

# TECHNICAL RESEARCH REPORT

Parameter Identification and Simulation of a Thin Film  
Conducting Polymer Gas Sensor

*by Yong Li, Raymond A. Adomaitis, Thomas J. McAvoy*

**TR 2001-35**



*ISR develops, applies and teaches advanced methodologies of design and analysis to solve complex, hierarchical, heterogeneous and dynamic problems of engineering technology and systems for industry and government.*

*ISR is a permanent institute of the University of Maryland, within the Glenn L. Martin Institute of Technology/A. James Clark School of Engineering. It is a National Science Foundation Engineering Research Center.*

**Web site <http://www.isr.umd.edu>**

# Parameter Identification and Simulation of a Thin Film Conducting Polymer Gas Sensor

Yong Li, Raymond A. Adomaitis<sup>\*</sup>, Thomas J. McAvoy  
Department of Chemical Engineering and  
Institute for System Research  
University of Maryland  
College Park, MD 20740

---

## Abstract

Thin film conducting polymer gas composition sensors can be used in industrial safety monitoring, environmental pollution control, and numerous other industrial applications. In this paper, a sensor system model is developed and this model is used to compare a lumped circuit to a transmission line formulation of the equivalent circuits describing the polymer film and electrodes; the sensor model includes the absorption/desorption process and the electric properties of the sensor. The simulation approach combines physically based modeling and parameter estimation, in which a subset of model parameters are estimated using published experimental data. The simulation results are found to be useful for interpreting conducting polymer sensor responses to different gas species.

*Keywords:* gas sensor, conducting polymer, parameter identification, simulation, boundary-value problem, transmission line model

---

## I. INTRODUCTION

Solid-state gas composition sensors, based on conducting polymer films, have been investigated by numerous researchers<sup>[1-2, 12-15]</sup>. Conducting polymer sensors can be used for industrial safety, environmental pollution control, and other industrial applications. Polypyrrole (PPY) is one of the most stable conducting polymers and sensors based on PPY films have been studied by a number of researchers. For example, Swann, Glidle and Gadegaard<sup>[1]</sup> measured the direct current (D.C.) resistance change of a PPY polymer when exposed to water, methanol, chloroform, and other chemical compounds. Likewise, Lin, Hwang and Lee<sup>[2]</sup> studied the D.C. resistance change of PPY polymer films exposed to N<sub>2</sub> and ammonia gases at different concentrations.

A D.C. based sensor usually employs arrays of different conducting polymers, and the pattern of the array response is used to distinguish between different gas species<sup>[13]</sup>. Amrani and Payne<sup>[12-15]</sup> have investigated an alternate gas-sensing technique based on high-frequency A.C. measurements. Measurements of the sensor electrical response characteristics at different frequencies using a single sensor element produce distinct patterns when the sensor is exposed to different gases or vapors, potentially providing similar

information to that which would otherwise be obtained using an array of sensors and D.C. measurements. However, analysis of the A.C. response is more complicated compared to measuring D.C. conductance because both the dielectric constant and conductivity change with frequency. Likewise, some physical properties of the sensor, such as resonant frequency, will change because of the absorption and desorption of target gas species in the sensing film.

There is growing interest in developing a fundamental understanding of the response of polymer film sensors to different gas species. Gardner, Bartlett and Pratt <sup>[11]</sup> presented an absorption/desorption model for a D.C. conducting polymer sensor, which consists of a thin uniform polymer film deposited on a pair of finite coplanar electrodes supported by an insulating substrate. It was assumed that the gas diffused into the film and was simultaneously adsorbed at sites randomly distributed throughout the film. The diffusion and adsorption equations were presented in terms of several fundamental dimensionless parameters, which described the underlying chemical and physical properties of the sensor.

Impedance analysis is a technique that has been employed by numerous workers interested in investigating the conduction mechanisms within conducting polymers <sup>[3-5]</sup>. Work has also been undertaken using high frequency techniques, in which the polymer is primarily used as microwave absorbing material <sup>[6]</sup>. Albery describes the charge transport mechanisms in conducting polymers attributable to the movement of the electrons and ions within the polymer film <sup>[7]</sup>. Other investigators have been interested in constructing transmission line-based models to describe the charge transport mechanisms in conducting polymers <sup>[8-9]</sup>.

In this paper, we compare a lumped circuit model to a transmission line model for representing the circuit formed by the sensor assembly. The transmission line model is used to simulate the electrical circuit response of the A.C. sensor because the operating frequency used in the published experimental data is from  $1 \times 10^8$  Hz to  $1 \times 10^9$  Hz, and in this frequency range, the wavelength of the electrical signal becomes comparable to the sensor physical dimensions. The simulated results for impedance, resistance, and capacitance responses

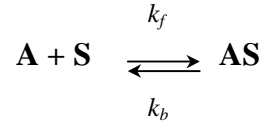
---

\* Author to whom correspondence should be addressed

are compared to the experimental values for the oxidizing and reducing gas species measured in [12]. We find that the absorption of all gas molecules can increase the capacitance of the sensor and a reducing gas will decrease the resistance of the circuit.

## II. MODELING THE ABSORPTION/DESORPTION PROCESS

The first step in developing a complete model for the PPY film sensor consists of describing the gas species sorption process. Gas diffuses into the conducting polymer sensing film and then reacts with it by an adsorption reaction. An adsorption reaction based on a Langmuir isotherm can be expressed as <sup>[21]</sup>



where A, S, and AS are the detected gas, the polymer film free sites, and the occupied sites of the sensing film, respectively.  $k_f$ ,  $k_b$  are the rate of forward and backward adsorption kinetics. We assume that the polymer contains a homogeneous adsorption site distribution. In most sensor configurations, the thickness of the sensing film is much smaller than the gap between two electrodes and the length of the electrodes, therefore, the sorbate concentration  $C$  and site occupancy  $\theta$  profiles are assumed to be only functions of distance  $x$  and time  $t$  as shown in Fig.1. The overall process can be expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - N_0 \frac{\partial \theta}{\partial t} \quad (1)$$

$$\frac{\partial \theta}{\partial t} = k_f C(1 - \theta) - k_b \theta \quad (2)$$

