Numerical Signal Analysis of Thermo-Cyclically Operated MOG Gas Sensor Arrays for Early Identification of Emissions from Overloaded Electric Cables

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Abstract: A thermo-cyclically operated multi metal oxide gas sensor (MOG) array is introduced together with a novel signal analysis approach (SimSens) for identifying the emissions from overheated isolation cable materials thereby detecting the fires originated in electrical cabinets at early stages. The MOG array can yield specific conductance signatures appropriate to specifically identify gases. The obtained results bear good capability for detection and identification of pyrolysis gas emissions at relatively low sample heating temperatures even before a visible color-change of the polyvinyl chloride (PVC)-isolation material. The dynamic conductance signals were evaluated using SimSens, a numerical analysis tool designed for simultaneous evaluation of conductance profiles. The results show promising pyrolysis gas identification and concentration determination capabilities in relation to the conductance profile shapes of model gases like carbon monoxide (CO) and propene. *Copyright © 2015 IFSA Publishing, S. L.*

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1. Introduction

In the current scenario, developing sensor systems for early detection of fires instigated by overloaded electrical circuits has gained great attention due to increased sensibility for security aspects. Metal oxide gas sensors (MOG) can be used as appropriate candidates for detection of conventional fires and smoke [1]. This type of gas sensor could be utilized for early detection of fires in electrical installations, as pyrolysis of cable materials leads to emission of distinct gas mixtures depending on insulation material composition [2-3]. Identification of those typical gas mixtures by thermo-cyclic operation of MOG sensor arrays and simultaneous sampling of conductance over time profiles (CTPs) together with numerical analysis of these profiles has been shown in the past to be an elegant and reliable method for detection of fires [3-8].

2. Outline of the SimSens Program

In many applications, a multitude of different gases may occur, which have to be identified and

analyzed simultaneously. One application of great interest is the abovementioned detection of fires due to electrical overload of cables at early stages of development. Depending on the various coating materials of the cables a variety of gases or gas mixtures can be emitted. These gases or gas mixtures according to the related coating materials have to be simultaneously identified and analyzed for early detection of such developing risk. The term "simultaneously" in this context means that the measurements are performed with only one sensor system and the instantaneous analysis is performed with only one analysis procedure covering all the different gases or gas mixtures, which may occur at a certain time but not at once.

The calibration and evaluation program SimSens was designed to meet these demands on simultaneous gas identification capability. SimSens is an extension of the well-introduced program ProSens [10-11], which was designed to analyze only one target gas or gas mixture under consideration.

Like ProSens, SimSens consists of a calibration part and an evaluation part. In the calibration part SimSens provides the mathematical calibration models for every gas to be analyzed. Each calibration model consists of functions for determination of the component concentration und of functions for calculating the related so-called theoretical CTP for substance identification. This means, the calibration part of SimSens provides calibration models for every gas or gas mixture under consideration, whereas ProSens calculates only one calibration model. The functions included in the calibration part of SimSens are parametric functions and the parameters are determined by multiple linear regressions of the CTP sample values versus concentration.

These parameters are transferred to the evaluation part of SimSens for the analysis of an unknown gas sample. Based on these parameters and the CTP of an unknown gas sample the evaluation part of SimSens calculates theoretical CTPs for each calibrated gas and compares these CTPs with the measured CTP.

If the measured CTP and one of the theoretical CTPs are close together, i.e., a difference value calculated from the sum of quadratic differences of every sample point of the measured CTP and the theoretical CTP is smaller than a pre-determined decision value, SimSens identifies the unknown gas sample as the related calibrated target gas.

Otherwise SimSens recognizes that the gas sample is none of the calibrated target gases. In case of identification, SimSens calculates the concentration of the gas sample based on the related calibration model.

Using these algorithms of numerical sensor signal analysis, SimSens has the capability to identify and analyze a variety of target gases or gas mixtures. This is due to the fact that in the calibration part of SimSens more than only one calibration model can be determined, namely one calibration model for each gas or gas mixture, which may occur in the considered application. Furthermore, in the evaluation part of SimSens, not only one gas or gas mixture can be identified, but all gases or gas mixtures, which are calibrated.

