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Modeling the CO gas response of PEDOT:PSS/ Fe(salen) thin film for a gas sensor

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Abstract. A thin film carbon monoxide (CO) gas sensor based on PEDOT:PSS/Fe(salen) was developed in this study using the spin coating technique on several glass pieces with interdigitated Au electrodes. The change in the electrical resistance of sensors with different dopant contents was measured in different ranges of CO gas concentrations and temperatures. It was found that Fe(salen) as a dopant element could significantly improve the performance of PEDOT:PSS-based sensors. Least Square Support Vector Machine (LSSVM) method was applied to predict the response characteristics of the films in different testing conditions. Modeling results showed satisfactory agreement with experimental findings.

1. Introduction

Many studies have investigated the process of monitoring carbon monoxide (CO), due to its toxicity, odorless, and colorless characteristics, and different gas-sensitive materials have been developed [1,2]. In this regard, the performance of polymer-based gas sensors has received much attention because of their low cost, ease of manufacturing, and ultimate responsibility [3–7]. PEDOT:PSS polymer (poly (3,4-ethylenedioxy) thiophene-poly (styrenesulfonate)) is one of the promising candidates for sensing polar species such as CO gas [6–8]. The performance of PEDOT:PSS-based sensors has been improved by incorporating various dopants. Javadpour et al. [7] added Fe, Al, and morpholine to PEDOT:PSS for enhancing the sensitivity of the sensors to the CO gas. Memarzadeh et al. [3] developed the PEDOT:PSS-based gas sensor with Co(salen) dopant for CO gas detection at room temperature. They found that the highest sensitivity was achieved at 1 wt.% of Co(salen) dopant. Arabloo et al. [9] investigated the effects of the presence of Fe(salen) dopant in the PEDOT:PSS-based sensor on CO gas monitoring. The developed PEDOT:PSS/Fe(salen) sensor exhibited high selectivity characteristics with good stability.

In spite of the vast experimental investigations performed on conductive polymers, there have been a few attempts at modeling their gas sensing behavior. Gardner et al. [10,11] developed a modeling approach based on diffusion and adsorption equations for predicting the conductance of polymer gas sensors. In their model, the governing equations are nonlinear differential equations with no exact analytical solution and, thus, must be solved by numerical techniques. In addition, approximate analytical expressions have been found for six limiting cases, including diffusion-controlled, reaction-controlled, and four intermediate processes. Gardner's model is complex and features a number of constant parameters that should be determined by fitting with the experimental data for each testing condition. Hwang et al. [12] presented a more simple model based on Langmuir isotherm for

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polymer-based gas sensors. However, their model did not consider the dynamic response of the sensors and only assumed the equilibrium state.

The Artificial Neural Network (ANN) is one of the commonly used methods for solving complex dynamic problems. This model can be simply implemented and has shorter computation time than other numerical methods [13,14]. A potential alternative to the traditional ANN model is the Support Vector Machine (SVM) model. SVM relies on the theory of statistical learning and convex optimization to make accurate predictions. The main advantage of the SVM over ANN is that this model often produces a unique global solution [15]. However, SVM uses computationally hard quadratic programming. Alternatively, Suykens et al. [16,17] proposed the Least Square Support Vector Machine (LSSVM) based approach, which solved a set of linear equations and had less computational complexity than standard SVM. This modeling technique was successfully applied in different fields of engineering. For example, Fang et al. [18] proposed a model based on LSSVM to predict electrical and mechanical properties of the Al-Zn-Mg-Cu alloy during thermal aging at various times and temperatures. Huang and Chen [19] applied a technique based on a fuzzy system for modeling the arc welding process. In that study, the basic functions of the fuzzy system were chosen using the SVM method. Fayazi et al. [20] applied the LSSVM modeling for the estimation of the natural gas viscosities at different temperatures and pressures. However, to the best knowledge of the authors, this method has not been applied for the response prediction of sensors.

