Modeling of Cu Doped Cobalt Oxide Nanocrystal Gas Sensor for Methane Detection: ANFIS Approach

A. Ahmadpour1, Z. Sheikh Mehrabadi1, J.R. Esfandyari2* and M. Koolivand-Salooki2

1Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Khorasan, Iran
2The Technical teacher of saveh education office, saveh, Iran
3Department of Chemical Engineering, omideh beranch, Islamic Azad University, omideh, Iran

Abstract

In this paper, Nano-sized copper-cobalt compound oxide powders have been prepared by sol-gel technique with different mole ratios of Cu/Co (from 0.00 to 0.15); Detection of the methane gas, the most chemically stable hydrocarbons, is done. The structural properties and morphology of powders were studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM). XRD analysis confirms that Co3O4 and (CuO, CoO) phases have been formed and mean grain size were decreased with increasing dopant (from 28 to 24 nm). According to TEM images it was found that the particles have cubic morphologies with nearly uniform distribution. Then an adaptive neuro-fuzzy inference system (ANFIS) models have been utilized for prediction of sensitivity values of the corresponded sensor. The results of ANFIS model show that the independent predicted Sensitivity values (S) compared to the measured target values have a good agreement. And also, high coefficient of sensitivity values of the corresponded sensor. The results of ANFIS model show that the independent predicted sensitivity values (S) compared to the measured target values have a good agreement.

Keywords: Nano particles; Cu/Co; ANFIS; XRD; TEM; FTIR

Introduction

Methane (CH4) is a major component of the widely used natural fuel gases in the industry and the private household. Explosion will occur when its concentration in air reaches to 5-16% (v/v); therefore the monitoring of CH4 in the industry is very important for safety reasons. In addition, it is also one of the greenhouse gases which so it needs to be monitored. However, CH4, is relatively difficult to detect at ambient conditions because its chemical reactivity is relatively low. The commonly used techniques for CH4 detection include gas chromatography (GC) [1-9], semiconductor devices [10-21], optical fiber sensors [22], electrochemical methods [23-24], and biochemical methods [25, 26].

Many Nano-sized pure and doped semiconducting oxides have been used for gas sensors [27-30]. Use of Nano-materials is interesting because of much greater surface area to the bulk ratio rather than course materials. In addition, when the grain size reduce to nanometer, especially when the dimensions become less than two times of the space-charge depth, a large fraction of atoms which will present in the surface and the surface properties become dominant. So, materials conduction type turns to surface conduction type [31-33]. The sensing mechanism depends on the changes in surface conductivity which is resulted from chemical reaction between target gases and the absorbed oxygen on the surface of the Nano-sized metal oxide. Consequently, it is important to enhance the rate of chemisorptions and surface reaction. Co3O4 is most active catalyst for oxidation of the methane [34]. So, it is a good candidate for the methane gas sensor. Addition of second component as doping is becoming one of the most interesting methods for optimization of the gas sensing properties in this type of sensors. These additives can act as catalysts in surface sites for adsorption of oxygen and detected gas or as promoters of the gas sensing characteristics [35]. The copper oxide has good catalytic activity for oxidation of the methane [34], so it was used as dopant for the methane gas sensor. For this reason, in this research, Nano-sized Cu-doped Cobalt oxides with different concentrations of the dopant have been prepared by the sol-gel method for the methane sensor application.

Material and Methods

The present paper covers an ANFIS modeling and experimental study of the gas sensing of the copper-cobalt compound oxide Nano particles. Experimental measurements have been made and Nano-sized powders have been prepared by the sol-gel technique with different mole ratios of the Cu/Co (from 0.05 to 0.15) for detection of the methane gas. The structural properties and morphology of the powders were studied by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM).

Adaptive network based fuzzy inference system

The ANFIS is a fuzzy Sugeno model placed in the framework of adaptive systems to facilitate learning and adaptation [36]. Sugeno type fuzzy inference systems (FIS) use a combination of least-squares and back propagation gradient descent methods, along with a hybrid learning algorithm to identify the membership function parameters and fuzzy IF–THEN rules based on a single output or singleton [37].

ANFIS represents a useful neural network approach for the solution of function approximation problems [38].

