Chemiresistor gas sensors based on conductive copolymer and ZnO blend – prototype fabrication, experimental testing, and response prediction by artificial neural networks

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ABSTRACT

Nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), and their derivatives generally known as nitrogen oxides (NOx) are primary pollutants in the atmosphere originated from natural and anthropogenic sources. The paper presents investigation of electric performance of novel chemiresistor NOx gas sensors. A novel material was utilized for active sensing layer-conductive copolymer and zinc oxide blend. The main advantage of the presented solution is low-cost and environment-friendly production. A series of this type of sensors was manufactured and tested experimentally. During the tests, the gas flow was controlled and signals of sensor responses, temperature, and humidity were computer-acquired using LabVIEW program. Sensor behavior for different thicknesses of the active layer has been investigated and interpreted. The research revealed that the electrical resistance of the sensors has changed in predictable manner depending on the gas concentrations. A recurrent artificial neural network architecture is proposed as a mathematical model to classify sensor responses to gas concentrations variation in a time-dependent regime. In this research, an enhanced method for gas concentration prediction is proposed using non-linear autoregression model with exogenous input (NARX). The performed simulations show good agreement between simulated and experimental data useful for predictions of sensor gas response.

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1 Introduction

Organic thin films devices have recently attracted significant attention for a wide variety of uses including printing inks, colorants, photoconductors, solar cells, electrochromic, and gas sensors. Microfabrication of gas sensors based on nanostructured materials and very low power consumption are indispensable technologies for modern society. Such sensors are used in various sectors including the mining industry for detection of mine methane, automotive for detection of combustion gases from vehicles, in medical applications for bioelectronic noses that mimics human olfaction, in air quality monitoring for estimation of greenhouse gas emissions. Chemical sensors are also used for the detection of gas, for water and soil pollutants, temperature, speed, magnetic field, and emission control. A chemical sensor is an electronic circuit element that changes in physical and chemical structure, when it absorbs in the surface layer a chemical stimulant. The electrical properties of the sensors are thus changed and subsequently converted into measurable quantities. Main pollutants such as nitrogen oxides (NOx), carbon dioxide (CO2), sulfur oxides (SOx), hydrocarbons (HC), carbon monoxide (CO), particulates matter (PM), lead (Pb), and volatile organic compounds (VOCs) can negatively impact climate and human health, causing respiratory illness. The industrial and high temperature combustion processes, the indiscriminate hazard chemical poison use in agriculture related to the continuous increase in technological progress, affect atmospheric characteristics leading to air pollution. Urban air pollution related to nitrogen dioxide NO2 is a worldwide concern. Long-term exposure to NO2 results in adverse human health consequences and causes many diseases of the respiratory and cardiovascular systems. Biological factors and genetic predisposition determine individual vulnerability and susceptibility. Pollution hazards influence individual vulnerability by age, sex, education, socioeconomic status, location residence, and occupation. Air pollution has a negative impact on people’s health and well-being, particularly on the most vulnerable populations such as children, women, and people living in developing countries. The economic costs of air pollution are enormous for sustainable development. Economic growth that accepts air pollution and ignores public health and environmental impacts is unethical and unsustainable. In addition, health care costs due to pollution-related diseases account for 7% of the national health budget [1]. The release of toxic chemicals and vapors is also an alarming threat to the ecosystems of the biosphere. Clean air and water are important elements for life on Earth, and air pollution also threatens the sustainability of Earth’s environment. The alarming trend of contaminant concentrations requires early detection and monitoring in urban environment. Passive diffusion tube sampling methods have been adopted to study the spatial and temporal variability of NO2 concentrations. The automated measurements applied to pipe extraction, preparation, and co-location are important considerations in assessing the measurements validity. Urban area hotspots for NO2 pollution provide precise spatial details of surrounding sampling sites and additional information on pollutant distribution, dispersion, and human exposure through urban environments. A single NOx diffusion tube approach facilitates the identification of NO2 hotspots by providing precise spatial details of where air quality is deteriorated through sampling over a 12-month period and covering all seasonal variability [2]. A bimodal distribution of NOx concentration and nitric oxide (NO) is related to seasonal variation and daily average [3]. Comparing trends in concentrations of these pollutants over diurnal or seasonal cycles, the temperature influences the NO2/NOx ratio. This data ratio is in line with that of several urban areas in the world [4]. Atmospheric Environment Automated Monitoring Station provides data on temporal and spatial variations useful for the estimation of NOx concentrations and their relationships with various pollutants and meteorological factors. A more relevant industrial chimneys and motorized vehicles presence contribute to an high concentration of NOx vapor. Diesel vehicle emissions are responsible for large amounts of nitrogen compounds in urban areas, especially when they move slowly and showed a potential increase in damage human health [5]. Many approaches in literature, comparing urban environments, provide an initial air quality and air pollution screening tool to support air quality assessment studies. The application of these empirical models for estimating the conversion rate from NOx to NO2 is the key for improving air quality and to reduce the potential impact on human health and ecosystems with air pollution reduction plans.