In the present study, PEDOT:PSS-based gas sensors with Fe(salen) dopants were fabricated by implementing the spin-coating process. The response of the sensors containing different concentrations of Fe(salen) to CO was studied by measuring the relative electrical resistance changes. The performance of the sensors was evaluated at different temperatures at various concentrations of CO gas. The LSSVM method was used for estimating sensor response curves in different testing conditions, and the results were compared to experimental data.

2. Materials and experimental procedure

A PEDOT:PSS aqueous solution containing Fe(II)(salen) and Fe(III)(salen) with different contents (0-1 wt.%) was prepared at room temperature (the details of the experimental procedure were reported in [9,21]). Then, the doped solution of PEDOT:PSS was coated on a glass substrate with Au electrodes using the spin coating process. The electrodes were interdigitated with 10.0 μm of gap width between them (Figure 1). The developed thin film sensors,

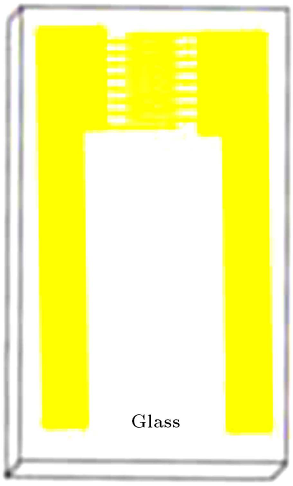

Figure 1. Glass substrate with Au electrodes used for coating.

with a thickness of 30 to 44 nm, were put in a test chamber and the CO gas flowed at 2.0-25.0 mL/sec. The variations of resistance of sensors were examined and recorded at different temperatures of 25-150°C.

3. Modeling approach

SVM is a supervised machine learning technique introduced in 1995 [22]. SVM was successfully applied to study classification and regression problems [16,17,23]. A major disadvantage of the original SVM is its high computational cost because of constrained optimization programming [16]. A modified version of the SVM known as LSSVM is then proposed to facilitate the solution of the standard SVM. As briefly discussed in the following section, a set of linear equations is considered in the LSSVM instead of quadratic programming problems, reducing the complexity of the optimization process [17].

Consider a dataset containing the N points $\{(x_1, y_1), (x_2, y_2), ..., (x_N, y_N)\}$, where x_i is the n-dimensional input vector and y_i is a scalar output value. The function:

$$y(x_i) = w^T \varphi(x_i) + b, \tag{1}$$

is applied to predict the output data from the input values. Here, w is a weight vector, $\varphi(x_i)$ is a nonlinear function used for regression, and b is a bias term. In the LSSVM model, the following optimization problem is considered [16]:

$$\min J = \frac{1}{2} w^T w + \frac{1}{2} \gamma \sum_{i=1}^{N} e_i^2, \tag{2}$$

subject to:

$$y(x_i) = w^T \varphi(x_i) + b + e_i \qquad i = 1, ..., N, \tag{3}$$

where γ is a regularization parameter, and e_i is the error of the ith data point. Through the Lagrange multiplier a_i, the above optimization problem is reformulated as follows [16]:

$$\min L = \frac{1}{2}w^T w + \frac{1}{2}\gamma \sum_{i=1}^{N} \{e_i^2 + a_i[y_i - w^T \varphi(x_i) - b - e_i]\}. \tag{4}$$

The optimum condition is obtained by differentiating the above equation from variables (b, w, e_i, a_i), resulting in the following:

$$\sum_{j=1}^{N} a_j = 0, \tag{5a}$$

$$y(x_i) = \sum_{j=1}^{N} a_j k(x_i, x_j) + b + \frac{a_i}{\gamma}, \quad i = 1, ..., N, \tag{5b}$$

where $k(x_i, x_j)$ is a kernel matrix. The radial basis function is commonly used as a kernel function in the LSSVM, which is defined as follows [24,25]:

$$k(x_i, x_j) = \exp(-\|x_i - x_j\|^2 \big/ \sigma^2), \tag{6}$$

where σ is the Gaussian function width.