where  $N_0$  is the total available adsorption site concentration in the conducting polymer, and  $D$  is the diffusivity of gas species in the polymer. The gas cannot diffuse through the substrate; hence the diffusive flux is equal to zero at the polymer film/substrate boundary ( $x = 0$ ):

$$\left. \frac{\partial C}{\partial x} \right|_{x=0} = 0. \quad (3)$$

We assume that the gas concentration at the polymer film surface is equal to the gas concentration in the gas phase. Therefore, the gas concentration at the polymer film/gas interface is given as

$$C|_{x=L} = C_0 f(t) \quad (4)$$

where  $f(t)$  is a unit amplitude square time function; the period is the same as the adsorption/desorption cycle time used in published experimental studies. The initial condition of this problem corresponds to zero initial concentration of the target gas species in the polymer film:

$$C|_{t=0} = 0 ; \theta|_{t=0} = 0 \quad (5)$$

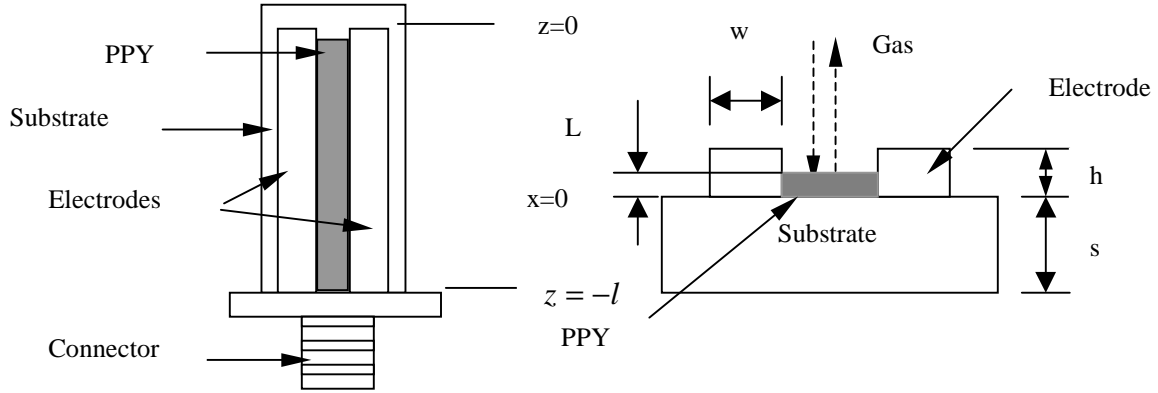


Figure 1 A representative PPY sensor system used by Amarani <sup>[12-13]</sup>

Dimensionless concentration ( $\eta$ ), time ( $\tau$ ), and length ( $\chi$ ) are defined as follows

$$\eta = \frac{C}{C_0}$$

$$\tau = \frac{t}{t_{cycle}}$$

$$\chi = \frac{x}{L}$$

where  $C_0$  is the gaseous species concentration in air when  $f(t)$  is equal to 1,  $t_{cycle}$  is the time of the adsorption or desorption cycle, and  $L$  is the thickness of the polymer film. Substituting the dimensionless terms into the modeling equations gives

$$\frac{\partial \eta}{\partial \tau} = D \cdot \frac{\partial^2 \eta}{\partial \chi^2} - n_0 \frac{\partial \theta}{\partial \tau} \quad (6)$$

$$\frac{\partial \theta}{\partial \tau} = t_{cycle} (K_f \eta (1 - \theta) - k_b \theta) \quad (7)$$

$$\left. \frac{\partial \eta}{\partial \chi} \right|_{\chi=0} = 0 \quad (8)$$

$$\eta \Big|_{\chi=1} = f(\tau) \quad (9)$$

$$\eta \Big|_{\tau=0} = 0 \quad (10)$$

where  $D = \frac{Dt_{cycle}}{L^2}$  ;  $K_f = k_f C_0$  ;  $n_0 = \frac{N}{C_0}$ .

PPY polymers can be prepared electrochemically to produce films in a highly doped state with intercalated anions. A positive charge and a radical, called a polaron, will be left on the polymer chain, and the polaron is the dominant charge carrier in PPY polymer<sup>[10]</sup>. Absorbed reducing gases will donate electrons and remove the positive charges from polymer backbone, resulting in a decrease in conductivity. Oxidizing gases will accept electrons and leave positive charges on the polymer chain, which results in an increase of conductivity. We assume that the change of the conductivity is linearly related to the site occupancy<sup>[11]</sup>:

$$\frac{\sigma_p(\chi, \tau) - \sigma_0}{\sigma_0} = S_\sigma \theta(\chi, \tau) \quad (11)$$

where  $S_\sigma$  is the conductance sensitivity of the polymer and  $\sigma_0$  is the base conductivity of the polymer in pure air. The conductance response of the polymer is given by:

$$\frac{G_p - G_0}{G_0} = \frac{\sigma_p - \sigma_0}{\sigma_0} = S_\sigma \int_0^1 \theta(\chi, \tau) d\chi \quad (12)$$

where  $G_0$  is the base conductance.

The absorption of gas molecules on the polymer chain can change the microstructure of the polymer<sup>[22]</sup>. The change of structure usually will facilitate alignment of the polymer with the applied field, which means it will increase the orientation polarization and subsequently increase the dielectric constant. We assume that the change of the dielectric constant is linearly related to the site occupancy:

$$\frac{\varepsilon_p(\chi, \tau) - \varepsilon_{p0}}{\varepsilon_{p0}} = S_\varepsilon \theta(\chi, \tau) \quad (13)$$

where  $S_\varepsilon$  is the dielectric sensitivity of the polymer and  $\varepsilon_{p0}$  is the initial dielectric constant of the polymer.

Capacitance is proportional to dielectric constant, so the capacitance response of the polymer is given by the equation below:

$$\frac{C_p - C_0}{C_0} = \frac{\varepsilon_p - \varepsilon_{p0}}{\varepsilon_{p0}} = S_\varepsilon \int_0^1 \theta(\chi, \tau) d\chi. \quad (14)$$

The conductance and capacitance response will be substituted into the transmission line model to calculate the electrical response of the sensor, such as the resistance and the resonant frequency of the sensor.