ANFIS structure

For simplicity, it is assumed that the fuzzy inference system under consideration has two inputs and one output. The rule base contains two fuzzy if-then rules of Takagi and Sugeno’s type [39] as follows:

Received October 31, 2011; Accepted February 22, 2012; Published February 27, 2012

Citation: Ahmadpour A, Mehrabadi ZS, Esfandyari JR, Koolivand-Salooki M (2012) Modeling of Cu Doped Cobalt Oxide Nanocrystal Gas Sensor for Methane Detection: ANFIS Approach. J Chem Eng Process Technol 3:124. doi:10.4172/2157-7048.1000124

Copyright: © 2012 Ahmadpour A, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
If x is A and y is B then z is f(x, y)

Where A and B are the fuzzy sets in the antecedents and z = f(x, y) is a crisp function in the consequent. f(x, y) is usually a polynomial for the input variables x and y.

Consider z = f(x, y) is a first-order Sugeno fuzzy inference system, which contains two rules.

Rule 1: If x is A1 and y is B1, Then: f1 = a1 x + b1 y + c1
Rule 2: If x is A2 and y is B2, Then: f2 = a2 x + b2 y + c2

ANFIS structure contains five layers excluding input layer.

Layer 0 is the input layer. It has n nodes where n is the number of inputs to the system.

Layer 1 is the fuzzification layer in which each node represents a generalized bell curve membership function value of a linguistic term as follows:

$$\mu_A(x) = \frac{1}{1 + \left(\frac{x - c_i}{a_i}\right)^{2n}}$$ (1)

Each node in Layer 2 provides the strength of the rule by means of multiplication operator. It performs AND operation.

Layer 3 is the normalization layer which normalizes the strength of all the rules according to the following equation:

$$O_{3j} = \frac{w_j}{w_1 + w_2}$$ (2)

Layer 4 is a layer of adaptive nodes. Every node in this layer computes a linear function where the function coefficients are adapted by using the error function of the multilayer feed-forward neural network.

Layer 5 is the output layer whose function is the summation of the net outputs of the nodes in Layer 4. The output f is computed as follows in Figure 1:

The first layer, every node i in this layer is an adaptive node with node function in Equation 1:

$$\mu_{Ai}(x) = e^{-((x-x^*)/\sigma^2)}$$ (3)

Where {x*} are σ premise parameters updated through hybrid learning algorithm and x is input variable. At least in the basic ANFIS method these parameters are not adjustable.

The second layer calculates the firing strength for each rule quantifying the extent which any input data belongs to that rule. The output of the layer is the algebraic product of the input signals as can be given as: [40-42]

$$O_{2j} = \omega_j = \mu_{A1}(x_1) \times \ldots \times \mu_{An}(x_n)$$ (4)

Figure 2 shows the ANFIS structure of T, Q and Ratio Cu/Co values as the three input parameters and two linguistic values (healthy or bruised) as the output parameters. After training the ANFIS model, predicted performance was tested.

**Experimental**

Nano-particles of copper-cobalt compound oxides were synthesized by sol-gel method. Systematically a proper amount of CoCl₂·6H₂O and CuCl₂·2H₂O dissolved in deionized water and ethanol. The initial solutions have been prepared with mole ratios of Cu/Co = 0.0, 0.05, 0.08, 0.10, 0.125 and 0.15. Then, citric acid (as complexing agent) was added in a mole ratio of C₆H₈O₇/CoCl₂·6H₂O = 5, and primary sol was prepared by adding ethylene glycol (as polymerizing agent) in the mole ratio six time over cobalt cation and was stirred for 20 minutes. The clear mixed solution was refluxed at 120°C in oil bath for 6 hours. The final sol ensuing from reflux was kept at 80°C for 17 hours in oil bath to evaporate volatile compounds and a wet gel was formed. For removing the other residual volatile component the gel was heated again directly on hotplate at 180°C for 3 hours and then 220°C for 30 minutes. Finally the dry gel was annealed in 450°C for 1 hour to eliminate organic component and the copper-cobalt oxides Nano-powder was obtained. For gas sensing measurements, usually nanopowders screen-printed on the electrodes, So, using a component as binder, in many cases ethylene glycol, is necessary. Choi and Min [34] reported that sensitivity of a Co₃O₄ sensor decreases with increasing of the ethylene glycol. Accordingly, sensors were fabricated by pressing followed by hot treatment. The same amount of each powders were pressed into pellets at a pressure of 7 ton and then heated in furnace for 2 hours at 800°C with heating rate of 2°C/min. Silver paste was used as electrodes on the two sides of one surface of pellets for recording of the resistant change.