Eqs. (5a) and (5b) represent $(N+1)$ equations with $(N+1)$ unknowns $(b, a_1, a_2, ..., a_N)$. By solving these equations, the LSSVM parameters can be determined.

4. Results and discussion

4.1. Experimental results

The experimentally determined resistivity (R) of the sensors is converted to the response of the sensor (S) through the following relation:

$$\%S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100, \tag{7}$$

where R_{gas} is the measured thin film resistance in gas, and R_{air} is the thin film resistance in the air. The response of PEDOT:PSS/Fe(salen) gas sensors for different doping contents that are determined experimentally is shown in Figure 2. From Figure 2(a), by increasing the Fe(II)(salen) content from 0 to 0.02 wt.%, the response of sensors increased. However, by increasing the dopant content to a greater degree, the response of the sensor to CO gas decreased, which could be associated with the interaction between the Fe(II)(salen) particles. Therefore, the maximum response was obtained at the dopant content of 0.02 wt.% Fe(II)(salen). From Figure 2(b), a similar trend can be observed for Fe(III)(salen) dopant. However, in this case, the maximum response occurred at the dopant content of 0.1 wt.%. According to the previous studies on the gas response of conductive polymers [5,9,26], for a given gas concentration and dopants type, there

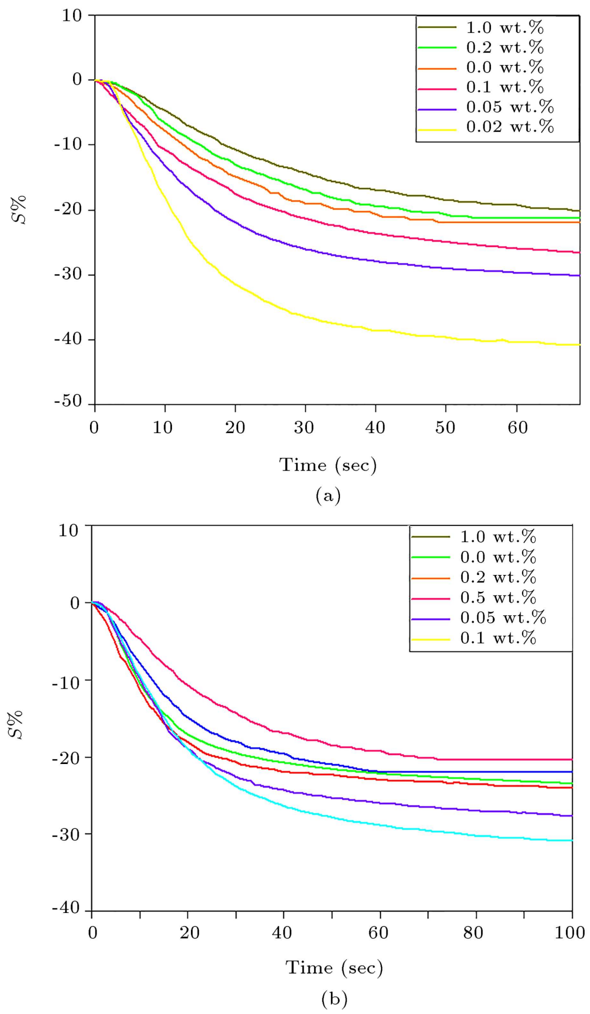

Figure 2. The effect of doping content on the measured sensor response: (a) Fe(II)(salen) and (b) Fe(III)(salen).

