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High temperature sensor array for simultaneous determination of O_2, CO, and CO_2 with kernel ridge regression data analysis

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Abstract

A sensor array comprising of three chemical gas sensors was evaluated to predict the concentrations of O_2, CO, and CO_2 in a gas stream with the sensors at 600 °C. The data analysis involved a non-linear multivariate regression method (kernel ridge regression, KRR) along with a searching algorithm to predict gas concentrations. The sensors in the array included a resistance-based 2% CuO/10% La_2O_3/TiO_2 sensor, and two potentiometric sensors, including a yttria stabilized zirconia (YSZ) sensor with a metal/metal oxide internal reference electrode, and a lithium phosphate-based sensor. In addition, the possibility of using the KRR algorithm to predict gas concentrations beyond the training data is explored.

Keywords: Exhaust analysis; Combustion sensors; Harsh environment; Fire safety

1. Introduction

Rapid detection and quantification of chemical species are important in optimization of industrial processes. For example, optimization of combustion processes can lead to significant energy savings, as well as minimization of emissions across power, chemical, steel and other manufacturing industries. Rapid detection and quantification of gases, such as CO, O_2 and CO_2 at high temperatures with the opportunity for feedback control can revolutionize combustion processes [1,2]. In addition, health, safety and national security needs also require sensor methodology to identify chemical species [3].

Most sensors used for detection of chemical species exploit optical or electrochemical methods. Electrochemical gas sensors have several advantages over conventional analytical instruments, such as infrared spectroscopy and chromatography, because of possible miniaturization, low acquisition and maintenance costs.

Traditionally, chemical sensing methods primarily rely on the inherent selectivity of the sensor to retrieve quantitative information or identify the presence or absence of analytes. However, in many cases, sensing elements cannot achieve the required selectivity. A strategy has been to couple an array of partially selective sensors to overcome challenges such as non-selectivity, non-linearity and non-stability (either known or projected sensor signal drifts) [4–6].

In most cases, statistical and signal processing techniques are necessary to decouple the mutual dependence between individual sensors. Essentially, these techniques can be divided into two categories: those for qualitative information acquisition and those for quantitative data extraction. The most popular representatives of the former are pattern recognition and artificial neural network (ANN) based approaches, while multi-component analysis and regression techniques fall into the second category.

Chemometric methods have been widely adopted for sensor array analysis. Jurs et al. [7] have provided a comprehensive review on computational methods for interpreting data from a chemical sensor array. A major pattern recognition approach is principle component analysis, PCA in short, and its extensions.

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Pardo et al. [8] reported employing PCA in electronic nose (EN) applications to differentiate diverse food products with satisfactory classification results. In principle, PCA reduces the raw data matrix into its corresponding eigenvectors and eigenvalues [7]. The amount of variance represented by eigenvectors is ranked according to the magnitudes of associated eigenvalues [8,9]. When applied as a classifier of gas mixtures, PCA ensures that properties of a gas mixture in most scenarios can be represented by a few principal components (PC), which contribute most of the variance. Therefore, these PCs can be used as indicators to identify the types or classes of the mixture under test. PCA is most effective in classification applications, especially in cases where data can be represented as clusters. However, PCA is not able to quantify the composition of a gas mixture.

On the other hand, multi-component analysis and regression methods are commonly regarded as traditional quantitative methods for sensor applications. For example, combining PCA with regression techniques overcomes PCAs inability of quantitative prediction and leads to a series of other closely related techniques, including principal component regression (PCR) and partial least squares (PLS) [10]. Although these techniques were originally developed as linear regression methods, their non-linear variants do exist for more general applications. However, a primary drawback of PLS/PCR is that they tend to be overly optimistic when the data are characterized by more measured variables than observations. In addition, they are most successful when sensor responses are known to be linear. Cao and Zhang [11] used linear regression equations combined with the least square method to determine explosive gases using a sensor array, with relatively large errors.