### III. THE EQUIVALENT CIRCUIT DEFINED BY AN A.C. SENSOR SYSTEM

The lumped formulation of an equivalent circuit of the A.C. sensor is shown in Fig. 2(a). Using the lumped circuit model, the impedance of the circuit is given by:

$$\begin{aligned} Z &= R_e + j\omega L_e + \frac{1}{\frac{1}{R_p} + \frac{1}{j\omega C_L}} \\ &= R_e + \frac{R_p}{1 + (\omega R_p C)^2} + j \left( \omega L_e - \frac{\omega R_p^2 C_L}{1 + (\omega R_p C_L)^2} \right) \end{aligned} \quad (15)$$

where

$R_e$  : resistance of the electrode;

$L_e$  : inductance of the electrode;

$C_L$  : capacitance of the sensor;

$R_p$  : resistance of the conducting polymer film;

$Z$  : impedance of the circuit.

The resonant frequency is given by <sup>[12]</sup>

$$f_r = \frac{1}{2\pi} \left( \frac{R_p^2 C_L - L_e}{L_e (R_p C_L)^2} \right)^{1/2}, \quad (16)$$

which is obtained by solving Eq.(15) with impedance  $Z$  equal to 0.

The capacitance and resistance of the polymer will change with frequency (i.e., additional coplanar capacitance becomes significant as well as self and mutual inductance), therefore the lumped circuit model cannot predict the experimental results over a large frequency range. The reason for the loss of accuracy is that at higher frequencies, the electromagnetic wavelength becomes comparable to the sensor dimensions and a transmission line model must be used instead of the lumped circuit model.

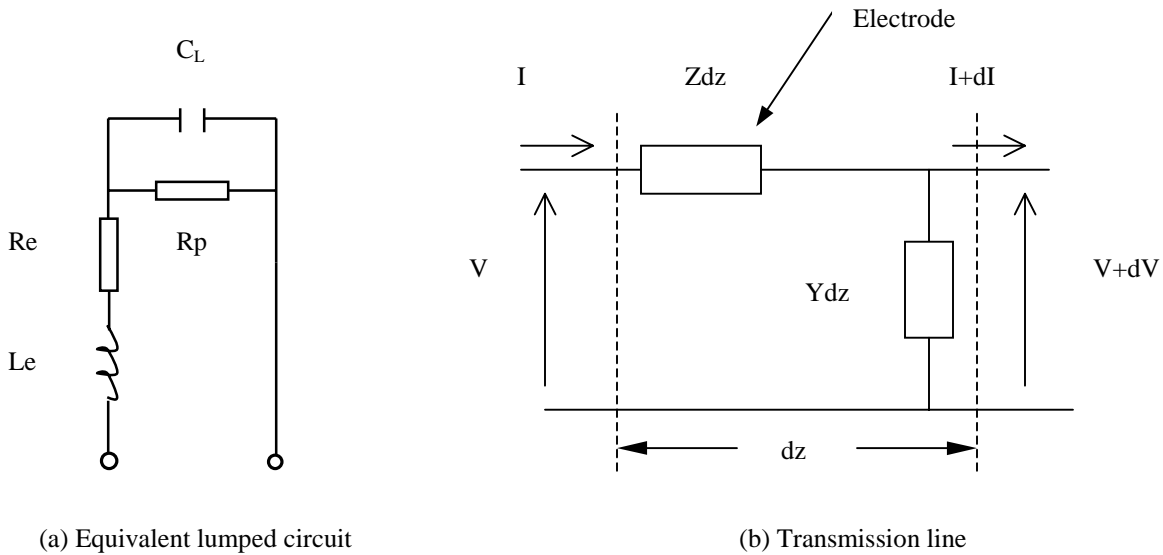


Figure 2. Lumped circuit and transmission line equivalent circuit diagrams

In the context of the sensor system shown in Fig.1, the transmission line consists of the parallel electrodes; the equivalent electrical circuit is shown in Fig. 2(b). The currents flowing in the electrodes are equal and opposite in the two electrodes, and a voltage difference exists between the electrodes. The current flow is affected by a distributed series inductance representing the induced voltage effects of magnetic flux surrounding the electrodes; the voltage between electrodes acts across the polymer film and substrate as a distributed capacitance. The impedance for the sensor is given by<sup>[23]</sup>

$$Z_i = Z_0 / \tanh(\gamma l) \quad (17)$$



where  $Z = R + j\omega L$ ;  $Y = G + j\omega C_{sensor}$ , and

$$Z_0 = \left( \frac{R + j\omega L}{G + j\omega C_{sensor}} \right)^{1/2} \quad (18)$$

$$\gamma = [(R + j\omega L)(G + j\omega C_{sensor})]^{1/2} \quad (19)$$

where

$R$  : the resistance per unit length;

$G$  : the conductance per unit length;

$C_{sensor}$  : the capacitance per unit length;

$L$  : the capacitance per unit length.

$C_{sensor}$  is the summation of four capacitances:

$$C_{sensor} = C_p + C_{gp} + C_a + C_s \quad (20)$$

where the individual capacitance contributions are defined by

$$C_p = \epsilon_p \epsilon_0 \frac{t}{a} \quad (21)$$

$$C_{gp} = \epsilon_a \epsilon_0 \frac{h-t}{a} \quad (22)$$

$$C_a + C_s = \epsilon_0 \frac{(\epsilon_a + \epsilon_s)}{2} \frac{k \left\{ \left[ 1 - \left( \frac{a}{a+2w} \right)^2 \right]^{1/2} \right\}}{k \left[ \frac{a}{a+2w} \right]}. \quad (23)$$

$\epsilon_0$  is the electric permittivity of free space, and  $\epsilon_a$ ,  $\epsilon_p$  and  $\epsilon_s$  are the dielectric constants of air, the polymer film, and substrate.  $k[x]$  is the complete elliptical integral of the first kind <sup>[12]</sup>.

The inductance of the overall sensor is given by <sup>[16]</sup>

$$L = \epsilon_0 \mu_0 \frac{1}{C_{air}} \quad (24)$$

where  $\mu_0$  is the magnetic permeability of free space, and  $C_{air}$  is the capacitance calculated using Eq.(20) when all dielectric materials are assumed to be replaced by air.

