Development of a neural network model for predicting the physical and chemical properties of materials from the technological parameters of their formation

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Abstract. A new approach for predicting the physical and chemical properties of materials based on the technological regimes of their formation is proposed. The developed method is applied to predict the response of the sensitive layer of a chlorine sensor based on the polyacrylonitrile film containing silver. The artificial neural network is constructed in the form of multilayer perceptron for predicting the gas sensitivity coefficient based on the technological parameters used for the material formation (mass fraction of the additives, wt.%, the temperature and time of the 1st and 2nd IR annealing steps). The adequacy of the developed model is proved: the root-mean-square error is $\sigma = 0.07$, the correlation coefficient is $R = 0.927$, and the mean-square error of the forecast is $\sigma_v = 0.11$. The sensitivity of the model for the mean square error of all the data is estimated to be $s = 0.09$.

1. Introduction
The prospect of using films of electrically conductive organometallic polymeric materials in chemical and biological sensors is the reason for intensive study of these properties of materials. Films of metal-containing polyacrylonitrile (PAN) are successfully used as a gas-sensitive layer of gas sensors operating at a temperature in the range of 17 – 32 °C [1]. The usage of PAN films is based on the adsorption-resistive effect, which consists in changing the resistance of the film material with selective absorption of gas molecules. A feature of PAN films is the ability to form polymer structures with a system of conjugated double bonds along the chain of macromolecules during heat treatment, which are characterized by increased electrical conductivity [2]. Thus, along with surface processes, structural changes in the linear polymer of PAN play an important part in the sensory response formation.

One of the problems that make it difficult to determine the criteria of the targeted synthesis of materials for solid-state gas sensors is the insufficient study of the effect of technological parameters of the material formation of PAN films obtained by the pyrolysis method under the influence of incoherent IR radiation on their electric, physical and gas sensitive properties. The development of technological bases for the controlled formation of nanocomposite films of metal-containing PAN is a laborious process for identifying the non-linear dependencies of the gas sensitive properties of PAN films on the given technological parameters [3-5].
2. Methodology
Films of the composition of Ag-containing PAN were formed by pyrolysis under the influence of incoherent IR radiation [6]. IR annealing was carried out using different temperature regimes in two stages. The first stage serves for the preliminary structuring of the PAN with the formation of a system of $C = N$-conjugated bonds at a temperature of 250 °C and 300 °C. The second stage of annealing, passing at a temperature of 350 and 450 °C, leads to the formation of also $-C = C$-bonds [7]. The time of exposure to IR radiation at each temperature varied $(2 \div 20$ minutes). The mass fraction of the modifying additive varied in the range of $0 \div 3$ wt. %

The construction of an analytical model of a complex object is problematic, and sometimes impossible, and the relationship and dependence of the physicochemical properties of objects on the given parameters is complex and nonlinear. The neural network approach is used to describe complex relationships between numerous factors or parameters of obtaining objects and their physicochemical properties [8-9]. The prediction of properties of objects using structural data by the neural network approach has been successfully applied in various fields of physical research. For example, to predict the temperature in a storage tank for liquids using solar energy [10], the neural network model was used in the form of a multilayer perceptron with back propagation of the error.

To predict the properties of materials using neural network modeling, one can single out the general sequence of steps required for any modeled object (figure 1).

![Figure 1. Algorithm for modeling of physical and chemical materials properties using neural networks.](image)

3. Results
As a method of a neural network constructing for analyzing the experimental data, the method of constructing a neural network in the form of a two-layer perceptron is used (figure 2). The neural network contains 5 input neurons and 1 output. The neural network was trained using an algorithm for back propagation of the error.

Each input neuron corresponded to one of the technological parameters (mass fraction of the additive (mass%), temperature and time of the 1st and 2nd stages of IR annealing). The output neuron corresponded to the predicted property ($S$, rel.). The adequacy of the synthesized models was proved: the standard error of $s_i = 0.07$, the correlation coefficient $R = 0.927$, and the mean square error of the forecast $s_v = 0.11$. The sensitivity of the model was estimated for a standard data error of $s = 0.09$.

The correlation coefficient $R$ determines the attributable fraction of the spread, $R^2$ is the fraction of the total spread relative to the gas sensitivity $S$, due to regression ($R^2 = 0.86$). The fact that the model explains by 86% the spread of data relative to the average, allows us to speak about the reliability of the model.
The root-mean-square errors of training $s_t = 0.07$ and test, $s_v = 0.11$ samples are approximately the same, which excludes retraining of the network. The accuracy of the calculations in the "learning" group and the "test" subgroup is the same (this is the forecast power), which indicates the stability of the model.