Another important approach is computational neural networks. In its simplistic form of a three-layer structure, the input layer corresponds to the individual sensors in an array. Each neuron cell represents a single sensor. The neurons in the output layer are related to the different classes in classification problems, or distinct permutations of the gas concentrations in quantification problems [7]. In the hidden layer, a weighted sum of the inputs and bias terms are combined and passed to a transfer function, for example, SIGMOD function, and then the results are delivered to the output layer. The number of neurons in the output layer depends on the number of classifications in many applications. Therefore, quantification using neural networks needs a large amount of cells, and it increases computational complexity and requires training data sets. More advanced neural networks, such as multilayer perceptron (MLP) and self-organizing maps can be used as a preprocessing unit to alleviate these difficulties [7].

Our interest has been in the development of high temperature electrochemical gas sensors, aimed towards combustion optimization, as well as fire detection. The research strategy has focused on developing selective sensors for O_2, CO_2, NO_x, CO and hydrocarbons [12–17]. Even with careful choice of electrodes, electrolytes and catalysts, cross-sensitivity to some gases, interference from humidity and temperature effects are observed. We have reported on a non-linear regression method (kernel ridge regression, KRR) to extract quantitative information for a two-sensor array for measuring CO and O_2 in harsh environments [18,19]. Kernel ridge regression (KRR) has the major advantage of obtaining the so-called kernel analytically and subsequently allows the number of basis functions to be virtually infinite. In addition, the required computational overhead and training data are decreased significantly. The basic idea of KRR is to model the multiple gas response functions of the sensors with the "kernel" regression model, a name derived from a mainstream supervised machine learning technique.

The goal of the present study was to expand KRR technique from the two-sensor array to three-sensor array and extract information regarding the concentrations of CO, CO_2 and O_2 from a three-sensor array. The sensors examined are a resistance-based anatase-based sensor (with La_2O_3 and CuO, labeled sensor I), and a potentiometric zirconia sensor (sensor II) and a lithium phosphate-electrolyte based sensor (sensor III). The signals from all three sensors were recorded in varying CO (250–600 ppm), O_2 (2–10%) and CO_2 (2–10%) at 600 °C and the data were analyzed by the KRR method. Improvements to the data analysis include development of an adaptive searching algorithm to retrieve gas concentrations with improved times and precision. In addition, the potential of the KRR method to predict concentrations beyond the training data set is evaluated with a two-sensor array.

2. Experimental section

2.1. TiO_2 sensor (sensor I)

Sensor I was made by mechanical mixing and heat treatment of commercial metal oxide powders. Commercial anatase (99.9%, Aldrich), La_2O_3 (Aldrich) and CuO (Aldrich) were weighed to achieve 2 wt% CuO–10 wt% La_2O_3–anatase, ball-milled and calcined at 800 °C for 6 h. This procedure has been outlined previously [20]. Alumina substrates with screen-printed gold interdigitated electrodes separated by 250 μm were used.

2.2. Pd/PdO internal reference stabilized ZrO_2 sensor preparation (sensor II)

This sensor was constructed as outlined in a submitted manuscript [21]. The electrolyte, ring and bottom wafer were cut from pre-formed and densified rods/tubes of 3 mol% yttria-stabilized tetragonal zirconia polycrystals (YTZP, $d_{avg} < 0.4$ μm) that were purchased from Custom Technical Ceramics Inc. (Arvada, CO). The 8 mol% cubic YSZ spacers ($d_{avg} \sim 8$ μm) were cut from a rod that was also purchased from Custom Technical Ceramics Inc. The YTZP green tapes were laser cut from sheets into rings the dimensions of which matched that of the YTZP ring (Nextech, Columbus, OH). The Pt wire to the inner reference electrode was sandwiched between two pieces of YTZP green tape in order to densify around the wire during joining. The internal reference was Pd/PdO obtained from Alfa. The sensor was compressed at 0.012 mm/min under a 1000 N full-scale load at 1287 °C. The resultant longitudinal compression was 263 μm. During the heating cycle, the load on the sample was balanced as not to exceed 5 N. Upon reaching the target temperature the system was left under a 5 N load for