The use of accurate monitoring systems and gas sensors has a crucial role for gas detection in
industrial environment, but also in buildings where a good air quality is required. These devices are usually equipped with a chemically selective layer that interacts with its surroundings as a sensor layer. As a result of the interaction, the sensing layer changes its properties, e.g., conductivities resulting from the adsorption of the analyte molecule on the surface of such a layer. Organic semiconductor gas sensor based on advanced nano- and microfabrication technology has the advantages in manufacturing, cost and room temperature, compared to other semiconductor gas sensors. The nanotechnologies contribution consists in new materials developing with a large active surface area for the absorption of gaseous molecules to improve sensing performance. Carbon-based nanomaterials such as graphene have been widely used for NO2 sensors at room temperature. Numerous approaches have confirmed efficiency of electrically conductive polymeric materials and graphene composite due to their excellent conductivity and large surface area, applied to gas sensor but also to electrochemical biosensors [6–10]. In recent laboratory studies, a series of polypyrrole/graphene oxide reduced and polypyrrole/graphene oxide covalently bound nanocomposites with 4-carboxybenzene diazonium aryl salt nanocomposites have been used to evaluate their resistive sensitivity chemical properties for detecting NO2 gases at room temperature. The synthesis of the nanocomposite ppy-graphene has been obtained by the addition of graphene in the polymeric solution and in the polymerization reaction process. Graphene and carbon-based nanofillers, in general, have been provided to improve the gas detection properties and to boost both sensitivity and specificity; however, the agglomeration of graphene affects the polymer matrix [11]. In addition, other compounds have been tested for the same application. Composites of carbon nanotubes and ZnO (CNTs&/ZnO) have exhibited better electrical performance under CO exposure with the improvement of the response time of 60% compared with ZnO [12]. ZnO nanostructures are ideal chemical compounds for operating sensing and selecting applications due to their multifunctional properties such as as high surface, high crystallinity, and organized molecular structure. In the recent development, ZnO nanocomposites for their temperature, stability, and flexibility have been applied to product NO2 gas sensors. These features led to many attempts to optimize the semiconductor’s properties for gas sensing applications by creating new morphologies and crystallographic shapes of ZnO [13]. Metal oxides such as ZnO and SnO2 rather cheap and simple had a considerable diffusion in the past [14]. Subsequently, alternative oxides were developed as active sensing layers for the detection of gas analytes, starting from oxides such as CuO, Ga2O3, TiO2, CoO, and binary systems obtained by coupling of other elements to oxides, such as NiO–Au or TiO2–Pt [15]. Furthermore, sensors equipped with mixed oxides such as BaT iO2 and non-stoichiometric oxides (Sn1-xT ixO2, Y:Ba:Cu:O, Bi:Sr: Ca:Cu:O) showed greater sensitivity and selectivity [16]. Semiconductor-based chemiresistor sensors are the most investigated sensor structures for the detection of combustible and toxic gases changing their electrical resistance as a result of the interaction between the semiconductor and the tested gas atmosphere [17]. Two-dimensional layered MoS2 nanostructure-based gas sensor synthesized by a solvothermal method for formaldehyde (HCHO) gas sensing applications and the poly (para-phenylene terephthalimide)—NiO@CuO gas sensor for the detection of NH3 achieved at room temperature were reported in [18, 19]. For detecting ppb-level NO2 concentrations at room temperature, and taking advantage from the influence of UV radiation on temperature and resistivity of ZnO layer, a novel sensor regenerated by UV light with suitable material of Sol-gel synthesized Al-doped ZnO was introduced in [20]. A portable gas-sensing system which is periodically irradiated with light from a pulsed ultraviolet light emitting diode (UV-LED) was fabricated for sensing ppb-level NO2 gas made of a composite iron oxide/multi-walled carbon nanotubes/tungstenoxide (Fe2O3/MWCNTs/WO3) material that was produced by a one-pot polyl method followed by metal organic decomposition (MOD) as reported in [21]. The artificial neural networks (ANNs) are bio-inspired computing systems for data processing [22] and have found wide a large field of applications related to sensors and sensing techniques, including gas sensors, thermal conductivity, water hybrid nanofluid, tellurite glass system [23–26]. The most common application are predictions based on sensor arrays input data, e.g., identification of gas mixtures, lubricant content or structure stress and utilizing of ANNs for calibration processes [27–32]. The electronic noses (ENOSE) system is capable of monitoring propane-2-ol, methanol, acetone,
ethylmethylketone, hexane, benzene, and xylene using an array of sensors and ANNs in environmental monitoring [33].