Phase formation and crystallinity were studied by X-ray diffraction using a D8 Advanced Bruker with Cu ka radiation (λ=0.15405 nm) in a 2θ range from 15° to 85° with a step size of 0.05°. The atomic link...
investigation was performed using Fourier transform infrared (FTIR) spectroscopy on a Bomem MB-154 spectrometer. Transmission electron microscopy (TEM) was carried out on a LEO 912 AB transmission electron microscope for determination of the particle shape and size. The prepared sensors were located in the testing chamber for gas sensing characterization. All sensitivity measurements were done in constant temperature in the range of 200-300°C and fixed quantity of sample gas of methane (3000 to 6000ppm). Electrical resistance of the sensor was monitored by a digital multimeter.

The sensitivity was defined as

\[(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}} \times 100\%\]

Where \(R_{\text{gas}}\) and \(R_{\text{air}}\) are the electrical resistance in clean air and in presence of the gas at the same temperature, respectively.

Result and Discussion

Experimental results

The XRD patterns of copper-cobalt oxides nanopowders with different mole ratio of copper have been shown in Figure 3. It reveals polycrystalline structure consisting of cubic Co₃O₄ (\(a=8.08400\)Å) in all samples and (CuO₀.₃CoO₀.₇)Co₂O₄ in which contain Cu.

Major XRD peaks are corresponded to (3 1 1) plane at 36.9° and it intensity does not change evidently by adding copper impurity in samples but it has become slight wider. Beside the strongest peak, also other peaks corresponded to (2 2 0) and (4 4 0) planes have got wider. It’s clearly identified that copper impurity decreases the crystallinity and enhances the amorphous state that lead to the decreasing of the crystalline size. No other phase has been created in samples with different Cu/Co mole ratios and it demonstrates that formed phase are stable and its formation is independent of copper quantity.

Mean particle’s size in major peaks is calculated using Scherrer’s equation.

\[D = \frac{k\lambda}{\beta \cos \theta}\]  

(5)

Where \(k\) is constant, depend on crystal morphology in the range of 0.89-1.39 and it is 0.9 in this calculation, \(\lambda\) is the x-ray wavelength, \(\beta\) is the line broadening at half the maximum intensity (FWHM) in radians and \(\theta\) is the Bragg angle of XRD peak. The particle size values are given in Table 1. It was varied between 24 and 28 and decrease as Cu/Co mole ratio increase to 0.15.

Figure 4 shows FTIR spectra of copper-cobalt oxide Nano-particles with different mole ratios of Cu/Co = 0.0, 0.05, 0.10, 0.15 (S₁, S₂, S₄ and S₆, respectively).

The bands at 576 and 668 cm⁻¹ are attributed to vibration of Co-O in the Co₃O₄. Any peak related to Cu-O could not be identified; it is probably Co-O peaks overlap Cu-O peak, and they have seen in very close wavelength. There is no peak that could be assigned to C-H which suggests that carbonate component removed completely from samples.

TEM images of cobalt oxide nanoparticles (S₁) and copper-cobalt oxide nanoparticles with Cu/Co = 0.15 (S₆) prepared by sol-gel method with different magnification are given in Figure 5.

It’s found that particles have cubic morphologies with uniform distribution. The average particle size was 30 nm in S₁ and 15nm in S₆, which decreases by increasing of the dopant. It has a good agreement with result of Scherre’s formula.

ANFIS comparative analyses and discussion

Two models of Sugeno, with an automatic extraction of data from FIS [GENFIS2] were used. The MATLAB software was adopted for comparison purposes. Moreover, the coverage threshold was fixes to 0.01. Table 2 shows experimental data and predicted data by ANFIS.