is an optimum concentration of the dopants at which maximum response is observed. This behavior may be related to the number of available interaction sites. In fact, at higher concentrations of the dopants, the excess material produced a shielding effect and a weak response. Figure 3 shows the measured response of the sensor to the optimum content of Fe(II)(salen) and Fe(III)(salen) dopants along with the response of pure PEDOT:PSS sensor. From this figure, the PEDOT:PSS sensor containing 0.02 wt.% of Fe(II)(salen) shows the highest response and can be a good choice for the CO gas sensors. Figures 4 and 5 show the effect of CO gas flow rate on the measured response of PEDOT:PSS with 0.02 wt.% Fe(II)(salen) and 0.1 wt.% Fe(III)(salen), respectively. According to Figures 4 and 5, by increasing the CO gas flow rate, the responsibility of sensors increased and the time to reach the maximum responsibility decreased. In fact, at a higher flow rate, the gas concentration in the test chamber increases, which in turn accelerates the gas absorption. The effect of environmental temperature

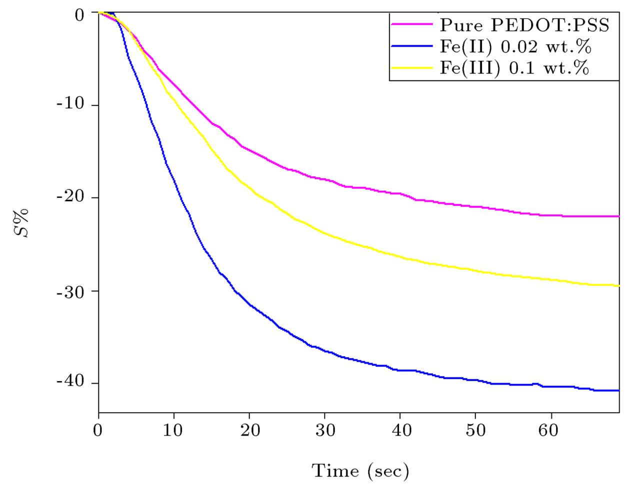

Figure 3. Comparison between the measured response of sensors containing optimum values of Fe(II)(salen) and Fe(III)(salen) dopants and that of pure PEDOT:PSS.

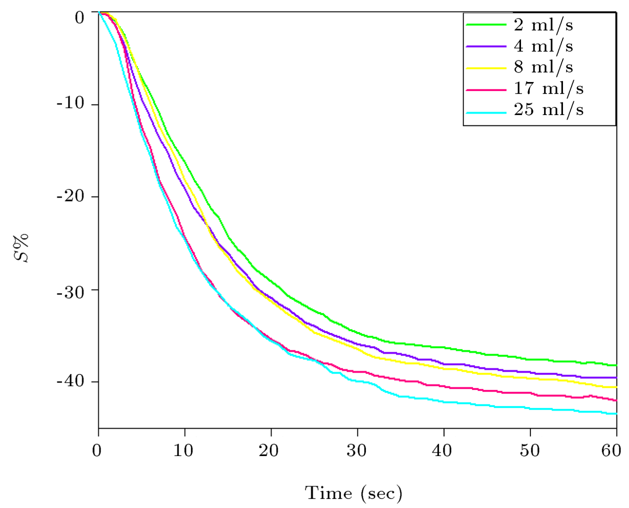

Figure 4. The effect of CO gas flow rate on the measured response of PEDOT:PSS with 0.02 wt.% Fe(II)(salen).

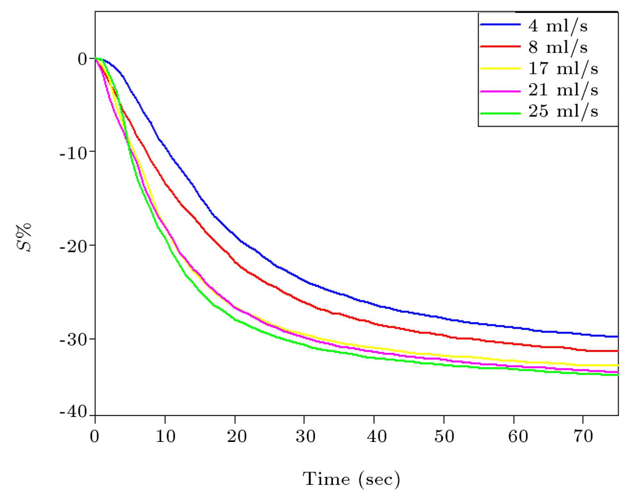

Figure 5. The effect of CO gas flow rate on the measured response of PEDOT:PSS with 0.1 wt.% Fe(III)(salen).