The resistance of the overall circuit is given as <sup>[16]</sup>

$$R = 2 \frac{\rho_e}{\delta_{skin} w} \quad (25)$$

where  $\rho_e$  is the copper electrode resistivity,  $\delta_{skin}$  is the skin depth of the electrode, and  $w$  is the width of the electrode. The conductance is defined by

$$G = \sigma_p \frac{t}{a} \quad (26)$$

where  $\sigma_p$  is the polymer conductivity found as the summation of the D.C. conductivity and the A.C. conductivity:

$$\sigma_p = \sigma_{a.c.} + \sigma_{d.c.} \quad (27)$$

where  $\sigma_{a.c.}$  is the A.C. conductivity and  $\sigma_{d.c.}$  is the D.C. conductivity.

#### IV. NUMERICAL SOLUTION

We use the MWRtools package <sup>[18-21]</sup>, which is a library of MATLAB language functions for implementing global spectral discretization methods for solving boundary value problems. In this study, Galerkin's method is used to solve the partial differential equations describing transport and sorption in the polymer film.

Because the boundary condition for the gas species concentration at the surface is not homogeneous, the trial function expansion used to represent concentration is split into two terms. One term satisfies the homogeneous boundary condition and the other satisfies the nonhomogeneous boundary condition:

$$\begin{aligned} \eta &= \eta_{\Omega} + \eta_{\partial\Omega} \\ &= \eta_{\Omega} + f(t)\chi^2. \end{aligned} \quad (28)$$

The dimensionless concentration  $\eta_{\Omega}$  and site occupancy  $\theta$  are expressed as follows:

$$\eta_{\Omega} = \sum_{i=1}^N a_i(\tau) \psi_i(\chi) \quad (29)$$

$$\theta = \sum_{i=1}^N b_i(\tau) \varphi_i(\chi) \quad (30)$$

where  $\psi$  and  $\varphi$  are the trial functions and  $a$  and  $b$  are the time dependent mode amplitude coefficients. Here we use the eigenfunctions of a Sturm-Liouville problem <sup>[18]</sup> as the trial functions  $\psi$  for concentration. The Sturm-Liouville problem is defined as:

$$\frac{\partial^2 \psi_i}{\partial \chi^2} = \lambda_i \psi_i \quad (31)$$

subject to boundary conditions

$$\left. \frac{\partial \psi}{\partial \chi} \right|_{\chi=0} = 0 ; \psi \Big|_{\chi=1} = 0.$$

Because there are no explicit boundary conditions for site occupancy  $\varphi$ , we can use a polynomial sequence  $\chi^n$  in the basis function expansion to define the site occupancy profiles in time. The eigenfunctions were obtained using the *sl.m* function, which is a MATLAB function in MWRtools package used to compute the eigenvalues and eigenfunctions of a Sturm- Liouville problem <sup>[18]</sup>. The coefficients  $a$  and  $b$  in Eq. (29) and (30) are calculated using the *odaepc.m* function, which is a polynomial collocation-based ODE/AE solver in the same computational package.

The fully discretized system is thus described by a large set of nonlinear algebraic equations, which are solved to find the site occupancy and concentration profiles of the polymer sensor exposed to a time dependent gas concentration. Using these simulation data, we then can compute the capacitance and conductivity change using Eq. (12) and Eq. (14). Substituting the capacitance change and conductivity change into the transmission line model, we finally obtain the resistance and resonant frequency change of the sensor.

## V. PARAMETER ESTIMATION

The final physical and chemical properties of conducting polymer films can vary depending on the polymerization process. Indeed, several chemical routes to synthesize pyrrole polymer films have been described leading either to insulating or conducting materials. Therefore, it is not possible to obtain accurate

values for many parameters in the model from empirical formulae or theoretical correlations. This means most parameters must be estimated from the experimental data. A Gauss-Newton <sup>[17]</sup> method and sets of published experimental measurements are used in this study to estimate a subset of model parameters. The objective function to be minimized in this parameter estimation procedure is defined as sum of the squares of the difference between the model predictions and experimental data:

$$q = \left[ Y - \tilde{Y} \right]^T \left[ Y - \tilde{Y} \right] = r^T r \quad (32)$$

where  $Y$  is vector of the measured data and  $\tilde{Y}$  is vector of the predicted value by the model.

Overall, the parameter estimation algorithm consists of the following steps:

- Step 1. Specify an initial estimate of the parameter vector,  $p_0$ .
- Step 2. Compute a search vector  $\Delta p$  by solving the following linear system:  $H\Delta p = -g$ , where  $g$  is the gradient of the objective function Eq. (32), and  $H$  is the Hessian matrix:

$$H_{k,j} = \sum_{i=1}^n \left( \frac{\partial r_i}{\partial p_k} \right) \left( \frac{\partial r_i}{\partial p_j} \right) \quad (33)$$

where  $n$  is the number of data points used in estimation.

- Step 3. Perform a line search along the search direction. That is, solve the one-dimensional optimization problem:

$$\min q(p_0 + \Delta p)$$

Step 4. Repeat Steps 2 and 3 until necessary and sufficient conditions for a minimum of  $q$  are satisfied.

## VI. PUBLISHED EXPERIMENTAL DATA

All the experimental data used in this study were obtained from the publication of Amrani, Persaud and Payne <sup>[12]</sup>. The impedance measurements of the sensor as a function of frequency and phase angle are shown in Fig.3. The change of capacitance of the sensor and the resistance change of the sensor for 100 ppm of three

species of volatile chemicals at 400 MHz are shown in Fig. 5 and Fig. 6. The relative change of resistance at different frequencies is shown in Fig 7.