![Figure 2. Structure of neural network.](image)

The sensitivity of the model was estimated by means of the mean square error of all data $s = 0.09$. An alternative way to verify the adequacy of the model is to test it.

The equation of the correlation dependence between the calculated and experimental values of the gas sensitivity of a silver-containing PAN is computed: $S_{\text{pred}} = 0.878S_{\text{exp}} + 0.078$. The visualization of the equation is shown in figure 3.

![Figure 3. Correlation of the calculated and experimental values of the gas sensitivity coefficient to chlorine of Ag-containing PAN films](image)

The optimum set of technological parameters for fabricating the Co-containing PAN films with the best values of gas-sensitivity to Cl$_2$ is established as follows: $\omega(\text{Ag}) = 0.05$ mass. %, $T_{\text{drying}} = 160$ °C, $t_{\text{drying}} = 30$ minutes, $T_{\text{IR-annealing1 phase}} = 250$ °C, $t_{\text{IR-annealing1 phase}} = 2$ minutes, $T_{\text{IR-annealing2 phase}} = 350$ °C, $t_{\text{IR-annealing2 phase}} = 28$ minutes.

Thus, a synthesized neural network can be used to predict the value of the gas sensitivity coefficient of Ag-containing PAN films in order to create an effective low-temperature gas sensor.

Experimental verification of the synthesized model was carried out (see table 1).
Table 1. Tests result of the synthesized model.

| ω (Ag), % | $T_{drying}$ | $T_{IR\text{-annealing}1}$ | $T_{IR\text{-annealing}2}$ | Gas Sensitivity $S$, r.u. | Absolute and relative error |
|-----------|-------------|-----------------|----------------|-----------------|---------------------------|
|           | $T_{drying}$, °C – min | $T_{IR\text{-annealing}1}$, °C – min | $T_{IR\text{-annealing}2}$, °C – min | Prediction | Experiment | Δ | δ, % |
| 0.05      | 160 – 30 | 250 – 28 | 0.75 | 0.69 | 0.06 | 8 |
| 0.75      | 160 – 30 | 300 – 20 | 0 | 0 | 0 | 0 |
| 0.75      | 160 – 30 | 150 – 3 | 400 – 2 | 0.13 | 0.15 | 0.02 | 13 |

4. Conclusion
A methodology for the synthesis of a neural network model has been developed for predicting the physical and chemical properties of materials taking into account the technological parameters of their formation. The developed method was used to predict the response of the sensitive layer of a chlorine sensor based on polyacrylonitrile containing silver.

It was shown that the use of the neural network approach allows reducing experimental work and establishing optimal technological parameters for obtaining gas sensitive materials to create efficient gas sensors.

References
[1] Bednaya T A, Konovalenko S P, Semenistaya T V, Perov V V and Korolev A N 2012 Izvestiya Vysshikh Uchebnykh Zavedenii. Electronica. 4 66 (In Russian)
[2] Jing M, Wang C, Wang Q, Bai Y and Zhu B 2007 Polym. Degrad. Stabil. 92 1737
[3] Semenistaya T V, Petrov V V, Kalazhokov K K, Kalazhokov Z K, Karamurzov B S, Kushkhov K V and Konovalenko S.P. 2015 Surf. Eng. Appl. Electrochem. 51 9
[4] Konovalenko S P and Semenistaya T V 2013 Izv. Sfedu. Eng. Sci. 1 178 (In Russian)
[5] Semenistaya T V, Petrov V V, Bednaya T A and Zaruba O A 2015 Mater. Today: Proc. 2 77
[6] Konovalenko S P, Bednaya T A, Semenistaya T V, Perov V V and Maraeva E V 2012 Inz. Vestn. Dona 4 chapter 2 URL:jvdon.ru/magazine/archive/n4p2y2012/1356 (In Russian)
[7] Zemtsov L M and Karpacheva G P 1994 Polym. Sci. 36 919 (In Russian)
[8] Kruglov V V and Borisov V V 2001 Iskusstvennye Nejronnye Seti. Teoriya i Praktika. (Moscow: Gorjachaja linija) (In Russian)
[9] Himmelblau D 1975 Prikladnoe Nelinejnoe Programmirovanie (Moscow: Mir) (In Russian)
[10] Géczy-Vig P and Farkas I 2010 Solar Energy 84 801