3D surface plots for the sensitivity values of nano sensor showing
the relationship between Temperature, Q, ratio Cu/Co and S are given in Figure 6:

A complete graphical comparison of experimental data used for testing or validating the predictions of ANFIS models are shown in Figures 7&8 for the train and the test data respectively. The coefficient of determination values (R²), which quantifies the degree of agreement between experimental observations and numerically calculated values were found greater than 0.96 for all output variables are shown in Figure 9&10. R² was defined as below:

\[
R^2 = \frac{\sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\left(\sum_{i=1}^{N} (x_i - \bar{x})^2\right) \left(\sum_{i=1}^{N} (y_i - \bar{y})^2\right)}}
\]

Table 3 reveals average relative error (ARE), absolute average relative error (AARE) and root mean square error (RMSE) for Nano Cu/Co respectively. ARE, AARE and RMSE are defined as below:

\[
ARE = \frac{1}{N} \sum_{i=1}^{N} \frac{|X_{\text{experimental}(i)} - X_{\text{calculated}(i)}|}{X_{\text{experimental}(i)}}
\]

![Figure 5: TEM images for Cu-Co oxides nano-crystals with different Cu/Co mole ratios prepared by sol-gel method; (a) Cu/Co mole ratio=0.0, (b) Cu/Co mole ratio=0.15.](image-url)
AARE = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{X_{\text{calculated}(i)} - X_{\text{predicted}(i)}}{X_{\text{predicted}(i)}} \right) \quad (8)

RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (X_{\text{calculated}(i)} - X_{\text{predicted}(i)})^2} \quad (9)

Conclusion

Copper-cobalt oxide Nano-sized powders with different mole ratio of Cu/Co from 0.0 to 0.15 were prepared by sol-gel technique for gas sensor application. Cubic Co₃O₄ and (CuO₀.₃CoO₀.₇₀)Co₂O₄ phases were firmly formed. The mean grain size varied from 28 to 24 by changing Cu/Co mole ratios from 0.0 to 0.15. The gas sensing performances of sensors were investigated in presence of methane gas. The results have shown that optimal operating temperature is 300°C in all sensors. Doping of metal oxide to Co₃O₄ altered the sensing behavior by influence defect chemistry and decrease particle size. The performance of the ANFIS Prediction and experimental results was measured using the average relative error (ARE), absolute average relative error (AARE), root mean square error (RMSE) and the Coefficients \(R^2\) values. The developed ANFIS model showed a good regression analysis with the \(R^2\) greater than 0.98. As the regression coefficients indicate the ANFIS approach could be considered as an alternative and practical technique to evaluate the sensitivity (S) based on the Q, temperature and ratio of Cu/Co with a high degree of accuracy.

References

1. Hugon O, Sauvan M, Benech P, Pijolat C, Lefebvre F (2000) Gas separation with a zeolite filter, application to the selectivity enhancement of chemical sensors. Sens Actuators B 67: 235-243.
2. Ohta K, Terai H, Kimura I, Tanaka K (1999) Simultaneous Determination of Hydrogen, Methane, and Carbon Monoxide in Water by Gas Chromatography with a Semiconductor Detector. Anal Chem 71: 2697-2699.
3. Janicki W, Chrzanowski W, Zwan P, Namieśnik J (2003) Automated analyser for monitoring the contents of hydrocarbons in gas emitted from exploratory bore-holes in the gas and oil industry. J Autom Methods Manag Chem 25: 141-147.
4. Hansen TL, Schmidt JE, Angelidaki I, Marca E, Jansen JC et al. (2004) Method for determination of methane potentials of solid organic waste. Waste Manag 24: 393-400.
5. Forsyth DS (2004) Pulsed discharge detector: theory and applications. J Chromatogr A 24: 63-68.
6. Maris C, Chung MY, Lueb R, Krischke U, Meller R, et al. (2003) Development of instrumentation for simultaneous analysis of total non-methane organic carbon and volatile organic compounds in ambient air. Atmos Environ 37: 149-158.

7. Rakshit A, Johri S (2003) Determination of dissolved volatile hydrocarbons in environmental aqueous samples by headspace-gas chromatography with flame ionization detection. Anal Lett 35: 10-13.