## VII. RESULTS AND ANALYSIS

The relaxation frequency ( $f_0$ ), static dielectric constant ( $\epsilon_{p0}$ ), and static conductivity ( $\sigma_{p0}$ ) are fundamental properties of a conducting polymer. These quantities can be estimated using the impedance data and phase angle data in Fig.3 and the transmission line model. Because the data in Fig.3 correspond to the base response, the absorption/desorption model is not used in this step of the parameter estimation process. We use the results of Singh <sup>[24]</sup> to derive initial guesses for the estimated parameter values listed in Table I. The physical dimensions of the sensor, which are used in the impedance calculation, are listed in Table II. Iterations of the parameter identification algorithm are continued until the difference between the experimental and simulated impedance values is less than 4% of the experimental impedance value, and then the phase angle data is used to further refine the parameter estimates. The impedance and phase angle simulation profiles are shown in Fig.3, and 11 data points are used to estimate the parameters given in Table III. Different initial guesses were selected as part of the identification procedure to verify that converged solutions to the parameter identification algorithm corresponded to a global minimum of the objective function rather than saddle points or local minima. The resonant frequency, as shown in Fig.4, is very close to the value measured by Amrani and Payne <sup>[12]</sup>.

Table I. Parameter initial guesses <sup>[24]</sup>

Parameters	Values
Relaxation frequency, $f_0$	6.111e10 Hz
Static dielectric constant, $\epsilon_{p0}$	126.69
Static conductivity, $\sigma_{p0}$	1.187e-3 Ohm <sup>-1</sup> m <sup>-1</sup>

Table II. Additional parameters <sup>[12][24]</sup>

$\epsilon_\infty$	10.0
Width of the polymer	1.4e-4m
Length of the sensor	2.5e-2m
The thickness of substrate	1.6e-3m
The thickness of PPY polymer	4.5e-5m

Table III. Estimated parameters with different initial guesses

Parameters	Initial guess			
	$f_0$ (Hz)	2.064e10	6.170e11	0.85e10
$\epsilon_{p0}$	2.032	949.70	480.41	9.643
$\sigma_{p0}$ (Ohm <sup>-1</sup> m <sup>-1</sup> )	4.967e-3	0.097	8.91e-2	2.180e-2
	Optimal value			
$f_0$ (Hz)	6.112e10	6.088e10	6.111e10	6.112 Hz
$\epsilon_{p0}$	126.69	126.69	126.69	126.69
$\sigma_{p0}$ (Ohm <sup>-1</sup> m <sup>-1</sup> )	1.876e-3	1.143e-3	1.183e-3	1.189e-3