Similar applications regarding sensor response prediction by artificial intelligence techniques are presented in [34–37]. An empirical formulation of the neural network model combines Least Absolute Selection and Shrinkage Operator (LASSO) and Regression and Nonlinear Autoregressive (NARX) models to regulate the data collected by the micro-air quality detector. LASSO-NARX model, is used for testing the correlation between the concentration of air pollutants and its influencing factors highlighting their relationship. The predicted value of each pollutant concentration in the LASSO regression and the LASSO-NARX model is constructed using the NARX neural network [38].

The following paper presents investigation on a completely innovative material utilized for active sensing layer-conductive copolymer and ZnO blend. In the present research, four chemiresistor gas sensors were fabricated and characterized by different thickness of the active sensing layer based on conductive copolymer and ZnO blend in laboratories of the Silesian University of Technology in Gliwice, Poland (Fig. 1 presents the microscopic images). All the developed sensor structures in the form of chemiresistors were tested experimentally. Figure 2 is the photograph of the chamber in which the four manufactured sensors were exposed to the flowing gas mixture. For this purpose, a gas server dosing gas analyte with a known concentration was used, through computer-controlled flow meters. The effect of the gas atmosphere on the structures made, manifested by a change in the resistance of the sensor layer, was measured using a precise multi-channel automatic resistance meter. In parallel, parameters of the gas atmosphere such as humidity and temperature were monitored. The entire setup was computer controlled. Sensor behavior for different thicknesses of the active layer has been investigated and interpreted.

The experiments revealed that the electrical resistance of the sensors has changed significantly depending on the gas concentrations. The next step was to investigate the predictability of the developed sensors. The goal was to find a numerical model that would mimic the behavior of the discussed chemoresistive gas sensors. Such model allows to better understand the sensor operation and perform further tests only by simulation. Combining gas sensors performance and data analysis allows to increase the efficiency of the sensing devices utilization [23–26].