3. Experimental Set

The principal sensing element used for pyrolysis gas identification studies is a four-fold sensor array on a 4×4 mm^2 alumina chip (Fig. 1), which comprises four micro-dispensed thick-film sensing layers of different SnO_2/additive-composites [3]. In operation, the sensor-chip is thermally modulated by applying a steady slope heater-voltage, which results in a periodic, nearly triangular temperature profile between 100 °C and 450 °C, at a cycle time of three minutes (Fig. 2).
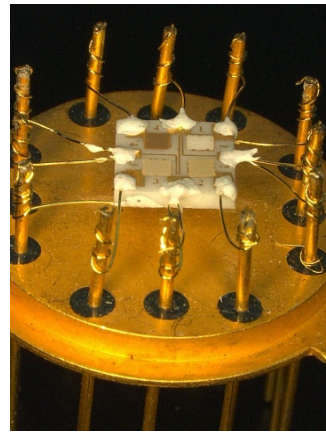

Fig. 1. Multi-sensor-array with four different layers dispensed on thin-film Inter-Digital-Electrodes. The chip is mounted on TO 8 header.
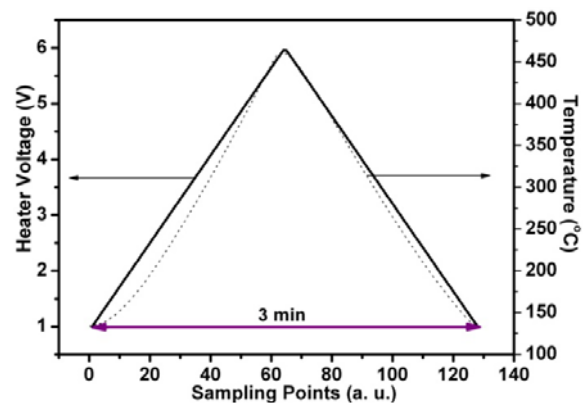

Fig. 2. Triangular heater voltage profile applied to operate the sensor array at thermo-cyclic mode (left ordinate) and corresponding temperature monitored by IR camera (right ordinate).

Operating MOG sensors thermo-cyclically and sampling of the conductance simultaneously yields gas specific CTPs [3-6], which enable identification

of the gas atmosphere from the characteristic CTP shapes.

Pure SnO_2, SnO_2/2 %ZnO-, SnO_2/1 %PtO- and SnO_2/1 %PdO-composites were selected systematically from a variety of material combinations by investigating their sensitivity performance. The various material combinations were investigated towards their specific conductance behavior to propene (C_3H_6), carbon monoxide (CO) and methane (CH_4) at different concentrations in synthetic air and 37.5 % (21 °C) relative humidity (r.H.) and were later exposed to pyrolysis gases as described in the following sections. These model gases were particularly selected as they are found to be the main components evolved during the pyrolysis of standard PVC-insulation cable materials. The selected sensing materials show optimal sensitivity, stability and gas identification capabilities towards model gases like CO and propene and to pyrolysis gases. The sensitivity to methane is very low and not further reported.

A detailed description of the sensor fabrication, experimental set up and generation of pyrolysis gases is depicted in refs [4], [6-7]. Pyrolysis experiments were conducted with 3.5 g of PVC isolated litz copper wires (LiY – 0.14 mm², AWG26, 2A current rating, yellow). The pyrolysis gases were generated by heating the samples in a quartz tube reactor and the evolving gas is carried to the sensor by a constant synthetic air flow. After the reactor, the constant flow is mixed with another adjustable flow of synthetic air in order to get varied gas concentrations. The reactor temperature was increased in a stepwise fashion starting from room temperature up to 170 °C. This fixed temperature was selected after several systematic experiments conducted below and above 170 °C. Evidently, the wire sample showed no visible change up to temperatures of 150 °C and even at 170 °C only a slight change of the sample by shrinking of insulation diameter is observed. At 200 °C discoloring takes place, the sample turns brown.

4. Results and Discussion

4.1. Sensor Response

An overview of the pyrolysis experiment with sensing pattern of a pure SnO_2 layer towards pyrolysis gas at different concentrations is given in Fig. 3. The pyrolysis gas was transported by a constant primary gas flow and diluted by a dilution flow of synthetic air. It is demonstrated that at 170 °C, an almost constant emission from the polymer material is observed over more than five hours. The absolute conductance-values presented here vary greatly depending on experimental parameter values. Several CTPs were recorded at a reactor temperature of 170 °C, while changing the dilution level to set defined relative concentrations. The CTPs at each concentration are highly

reproducible at the repeated cycling by showing similar baseline and peak conductance values (Fig. 3, inset).
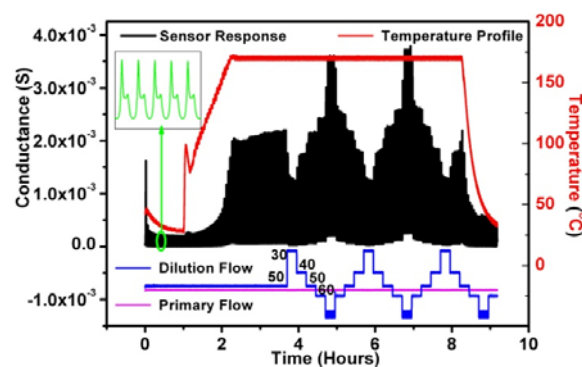