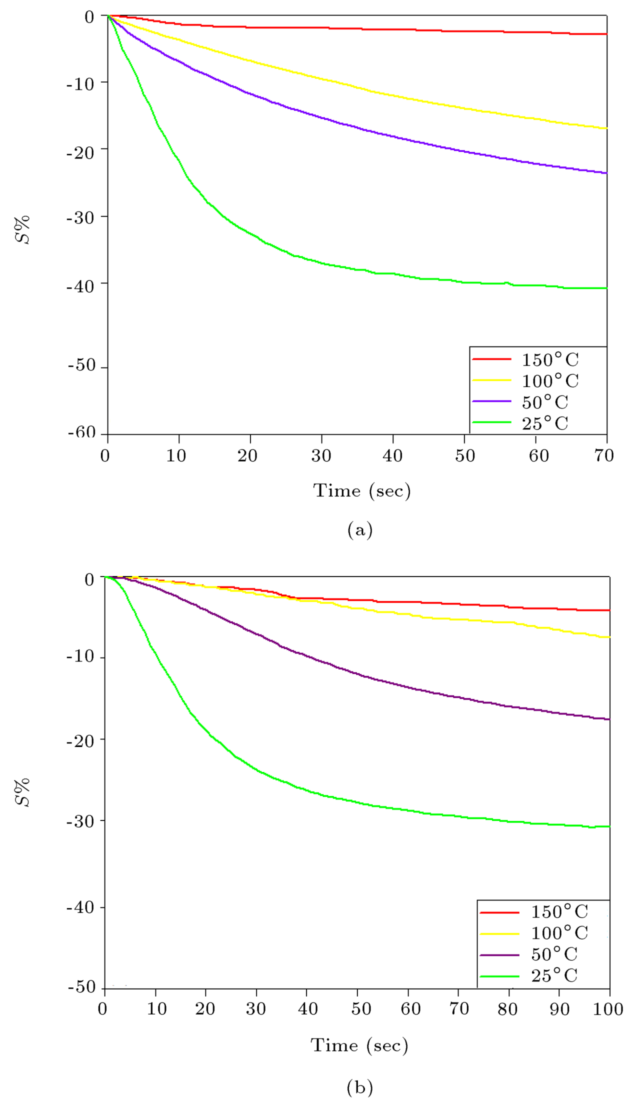

Figure 6. The measured response of sensors at different testing temperatures and for different doping types: (a) Fe(II)(salen) and (b) Fe(III)(salen).

on the response of the measured sensors is shown in Figure 6. According to the results depicted in Figure 6, the response decreases as temperature increases. These results are also in agreement with those obtained by Tai et al. [27]. The gas-sensing mechanism in conductive polymers involves two steps: the adsorption of gas molecules in sensing material and the reaction between them [28]. Temperature can influence both the absorption and reaction steps. At low temperatures, adsorption predominates desorption. However, increasing temperature will reduce the number of gas molecules bound to the film surface and shift the equilibrium to desorption [27–29]. Moreover, at higher temperatures, the reaction step is accelerated [28]. Here, the sensor response reduces as temperature increases, which shows that the adsorption/desorption is the predominant step in the sensing mechanism.