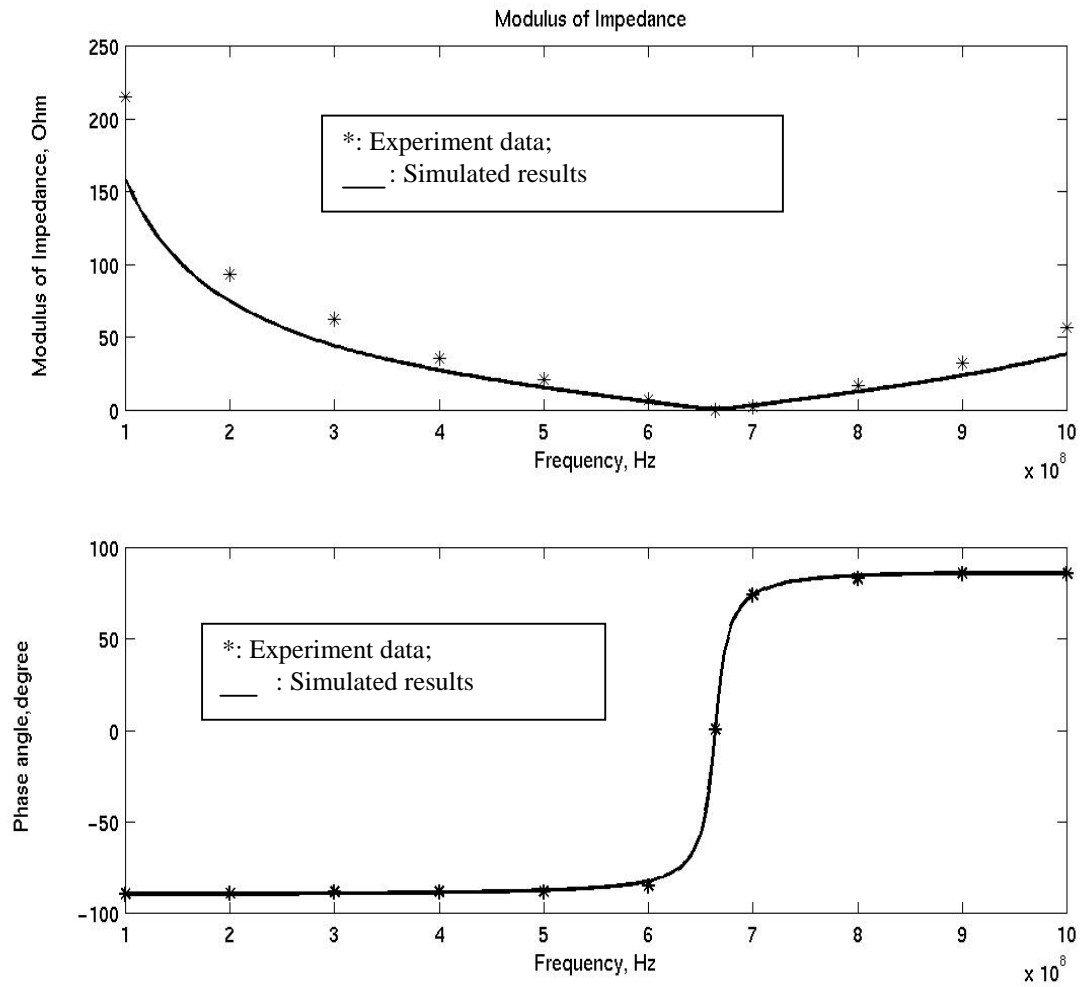


Figure 3 Impedance and phase angle versus frequency of the gas sensor

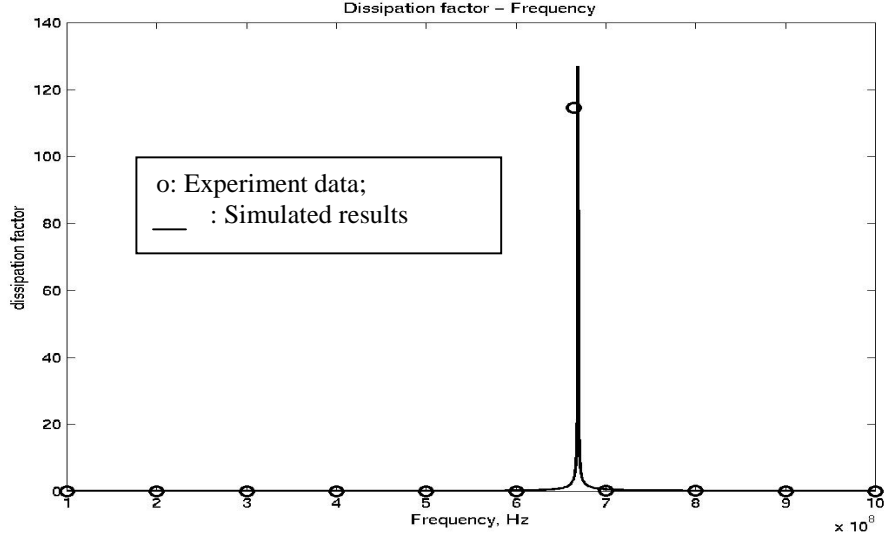


Figure 4 The dissipation factor versus frequency response

The frequency of the published experimental data ranges from  $1 \times 10^8$  to  $1 \times 10^9$  Hz. From Amrani and Payne<sup>[12]</sup>, the measured lumped capacitance  $C$  was 10.78 pF, the inductance  $L_e$  was  $4.9e-9$  H, and the resistance  $R_p$  was  $1.93 \text{ k}\Omega$ . Therefore the resonant frequency computed by Amrani using a lumped circuit model is

$$f_r = \frac{1}{2\pi} \left( \frac{(1.93e3)^2 * 10.78e(-12) - 4.9e(-9)}{4.9e(-9) * (1.93e3 * 10.78e(-12))^2} \right)^{1/2} = 692.446 \text{ MHz}$$

The resonant frequencies predicted by both models of this study are shown in Table IV. As can be seen from Table IV, the transmission line model produces a more accurate prediction. Additionally, when each model is used to predict the impedance change, the advantage of the transmission line model becomes even more apparent.

Table IV. Resonant frequency

	Resonant frequency values
Measured value	663.78MHz
Value predicted by lumped circuit model	692.446 MHz
Value predicted by transmission line model	668.83 MHz

The second set of parameters, including the diffusivity of gas species in the polymer ( $D$ ), the rate of adsorption ( $K_f$ ) and desorption ( $k_b$ ) of the gaseous species, and gas dielectric constant sensitivity coefficient ( $S_\epsilon$ ) of the polymer, are estimated using the capacitance responses of the PPY polymer sensor for ethyl acetate,

acetone and methanol <sup>[12]</sup> as shown in Fig. 5. The third set of parameters, which includes gas conductivity sensitivity,  $S_\sigma$ , is estimated using the resistance responses shown in Fig. 6. We use Sabara's <sup>[21]</sup> results as our initial estimates for  $D$ ,  $K_f$ ,  $k_b$ , and  $S_\sigma$  in the parameter identification procedure. The numerical implementation of the parameter identification is the same as described previously, and the final values of the estimated parameters are shown in Table V. The simulated responses of capacitance and resistance using these parameter values are shown in Fig. 5. and Fig. 6.

Table V. Estimated parameters

Parameters	Values		
	Methanol	Acetone	Ethyl acetate
The diffusivity of gas, $D$ ( $\text{m}^2\text{s}^{-1}$ )	0.335e-15	3.1775e-15	1.5429e-15
Rate of adsorption, $K_f$ ( $\text{s}^{-1}$ )	6.5034e-1	0.7495e-1	1.1191e-1
Rate of desorption, $k_b$ ( $\text{s}^{-1}$ )	3.5563e-1	2.4860e-1	2.8471e-1
Gas sensitivity for conductivity, $S_\sigma$	-28.3719	-25.3451	-7.5141
Gas sensitivity for permittivity, $S_\epsilon$	4.5345	5.1076	6.9164

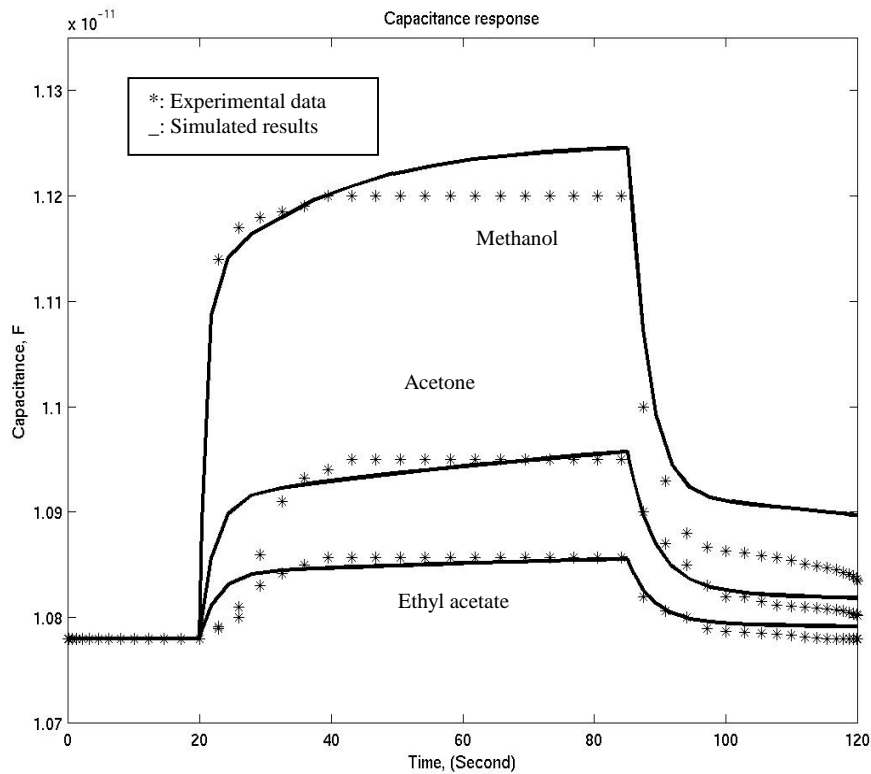


Figure 5. The capacitance response of PPY sensor at 400mHZ to 100 ppm pulses of methanol, acetone and ethyl acetate vapors