Fig. 3. Measurement sequence of a pure SnO_2 layer exposed with pyrolysis gas of a heated PVC-coated wire with temperature profile and gas flows. The numbers relate the pyrolysis gas concentrations in percent. At each concentration, the heater cycles 10 times. The inset and the oval in green show the reproducibility of the profiles with stable baseline and maximum conductance at repeated temperature cycles.

The CTPs measured by different sensitive materials to model gases (CO and propene) and pyrolysis gases at different concentrations are visualized in Fig. 7 for comparison. In the very most cases they show very specific features with respect to gas identification capabilities.

The thermo-cyclically driven array of four different gas sensitive SnO_2/additive-composites exhibits four different profiles to an exposed gas, which in fact can enhance the gas identification capability compared to conventional mono-sensors operated at isothermal mode. For example, in consideration of propene and CO response, the different sensing materials show completely different CTP shapes (Fig. 7, 1st and 2nd column). In case of pyrolysis gas, although the profile shapes of all materials look similar with two distinctive conductance peaks at the temperature rising and dropping regions, the conductance peak positions are dependent on temperature. Also, by the CTP-features of each sensor the pyrolysis gases can be clearly distinguished from the model gases (Fig. 4, rows).

4.2. Data Analysis

To demonstrate the performance of the sensor system and the procedure SimSens, it was assumed that besides pyrolysis gases propene and CO as interfering atmospheres may occur. The goal is to distinguish between the different gas atmospheres, this means to recognize whether an unknown gas sample is one of the considered gases. In case of identification, additionally, the concentration of the gas has to be determined. The analysis model is

based on the CTP-data of all four gas sensitive layers of the chip (Fig. 4), which are simply linked together to one "extended CTP" (ECTP) as visualized in Figs. 5-7.
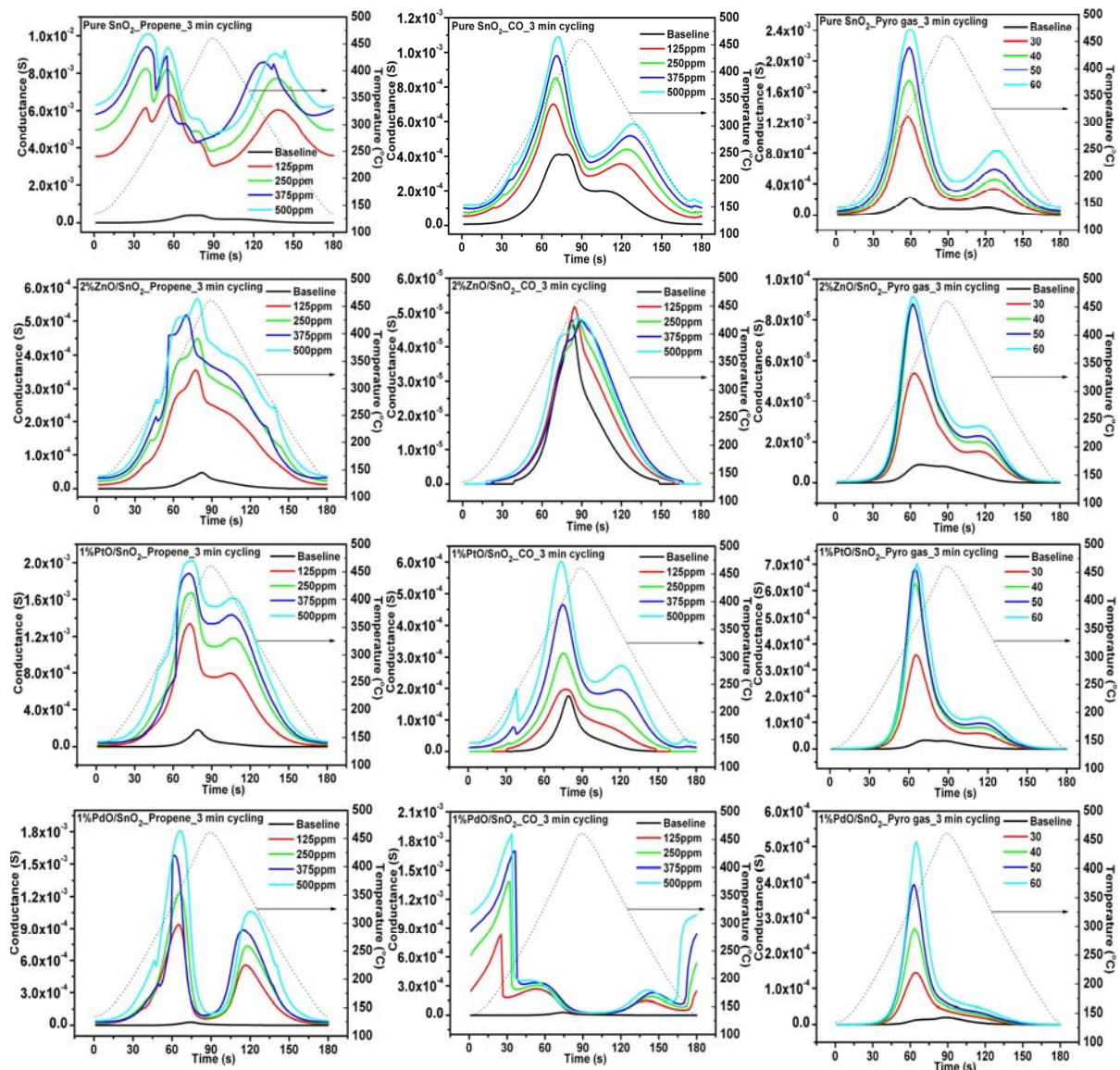