The novelty of the presented research has been addressed in a numerical model that mimics the described new type of gas sensor. A nonlinear autoregressive network with exogenous inputs

Fig. 1 The interdigital transducers examined under the microscope Nikon Eclipse E2000 (objective 5 × 0.15) on the left and SEM (Inspect S50, FEI, USA) image of elaborated organic–inorganic sensing layer on ITD substrate on right side.
(NARX) has been trained to mimic the behavior of the considered chemiresistor sensors. Such approach has allowed to have an efficient prediction of the sensor response to the given time-dependent concentrations of NOx, temperature, and humidity. The goal was to determine a model that simulates the fabricated sensors as accurately as possible. For this reason, a model optimization procedure was applied. In finding the best possible neural network, hyperparameter optimization was performed considering two criteria: minimizing the mean-square error between the predicted and experimentally measured sensor responses and minimizing the model itself (the number of neural neurons). In this way, relatively simple and accurate predictor was obtained and tested. Tests were performed using data with white Gaussian noise added to ensure the model that had the necessary generalization abilities and was not overfitted.

Details about the fabrication process of the chemiresistor sensors are given in Sect. 2. Section 3 contains the description of the experimental setup and measured results. Section 4 covers the general information about the applied approach for sensor response prediction, the ANN training, and testing. Section 5 closes with the conclusions.

2 Sensors fabrication

Chemiresistor sensor can be easily manufactured with common and well-known laboratory techniques, using low-cost and novel organic–inorganic material blends, which when applied to the substrate in the form of a thin layer, actively change the electrical resistance in the presence of different gaseous atmospheres. Chemoresistor-based array can be integrated as organic transistors and organic semiconducting materials (defined as an organic field-effect transistor (OFET)), made on flexible and stretchable substrates requiring a sensor device structure and flexible transducers for electronic biosensing. In our case, the chemiresistors were prepared on n-doped (0.02 Ω/cm) Czochralski (CZ)-grown silicon wafer with 195 nm thick thermal oxide (SiO2). The interdigital electrodes were formed on the top of the dielectric layer by physical vapor deposition (PVD) process. The deposition of thin chromium layer (20 nm) by thermal evaporation was made to improve the adhesion of thermally evaporated gold thin films (100 nm). The interdigitated electrodes were realized by photolithography process. In this work, 3 × 10 μm interdigital transducers were used, in which the electrode width was 3 μm, and the gap between the electrodes was 10 μm. After the process of washing and preparation of the substrates for the application of the sensor layer, they were inspected under the microscope Nikon Eclipse E2000 with objective LU Plan Fluor 5 × 0.15, and then, the active layer was deposited on the substrate. A conductive comb-graft copolymer called SilPEG H6 was dissolved in chloroform (CHCl3, POCh)—2.5 mg per 1 ml was sonicated and stirred for 30 min. ZnO nanomaterial (1 mg), which was obtained by hydrothermal method, was also dispersed in chloroform (5 ml) for 30 min using the ultrasonic. ZnO and the solution of the graft comb copolymer were mixed together under ultrasonic dispersing for 10 min [39–42]. The obtained dispersion of the organic–inorganic blend was applied on each substrate using drop coating method in ambient condition. A wire bonder (53XX-BDA, F&K DELVOTEC) was then used to provide electrical connection between the elaborated sensors and the rest of the measuring system, using 25 μm gold wire. Morphology and topography
characterization for obtained blend thin film and ZnO nanomaterial distribution was made using Scanning Electron Microscopy Inspect S50, FEI, USA (Fig. 1).

3 Sensor measurement setup

3.1 Measurement gas chamber

The gas-sensing measurements were carried out by placing the chemiresistor gas sensors in the gas chamber. The measurement gas chamber, with 4 mm diameter inlet and outlet pipes, has been made of chemical-resistant materials such as polytetrafluoroethylene (PTFE) and stainless steel. In the measuring chamber, quartz windows were used, through which the structures were illuminated with UV LEDs ($\lambda = 390$ nm) as illustrated in Fig. 2 on the left. Four chemically resistor structures of gas sensors (Fig. 2, right) were placed on a base, which was equipped with a Pt100 sensor, in order to monitor temperature changes.