4.2. LSSVM modeling results of gas response prediction

The experimental data presented in Figures 2 to 6 were used to construct a general and precise model to estimate the sensor response in different testing conditions at different levels of dopants. In doing so, temperature, gas flow rate, dopant content, and exposure time were taken as the input parameters, and the absolute values of the sensor response were assigned as the target (output) variable. During the model implementation, the experimental data were randomly divided into two sets of training and testing data. For training the model, 65% of data points were used and the remaining data were applied to assess the proposed model capability to predict the unseen data. MATLAB software was utilized for programming. The values of model parameters, i.e., γ and σ, significantly affect the performance of the model. In the present study, the optimum values of parameters were achieved by applying the Coupled Simulated Annealing (CSA) algorithm [30]. The predicted optimum values of γ and σ were found to be 5.25×10^{10} and 0.3257 for Fe(II)(salen) and 1.16×10^{10} and 0.9896 for Fe(III)(salen) dopants, respectively. In order to evaluate the precision of the developed model, several statistical parameters including coefficient of determination (R^2), Root Mean Square Error (RMSE), and Average Absolute Relative Deviation (AARD) are considered as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (p_i - t_i)^2}{\sum_{i=1}^{N} (p_i - \bar{t})^2}, \tag{8a}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (p_i - t_i)^2}{N}}, \tag{8b}$$

$$\%AARD = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{(p_i - t_i)}{t_i} \right|, \tag{8c}$$

where p_i is a predicted value, and t_i is the corresponding experimental value. $\bar{t}$ is the average value of the experimental data. The values of statistical parameters for the constructed models are reported in Table 1.

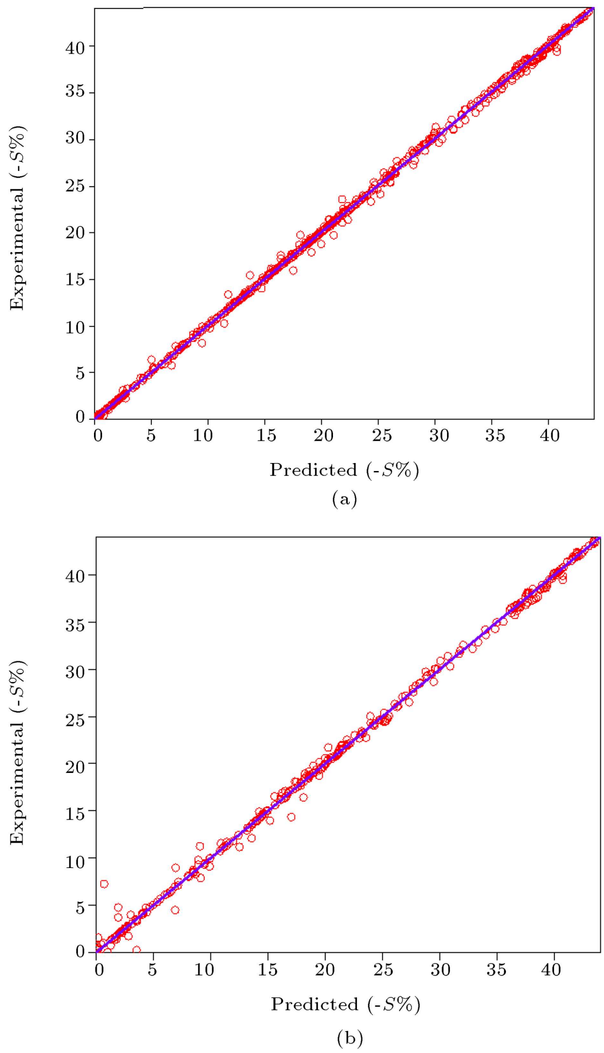

Figure 7. Predicted CSA-LSSVM model against experimental data for Fe(II)(salen): (a) Training data and (b) testing data.

According to the results summarized in Table 1, the high R^2 values and low values of RMSE and AARD show that the predicted error is quite low and the model is reliable and accurate for the prediction of gas sensor responses. Figures 7 and 8 show plots of the developed model predictions against the experimental (target) data. As is shown in these figures, the data points lie on a line with a unit slope, showing that the proposed modeling approach is robust and precise.

Table 1. The values of statistical parameters of the developed Least Square Support Vector Machine (LSSVM) model for gas response prediction.