Fig. 4. Matrix representation of the comprehensive sensor responses: Conductance over time profiles (CTP) of the four sensing layers (in columns) when exposed to various concentration of propene, CO and pyrolysis gas (in rows). The propene and CO concentrations are given in ppm and the pyro gas concentration is given in percentages in relation to the dilution flow used, (see caption of Fig. 3 for more details).

For the calibration model of pyrolysis gas, the CTPs of pyrolysis gases at 30 %, 40 % and 60 % relative gas concentrations (Fig. 3 and Fig. 4) were used and for the calibration model of propene and CO, the CTPs were taken at the corresponding concentrations 125 ppm, 250 ppm and 500 ppm.

To test the capability for identifying the gas component/mixture and to determine the associated concentrations, three gas samples were measured and evaluated by SimSens. These are pyrolysis gas at 50 % relative concentration, propene and CO at 375 ppm.

The following figures show that the pyrolysis gas sample at 50 % relative concentration could be clearly recognized as a pyrolysis gas. This is due to the fact that in Fig. 5 the difference between measured CTP and calculated CTP on the basis of the pyrolysis calibration model is very small. In Fig. 6 and in Fig. 7, the differences between measured CTP and calculated CTP based on the calibration model of propene, respectively CO, are much higher. Analogous results were obtained when evaluating the propene sample and the CO sample.

Of course, the decision of identification is not based on a visual impression. For substance identification, a difference value D is calculated as a measure of the difference between measured CTP and calculated CTP.
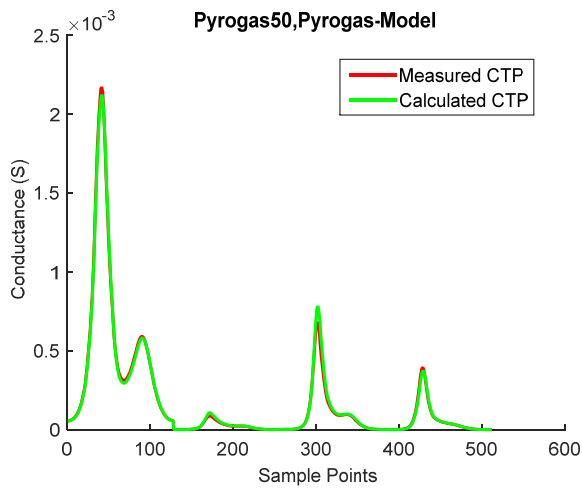
Fig. 5. Measured ECTP of pyrolysis sample at 50 % dilution and associated calculated ECTP based on the pyrolysis calibration model.
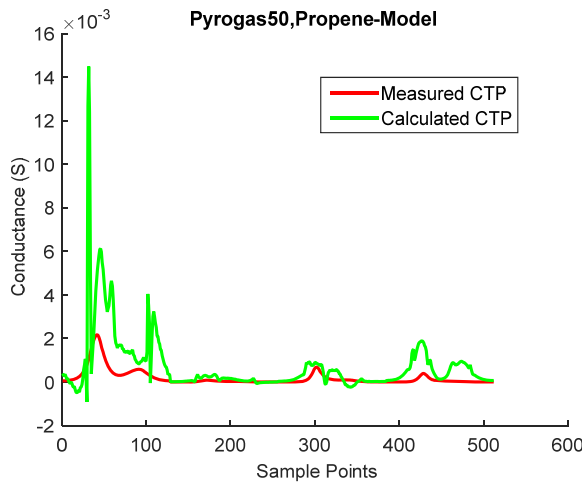