3.2 Experimental characterization

The characterization of gas sensors and gas measurement systems requires a versatile gas mixing apparatus constituted by gas mixing, humidification, and gas measurement. The flow of the carrier gas, which here was synthetic air, was controlled by Bronkhorst EL-FLOW mass flow controllers which allow the flow set point to be adjusted. Relative humidity during the measurement was 6%. All measurements were made by stimulating the elaborated sensing structures with LED UV diodes. The temperature in gas chamber was controlled and measured using a proportional integral-derivative (PID) controller SR94 (Shimaden, Tokyo, Japan), and it was 24 °C/room temp. The sensor resistance data were collected and measured by a digital multi-switch unit 34970A (Agilent, Santa Clara, CA, USA) with current source of 500 nA within the range of 100 MΩ. The proposed automated system for performing electrical and gas sensing characterization taking into consideration the gas sensor chamber, data acquisition, and signal pre-processing, is presented in Fig. 3. During the tests, the gas flow (opening and closing valves of synthetic air and NOx) was controlled and signals of sensor responses, temperature, and humidity were computer-acquired using LabVIEW program.

3.3 Measurement setup for gas sensing characterization

For the optical characterization of the sensitive layers toward gas mixtures, a gas test bench was used. The test bench consists of digital mass flow controller interface, gas test chamber with the designed sensors, pressurized gas cylinders, digital interface, PC, and Keithley measurement setup (Fig. 4).

Preliminary to gas-sensing measurements, the gas chamber was illuminated by UV light for 1 or 2 h under synthetic airflow to achieve stabilization of the sensor active surface and a steady baseline resistance. The flow rate across the sensing chamber was set to 200 ml per hour for synthetic air flow meter counter 1 and 200 ml per hour for synthetic air flow meter counter 2 and kept constant for the whole measurement process. After 2 h (circa $0.5 \times 10^4$ s) with three times repetition of flow cycle corresponding to circa 10 h, the chemiresistor gas sensors were exposed to low concentrations of nitrogen dioxide (500 ppb) under constant UV light and dry synthetic air flow. The time plot of the NOx gas and synthetic air flow counter 2 are presented in Fig. 5. For periods when NOx flow was opened, synthetic air counter 2 was closed. Synthetic air counter 1 was always open. Before arriving in the gas sensing chamber, the target gas were mixed first in a gas mixing chamber, which
is at a constant pressure and humidity to avoid interference from humidity and non-uniform pressure. A physico-chemical interaction is created between oxides of nitrogen (NOx) and sensitive materials on substrate of chemiresistors in the presence of UV light. The nitrogen dioxide molecule gets adsorbed on the surface of ZnO/graft comb copolymer, it traps electronic charge from the conduction band of the nanomaterial which results in an increase in the resistance of the sensor.

The sensor response ($R$) is defined by the percentage ratio of the chemiresistor resistances that change on the surface of the gas sensor after and before being exposed to NO$_2$ as shown in the following formula:

$$R = \left( \frac{R_g - R_a}{R_a} \right) \cdot 100\%$$  \hspace{1cm} (1)

where $R_a$ is the measured sensor resistance in synthetic air carrier gas at stationary state and $R_g$ is the sensor resistance measured in presence of the target gas (NO$_2$).

Four sample gas sensors were prepared, with different volume of ZnO/graft comb copolymer deposited as sensitive layer on surface of chemiresistors: 2 µL (sample 1), 4 µL (sample 2), 6 µL (sample 3), and 8 µL (sample 4). In the experiment, the resistance values for the gas response of the sample sensors are measured at various concentrations. All four sensors have showed under nitrogen dioxide and dry synthetic air in the gas chamber response as shown in Fig. 6 where both actual resistance values $R_g$ and relative values $R$ are presented against time. An increase of sensor response can be observed when
increasing the active layer thickness. During the exposure to the concentration of analyte, in our case exposition of NO₂ on sensor substrate, the sensors’ resistances increased nonlinearly. The sensors’ resistances drop in the presence of synthetic air flow.