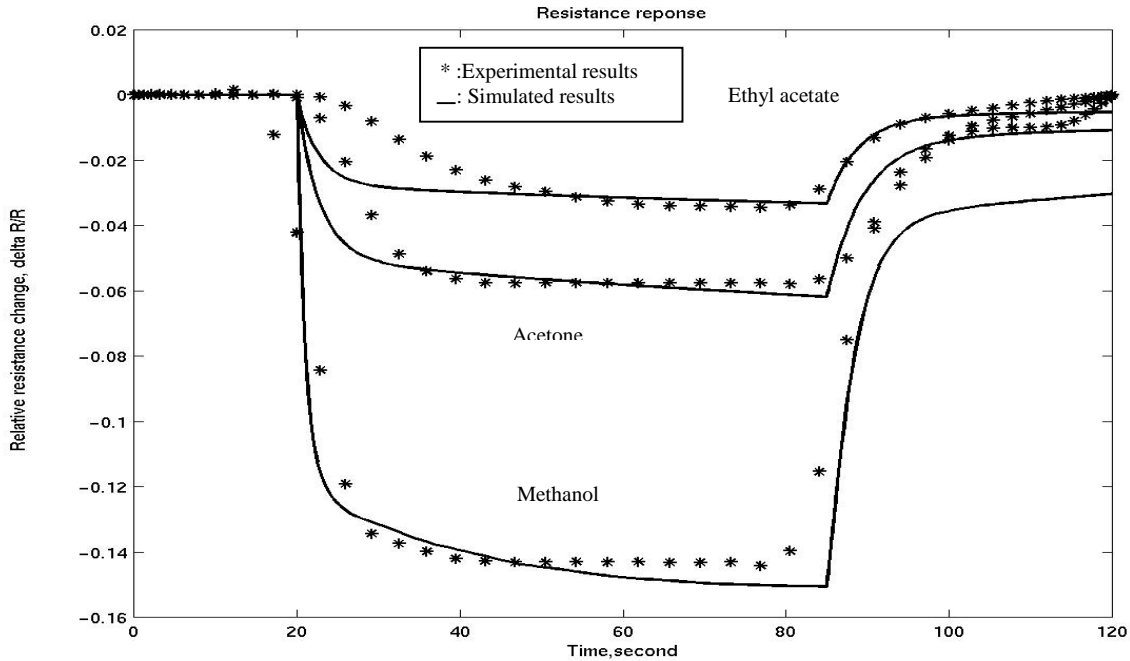


Figure 6. The resistance response of a PPY sensor at 400 MHz to 100 ppm pulses of methanol, acetate and ethyl acetate vapors

Methanol is the smallest molecule of the three gases in this study, which means methanol molecules may diffuse more easily into polymer film producing a faster response relative to the other two gas species. Additionally, the  $-OH$  group of the methanol molecule can strongly interact with the polymer, increasing this gas species' effect on the electrical response of polymer film compared to the other two gas species. As shown in Table V, the model of sensor response to methanol has the largest values of  $K_f$ ,  $k_b$ , and  $S_\sigma$ , and correspondingly, methanol has the largest capacitance and resistance response of three gas species shown in Fig. 5 and Fig. 6.

The relative change of resistance is frequency dependent. The predicted resistive responses with different operating frequencies and the experimental data from Amrani [12] are shown in Fig. 7. As can be seen in this figure, the largest relative change is approximately 18% when the sensor operating frequency is 200 MHz. Therefore, the model correctly predicts that the sensor will have the largest resistance response to methanol if the sensor is operated at 200 MHz.

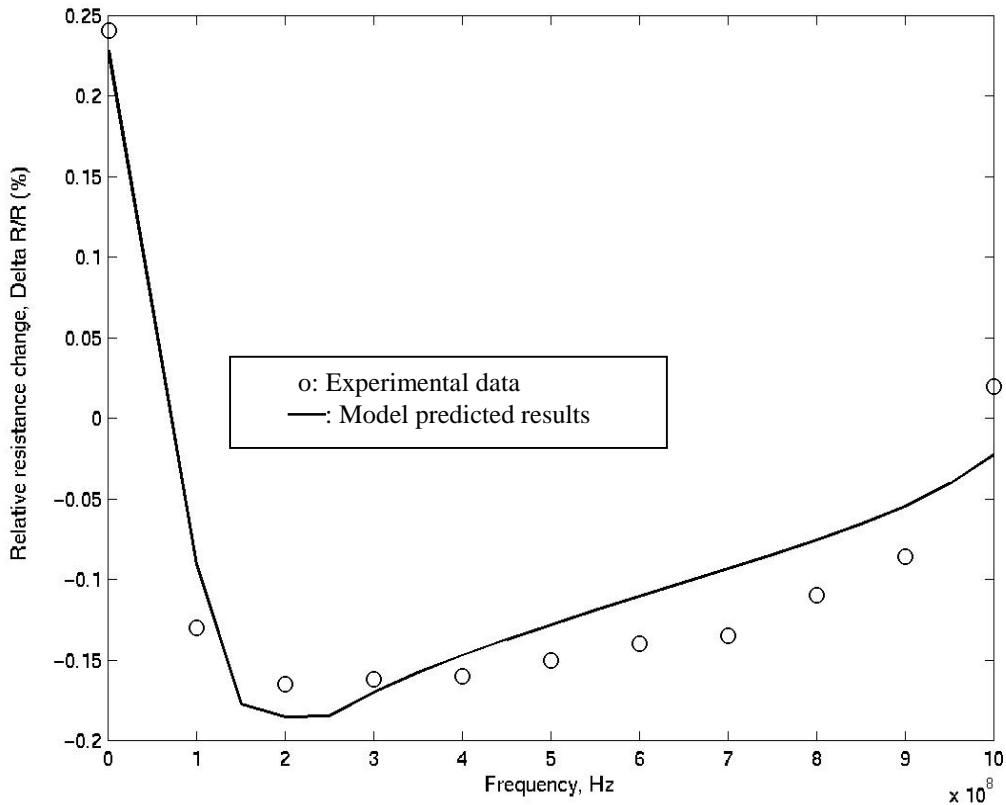


Figure 7. The resistive relative change of the sensor to 100 ppm concentration of methanol.