Fig. 6. Measured ECTP of pyrolysis sample at 50 % dilution and associated calculated CTP based on the propene calibration model.
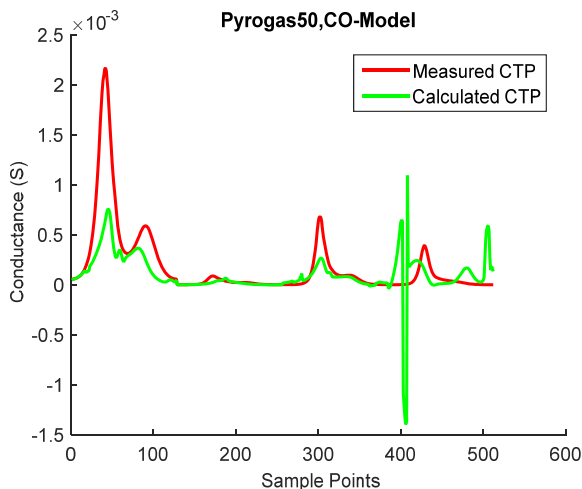

Fig. 7. Measured ECTP of pyrolysis sample at 50 % dilution and associated calculated CTP based on the CO calibration model.

D is the relative sum of quadratic differences of every sample point of the measured CTP and the theoretical CTP. If the difference value is smaller than a so-called decision threshold value eps, the sample under consideration is identified as the associated gas. In this investigation, the decision threshold value was set to eps=4.e-01.

In Table 1, only the red bold numbers are smaller than the decision threshold value. Therefore, the pyrolysis sample could be identified as a pyrolysis gas, the propene sample as a propene gas and the CO sample as a CO gas.

After identifying the gas samples, SimSens calculates the associated gas concentrations. The evaluation results are given in Table 2.

Table 1. Difference values between measured CTPs and theoretical CTPs.

	Pyrolysis Model	Propene Model	CO Model
Pyrolysis 50 %	**2.2e-03**	6.6e+02	8.7e+06
Propene 375 ppm	9.9e+01	**1.3e-02**	1.5e+05
CO 375 ppm	1.0e+00	4.3e+02	**1.7e-01**

Table 2. Comparison of dosed and analyzed concentration values and relative deviation. About the meaning of concentrations in % see Fig. 3.

Sample	Dosed Conc.	Calculated Conc.	Relative Error
Pyrolysis 50 %	50 %	47,6 %	4,7 %
Propene 375 ppm	375 ppm	388,8 ppm	3,7 %
CO 375 ppm	375 ppm	379,6 ppm	1,2 %

The concentration values estimated by the calibration model deviate from the experimentally adjusted values by less than 5 % in all cases.

5. Conclusions and Outlook

The thermo-cyclic operation of MOG array combined with simultaneous numerical analysis of the CTPs has been shown to be an elegant way for identification of gas mixtures. In this study, the pyrolysis gases emitted by heated PVC-based insulation materials are recognized by well reproducible CTPs, even at temperatures where no color change of the sample material could be observed. These CTPs are well distinguishable from those obtained for two model gases, CO and propene. The results look promising considering the aim of early fire detection with high sensitivity.

The acquired CTPs were numerically analyzed employing the SimSens algorithm and the results showed very good identification capabilities and concentration estimation accuracy, which can lead to better incident identification and a very sensitive, more robust detection with a low false alarm rate.

In case of field applications, gas detection experiments for fire or any other dangerous gases using MOG sensors may have to be conducted in a real environment, where indefinite and unspecific but typical gas mixtures are present. In such cases, the numerical analysis of data using SimSens of a thermo-cyclically operated MOG-array will be of great advantage because the CTPs of four sensitive layers provide numerous gas specific features. To enable these advanced field applications, a microprocessor-based sensor system has to be devised, featuring the necessary means.

Acknowledgements

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