	Fe(II)(salen)		**Fe(III)(salen)**	
Statistical parameters	**Training data**	**Testing data**	**Training data**	**Testing data**
R^2	0.9994	0.9987	0.9982	0.9984
% AARD	1.8252	6.2411	3.2404	5.6233
RMSE	0.3302	0.4522	0.4406	0.4201

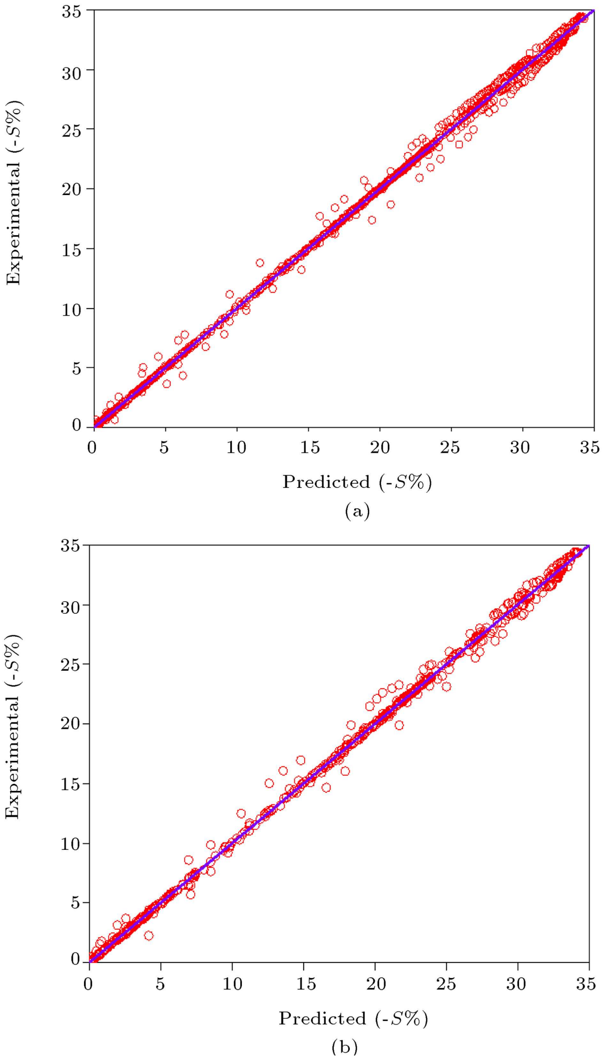

Figure 8. Predicted CSA-LSSVM model against experimental data for Fe(III)(salen): (a) Training data and (b) testing data.

These results imply that the gas response predictions by LSSVM models are in very close agreement with experimental data for all the training and test sub-datasets.

5. Conclusion

In the current research, the CO gas response of the PEDOT:PSS-based gas sensor with different contents of Fe(salen) dopants was studied at different temperatures and gas flow rates. The main results are given below:

- The presence of Fe(salen) dopants has a great impact on the gas response of PEDOT:PSS-based thin films. The maximum response is obtained at the dopant content of 0.02 wt.% and 0.1 wt.% for Fe(II)(salen) and Fe(III)(salen), respectively;
- The PEDOT:PSS gas sensor with the optimum content of Fe(II)(salen) (0.02 wt.%) shows the highest gas response in comparison with pure PEDOT:PSS and the sensor with Fe(III)(salen) dopants. Hence, the PEDOT:PSS-based sensor containing 0.02 wt.% of Fe(II)(salen) can be a good choice for the CO gas sensor;
- The response of the developed gas sensors to CO gas increases by increasing the gas flow rate, while it decreases with an increase in the ambient temperature;
- A modeling approach based on the Least Square Support Vector Machine (LSSVM) framework was proposed for the prediction of the response of the gas sensors at different dopant contents, flow rates, and testing temperatures. All in all, the model reproduced the experimental data with excellent accuracy.

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