### VIII. CONCLUDING REMARKS

The absorption/desorption process and equivalent electric circuit models of a thin film A.C. sensor were studied in this paper. Simulation results demonstrated a good match with published experimental data for three species of reducing gases. It was found that the transmission line model used in this study produced more accurate simulation results compared to a lumped circuit model because of the high operating frequency used in the published experimental data. It was also found that the molecule size and the polarity of gas species both have a strong effect on the electrical response of the sensor. Using the model developed in this paper, it is possible to find the optimized sensor operating frequency by locating the frequency corresponding to the

maximum sensor sensitivity to a specific gas species. Likewise, the model can be used to guide the design of sensors to optimize the sensor selectivity and speed of response to different gas mixtures.

### ACKNOWLEDGMENTS

This research was supported by the National Science Foundation through grant CTS 9616085 and by the Small Smart Systems Center at the University of Maryland.

### REFERENCES

1. M.J. Swann, A. Glidle, N. Gadegaard, L. Cui, J.R. Barker, J.M. Cooper, Distribution of adsorbed molecules in electronic nose sensors, *Physica B* 276-278 (2000) pp. 357-358
2. C.W. Lin, B.J. Hwang, C.R. Lee, Sensing behaviors of the electrochemically co-deposited polypyrrole-poly(vinyl alcohol) thin film exposed to ammonia gas, *Materials Chemistry and physics* 58 (1999) pp.114 –120
3. T. Amemiya, K. Hashimoto, A. Fujishima, Frequency-resolved Faradaic processes in polypyrrole films observed by electromodulation techniques – electrochemical impedance and color impedance spectroscopies, *J. Phys. Chem.* 97(1993) pp. 4187-4191
4. T. Amemiya, K. Hashimoto, A. Fujishima, Faradaic charge transfer with double-layer charging and/or adsorption-related charging at polymer- modified electrodes as observed by color impedance spectroscopy, *J. Electroanal. Chem.* 377 (1994) pp. 143-148
5. G.S. Popkirov, E. Barsoukov, In-situ impedance measurements during oxidation and reduction of conducting polymers – significance of the capacitive currents, *J. Electroanal. Chem.* 383 (1995) pp. 155-160
6. L. Olmedo, P. Hourquebie, F. Jousse, Microwave absorbing materials based on conducting polymers, *Adv. Mater.* 5 (1993) pp. 373-377
7. P.A. Topart, M.A.A. Noel, High-frequency impedance analysis of quartz-crystal microbalances coated with conducting polymers, *Anal. Chem.* 66 (1994) pp. 2926-2934
8. W.J. Albery, C.M. Elliott, A.R. Mount, A transmission line model for modified electrodes and thin layer cells, *J. Electroanal. Chem.* 288 (1990) pp. 15-34
9. W.J. Albery, A.R. Mount, A further development of the use of transmission-lines to describe the movement of charge in conducting polymers, *J. Electroanal. Chem.* 388 (1995) pp.1-9

10. Y. Shen, K. Carneiro, Characterization of the transport properties of conducting polypyrrole films, *Synthetic Metals* 18 (1987) pp. 77-83
11. J.W. Gardner, P.N. Bartlett, K.F.E. Pratt, Modeling of gas-sensitive conducting polymer devices, *IEEE Proc. Circuits Devices Syst.* 142(5) (1995) pp. 321-333
12. M.E.H. Amrani, K.C. Persaud, P.A. Payne, High-frequency measurements of conducting polymers: development of a new technique for sensing volatile chemicals, *Meas. Sci. Technol.* 10 (1995) pp.1500-1507
13. F. Musio, M.E.H. Amrani, K.C. Persaud, High-frequency A.C. investigation of conducting polymer gas sensors, *Sens. Actuators B* 23 (1995) pp.223-226
14. M.E.H. Amrani, R.M. Dowdeswell, P.A. Payne, K.C. Persaud, An intelligent gas sensing system, *Sens. Actuators B* 44 (1997) pp.512-516
15. M.E.H. Amrani, P.A. Payne, Multi-frequency interrogation technique applied to conducting polymer gas and odour sensors, *IEEE Proc. – Sci. Meas. Technol.* 146(2) (1999) pp.95-101
16. E. Bogatin, A closed form analytical model for the electrical properties of microstrip interconnects, *IEEE Transactions on Components, Hybrids, and Manufacturing Technology* 13(2) (1990) pp.258-266
17. V.J. Law, Y. Sharma, Computation of the gradient and sensitivity coefficients in sum of squares minimization problems with differential equation models, *Computers & Chemical Engineering* 21(12) (1997) pp.1471-1479
18. R.A. Adomaitis, Y.-h. Lin, A collocation/quadrature-based Sturm-Liouville problem solver, *Appl. Math. Comp.* 110 (2000) pp.205-223
19. R.A. Adomaitis, Y.-h. Lin, H.-Y. Chang, A computational framework for boundary-value problem based simulations, *Simulation* 74 (2000) pp.28-38
20. Y.H. Lin, H.Y. Chang, R.A. Adomaitis, MWRtools: a library for weighted residual method calculations; *Computers & Chemical Engineering*, 23(8) (1999) pp.1041-61
21. A. Sabadra, Parameter identification and simulation of a conducting polymer gas sensor, M.S. Thesis, University of Maryland, College Park 2000.
22. C.C. Ku and R. Liepins, *Electrical properties of polymers*, Munich, New York, 1987.
23. R.W.P. King, *Transmission-line theory*, Dover, New York, 1955.
24. R. Singh, R.P. Tandon, V.S. Panwar, S. Chandra, Low-frequency AC conduction in lightly doped polypyrrole films, *J. Appl. Phys.* 69(4) (1991) pp.2504-2511