8. Kaminiski M, Kartanowicz R, Jastrzebski D, Kaminski MM (2003) Determination of carbon monoxide, methane and carbon dioxide in refinery hydrogen gases and air by gas chromatography. J Chromatogr A 989: 277-283.

9. Worthy DEJ, Levin I, Trivett NBA, Kuhlmann AJ, Hopper JF, et al. (1998) Seven years of continuous methane observations at a remote boreal site in Ontario, Canada. J Geophys Res 103: 15995-16007.

10. Seiyama T, Kato A, Fujishi K, Nagatani M (1962) A new detector for gaseous components using semiconducting thin films. Anal Chem 34: 1502-1503.

11. Fleischer M, Kornely S, Weh T, Frank J, Meinzer H (2000) Selective gas detection with high-temperature operated metal oxides using catalytic filters. Sens Actuators B 69: 205-210.

12. Flaglia G, Comini E, Sberveglieri G, Rella R, Siciliano P, et al. (1998) Square and collinear four probe array and Hall measurements on metal oxide thin film gas sensors. Sens Actuators B 53: 69-75.

13. Benouis M, Jaffrezic-Renault N, Dutasta JP, Cherif K, Abdelghani A (2005) Study of a new evanescent wave optical fibre sensor for methane detection based on cryptophane molecules. Sens Actuators B 107: 32-39.

14. Tournier G, Pijolat C (1999) Influence of oxygen concentration in the carrier gas on the response of tin dioxide sensor under hydrogen and methane. Sens Actuators B 61: 43-50.

15. Llobet E, Orts J, Vilanova X, Brezmes J, Correig X (1999) Selective methane detection under varying moisture conditions using static and dynamic sensor signals. Sens Actuators B 60: 106-117.

16. Pijolat C, Pupier C, Sauvan M, Tournier G, Lalauze R (1999) Gas detection for automotive pollution control. Sens Actuators B 59: 195-202.

17. Quanta R, Rella R, Siciliano P, Capone S, Epifani M, et al. (1999) A novel gas sensor based on SnO2 thin film for the detection of methane at low temperature. Sens Actuators B 58: 350-355.

18. Licznierski BW, Nitsch K, Tetrycz H, Szeczowka PM, Wisniewski K (1999) Humidity insensitive thick film methane sensor based on SnO2/Pt. Sens Actuators B 57: 192-196.

19. Schmid W, Barsan N, Weimar U (2003) Sensing of hydrocarbons with tin oxide sensors: possible reaction path as revealed by consumption measurements. Sens Actuators B 89: 232-236.

20. Gajdosik L (2002) The derivation of the electrical conductance/concentration dependency for SnO2 gas sensor for ethanol. Sens Actuators B 81: 347-350.

21. Saha M, Banerjee A, Halder AK, Mondal J, Sen A, et al. (2001) Effect of alumina addition on methane sensitivity of tin dioxide thick films. Sens Actuators B 79: 192-195.

22. Llobet E, Rubio J, Vilanova X, Briznies J, Correig X, et al. (2001) Electronic nose simulation tool centered on Spice. Sens Actuators B 78: 419-429.

23. Hammerichin O, Lund H, Hammerich O (2000) Organic Electrochemistry. (4thedn), Marcel Dekker, NY.

24. Lu Y, Li J, Han J, Ng HT, Binder C, et al. (2004) Room temperature methane detection using palladium loaded single-walled carbon nanotube sensors. Chem Phys Lett 391: 344-348.

25. Damgaard LR, Revsbech NP (1997) A microscale biosensor for methane containing methanotrophic bacteria and an internal oxygen reservoir. Anal Chem 69: 2262-2267.

26. Damgaard LR, Revsbech NP, Reichardt W (1998) Use of an oxygen-insensitive microscale biosensor for methane to measure methane concentration profiles in a rice paddy. Appl Environ Microb 64: 864-870.

27. Xiangfeng Ch, Donglia J, Yua G, Chenmoua Zh (2006) Ethanol gas sensor based on CoFe2O4 nano-crystallines prepared by hydrothermal method. Sens Actuators B 120: 177-181.