The operating temperature of gas analyte in the gas mixing chamber was measured by a sensor and recorded during the data acquisition process. The temperature conditions were maintained stable as the temperature changed between 23.5 °C and 24.6 °C, with average value of 23.7 °C. At first stage, the temperature slightly increased by the synthetic air gas injection, than the chamber cooled down during the nitrogen oxide gas flow, as observed in Fig. 7. The probable cause was due to the changing of gas pressure. During the measurements, the UV light constantly illuminated the sensing structures.

The humidity was measured inside the gas mixing chamber. The measured value of humidity oscillated around 3.5%, both during the dosing of the carrier gas and the gaseous analytes, and it was stable throughout the measurements.

4 Artificial neural networks approach and results

4.1 Artificial neural networks

ANNs are bio-inspired computing systems that mimic the principles of operation of an animal brain. ANN is a system of connected units, called artificial neurons, that are basically a mathematical models of biological neurons. Each neuron receives input signals, processes it by a nonlinear function of the weighted sum of the inputs, and outputs the processed information. The model of a single neuron $i$ is presented in Fig. 8. The artificial neuron performs the following function $\phi$: 

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Fig. 6 The comparisons of the transient responses of chemiresistor gas sensors with sensitive layer of ZnO and the graft comb copolymer: a actual sensor resistance values, b relative sensor response values
\[
y_i = \varphi(e) = \varphi \left( \sum_{j=1}^{N} w_{ij}x_j + B \right)
\]

where \(x_j\) \((j = 1, 2, ..., N)\) are the inputs, \(y_i\) is the output, \(e\) is the neurons net value, \(w_{ij}\) is the weight for each input \(j\), \(B\) is the bias, and \(\varphi\) is the neuron’s activation function.

The networks are normally organized by layers of artificial neurons, where the signals go from the input layer, through one or more hidden layers, to the output layer. If the information moves only forward (to subsequent layers), such model is called a feedforward neural network. If there are feedback signals, the networks are considered to be recurrent. The weights \(x_{ij}\) of all the neurons are adjusted in a training process, where the general error of the network’s predictions is minimized. The ANNs are considered as efficient predictors because of their advantages (high resistance to noise and distortion of input signals, ability to identify significant and hard to deterministically describe connections between data) and, therefore suitable to represent complex issues [36, 43, 44].

The numerical tests have shown that the response of the sensor is dependent of the previous states of the sensor. For this reason, nonlinear autoregressive network with exogenous inputs (NARX) was applied as the predictor. If \(Y(t)\) denotes the output of a neural network, where \(t\) is a set of discrete time steps \((t = 0, 1, 2, ...),\) the operation principle of one-step ahead NARX could be described by the following nonlinear function \(F:\)

\[
Y(t + 1) = F(Y(t), Y(t - 1), ..., Y(t - d_y), u(t), u(t - 1), ..., u(t - d_u))
\]

where \(u(t)\) is the input to the network at time \(t\), and \(d_u\) and \(d_y\) are the lags of the input and output, respectively.

### 4.2 Sensors response prediction using artificial neural network approach

The ANN proposed in this paper is developed in order to predict the sensor responses related to manufactured four chemisensors with different thicknesses of the active layer, corresponding to the volume of 2, 4, 6, and 8 \(\mu\)L of the injected blend in function of temperature, humidity, and concentrations of gases. A schematics of numerical model based on neural network is reported in Fig. 9. In this neural network model, the input vector \(u(t)\) is constituted by air and NO\(_x\) concentrations flow,
temperature, and humidity. The target vector $Y(t)$ is constituted by four gas sensor responses.

The experimental data have shown that recurrent neural network is well-suited predictor mathematical model given that the sensor output is dependent on the state of the sensor response in previous time moments. The reference data are a time series that consists of 21,614 data samples with constant time step of 2 s. Two-layered recurrent ANN with single delay, symmetric sigmoid activation function in the hidden layer and linear activation function in the output layer was adapted as the prediction model.

