.3 environment. A genetic algorithm [11] was used to search for candidate optimal models. A Levenberg-Marquardt algorithm used for final parameter tuning has already been implemented in MATLAB as the LSQNONLIN routine. This routine requires the start values of the parameters, the function to minimise and stopping criteria as input arguments. It outputs the fitted parameters, the fitting error and whether successful convergence has occurred.

Common to both of these optimisation stages was the simulation script that produced, based upon specific parameters values, a simulation of two sets of six sensors representing the six experimental sensors reacting to the two solvents. The two sets of six responses for each experiment are interrelated. These relationships are that pairs of sensors share the same chemical characteristics and that, between two exposures, a sensor retains the same physical characteristics. These relationships were manifested in the simulation by common parameters representing common characteristics.

Figure 2. Example of the model fitted to an experimental dataset.
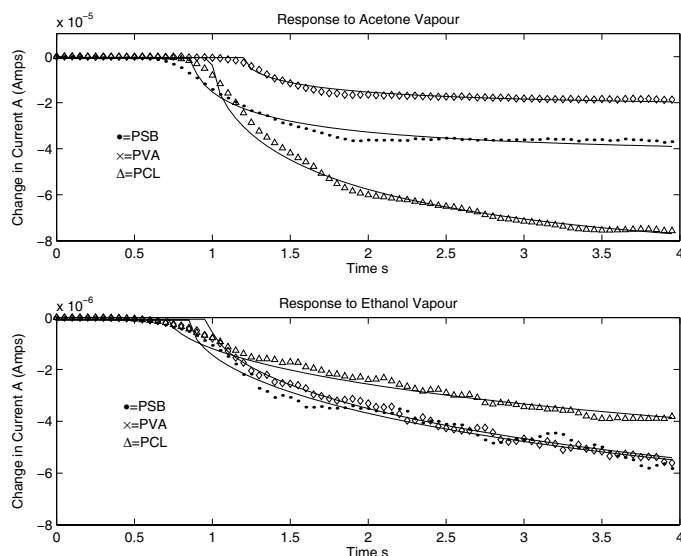

RESULTS AND CONCLUSIONS

The model fitted to the experimental data well. Figure 2 shows an example of the model fit compared to the real data, the change in current is plotted so that all the responses may be viewed on the same scale. This fit has a sum of squares error of 1.944. The error was weighted with respect to the magnitude of the response and so an average point wise error of 4.5% was estimated. This is considered to be very good given that:

- The constraints on the parameters and the model to fit all 12 responses simultaneously.
- The difference in magnitude of response to acetone and ethanol.
- The data were noisy.

There are some disparities between the model and experimental responses. The model predicts more rapid initial dynamics than are actually observed. The reason for this is probably the nature of the error in the quasi-steady state approximation, which naturally assumes rapid dynamics. This would account for this rapid change in current at the beginning of the simulation.

The rate constants in the model relate to the progress of the solvent diffusion front through the polymer films. The acetone responses are clearly affected by the humidity and temperature of the atmosphere. This is shown in Figures 3, 4 and 5. The rate of reaction reduces with humidity, suggesting a competitive process. Note the discrepancy in the trend in Figure 5. This may be due to other factors affecting the rate of response or the sensor characteristics changing with time. The increase in diffusion rate is temperature dependent as was expected. There are two possible effects contributing to this. The first is that mass action is temperature dependent
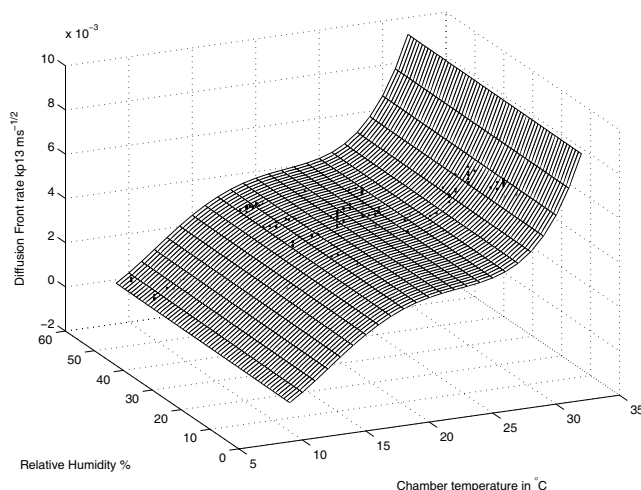
Figure 3. PSB based sensor diffusion front rate temperature and humidity dependence.
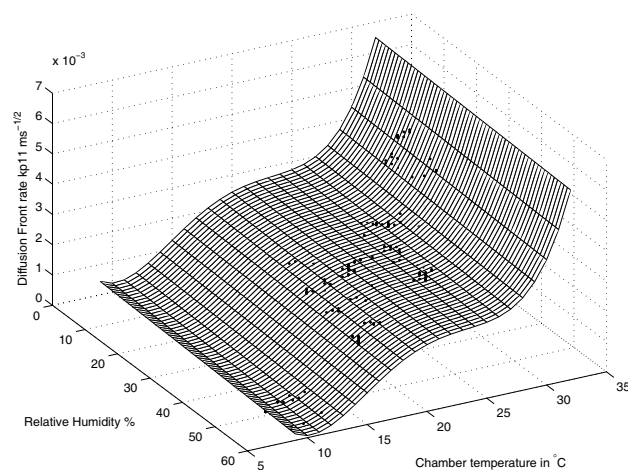
Figure 4. PVA based sensor diffusion front rate temperature and humidity dependence.
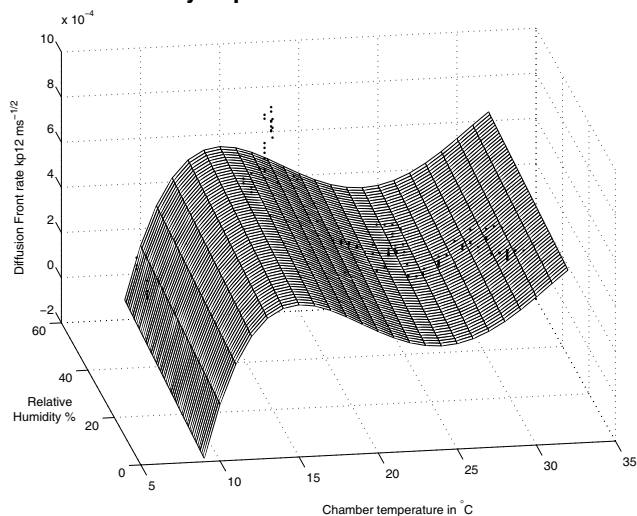
Figure 5. PCL based sensor diffusion front rate temperature and humidity dependence.

and so reactions will tend to equilibrium more quickly at a higher temperature. Secondly it is assumed that diffusion is concentration dependent. It is also known that the sample concentration will increase with temperature, so this could also explain the observed behaviour. The temperature effects were accounted for by fitting a 4th order polynomial to the temperature/k_p data in order to incorporate the sigmoidal type dependency.

This novel model has been shown to closely fit the experimental data. It has been demonstrated that it can be used to analyse the temperature dependencies of the system response. More than this, the model demonstrates how physical, fabrication dependent, characteristics may be separated from the underlying chemistry of the sensor.

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