The number of neurons in the hidden layer was optimized, taking into account two criteria – minimal number of neurons (small model) and maximal accuracy. It was assumed that the number of hidden neurons should be between 1 and 30. For every possibility, 500 attempts to train the network were made, from which the most accurate network of given size was chosen. Levenberg–Marquardt algorithm was used for training, where 60% of the reference data were used for training, 20% for testing, and 20% for validation. The accuracy is defined as the average mean squared error (MSE) between the reference and predicted output from five tests where each time a small white Gaussian noise is added to the inputs in order to ensure that the network is not overfitted.

As result of the optimization process, seven Pareto-optimal artificial neural networks were obtained. The Pareto front is presented in Fig. 10, and the performances of the obtained networks are listed in Table 1.

![Prediction model schematics](image)

**Fig. 9** Prediction model schematics

![Pareto front](image)

**Fig. 10** Pareto front

| Number of hidden neurons | MSE     |
|--------------------------|---------|
| 1                        | 0.1928  |
| 2                        | 0.1613  |
| 3                        | 0.1575  |
| 4                        | 0.1345  |
| 5                        | 0.0668  |
| 6                        | 0.0660  |
| 7                        | 0.0380  |
| 8                        | 0.0375  |
| 9                        | 0.0373  |

**Table 1** Parameters of Pareto-optimal networks
Figure 10 indicates that the assumed limits of the domain search of hidden neurons number were sufficient. The accuracy of ANNs bigger than 9 hidden neurons was of irrelevant increase, and no Pareto-optimal network was found for greater number of hidden neurons than 23. The ANN with 9 neurons in the hidden layer was taken for further consideration, as its performance is similar and of the same order of magnitude as of the larger found models. The architecture of the ANN is presented in Fig. 11, and the plot of training performance is shown in Fig. 12. Best validation performance (MSE) of 3.10e-5 was achieved ad epoch 226.

The chosen ANN was tested using input data with white Gaussian noise added to ensure that the model is not overfitted. The time plots with comparison of ANN predictions and targets are presented in Fig. 13. The MSE between the targets and outputs in the test was 0.0388. The achieved compliance between predictions and targets for transient and noisy data can be considered as satisfying. This proves that the novel type gas sensors behave in a predictable manner. A reliable numerical model of the sensors was obtained that can be utilized in future simulations.

5 Conclusion

A novel type of gas sensor chemiresistor sensors based on Copolymer and ZnO blend is presented in this paper. The production involves low-cost materials and well-known laboratory techniques. Experiments revealed that the active layer, based on innovative organic–inorganic material blend, actively changed the electrical resistance for different gas concentrations in a predictable manner. Data acquisition system was used in order to perform electrical and gas sensing characterization to acquire, in real time, the signals of the sensors responses that were dependent on the air and NOx gas flows, as well as on the temperature and humidity in a stainless steel gas chamber. The test stand consisted of digital mass flow controller interface, gas test chamber with the...
fabricated sensors, pressurized gas cylinders, digital interface, and DAQ system. During the tests, LabVIEW program was developed to control all testing parameters and measurements and to manage the transport gas flow rate. An artificial neural network (ANN) was developed in order to mimic the behavior of the tested sensors as accurately as possible. A robust hyperparameter optimization was performed with two criteria – minimal size of the numerical model and its maximal accuracy. The network chosen for consideration, with 9 neurons in the hidden layer, has proven to be of satisfactory accuracy, both in the training process and in the further testing where noise was added to the inputs. Fig. 12 clearly shows that the obtained network has the ability to generalization and has not been overfitted. The utilized gas sensors’ modeling methodology and further strengthening of sensing performances (in terms of sensitivity, response, and recovery time) can ensure the development of large-scale production of sensors to be used for gas pollution detection.

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**Author contributions**

All authors contributed to the study conception and design. Sensor fabrication, experimental setup, and data acquisition were performed by PK and GLS. The processing of data was performed by all authors. Sensor response prediction using artificial neural networks was done by WM and GC. The first draft of
the manuscript was written by PK, GLS, and WM. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest  The authors declare that they have no conflict of interest.

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