Electrochimica Acta 283 (2018) 141–148

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Automatic signal decoding and sensor stability of a 3-electrode mixed-potential sensor for NO_x/NH_3 quantification

Lok-kun Tsui [a, *], Angelica Benavidez [a], Ponnusamy Palanisamy [b], Lindsey Evans [c], Fernando Garzon [a, c]

[a] Center for MicroEngineered Materials, University of New Mexico, Albuquerque, NM, 87106, USA
[b] ESL ElectroScience, King of Prussia, PA, 19406, USA
[c] Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM, 87106, USA

ARTICLE INFO

Article history:
Received 7 May 2018
Received in revised form
18 June 2018
Accepted 20 June 2018
Available online 22 June 2018

Keywords:
NO_x
NH_3
Mixed potential sensor
Artificial neural network

ABSTRACT

Sensors to detect mixtures of NO_x/NH_3 are needed to monitor emissions of diesel automobiles where a selective catalytic reduction system uses an NH_3 mediated reaction to reduce NO_x. We report on the application of a three electrode $La_{0.8}Sr_{0.2}CrO_3$, $Au_{0.5}Pd_{0.5}$, Pt mixed potential sensor using yttria-stabilized-zirconia (YSZ) as a solid electrolyte to NO_x/NH_3 sensing. Artificial neural networks were used to automatically decode the concentrations of NO_x/NH_3 and errors of less than 15% are achieved. The optimal architecture for ANN decoding and the maximum density of training data points are also determined. The stability of the sensor was monitored by electrochemical impedance spectroscopy. The impedance associated with YSZ oxygen ion conduction and the electrochemical reactions at the three-phase interface are tracked over a period of over 100 days.

1. Introduction

Lean burn diesel engines can achieve higher fuel efficiency but require a complex catalytic reaction system to control hydrocarbon (HC), CO, and NO_x (NO and NO_2) emissions [1]. NO_x has been identified as an environmental pollutant causing ozone damage and acid rain as well as a harmful chemical to the respiratory system [2]. Selective catalytic reduction (SCR) uses urea (NH_2-CO-NH_2) which is converted into NH_3 (equation (1)) to mediate a reduction reaction of NO_x to N_2 by the reactions in equations (2) and (3) [3,4]. At the end of the emissions treatment stream excess NH_3 is eliminated at the ammonia oxidation catalyst (AOC) reactor producing N_2 in equation (4).

$$NH_2\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \quad (1)$$

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6H_2O \quad (2)$$

$$4\ NH_3 + 2\ NO_2 + O_2 \rightarrow 3\ N_2 + 6H_2O \quad (3)$$

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6H_2O \quad (4)$$

There is a need to develop sensors to quantitatively and continuously monitor the performance of SCR and AOC systems in real time [5]. Prior to the introduction of gases to the SCR, a diesel oxidation catalyst system has already eliminated HC and CO, so the main gases of interest to SCR and AOC monitoring are NO_x and NH_3. Deploying sensors which can monitor the emissions of NO_x and NH_3 at the output of the exhaust stream would enable the fine tuning of these catalytic systems in real time for improved efficiency and alert the vehicle owner of problems without requiring an external emissions measurement.

The numerous approaches to the design of NH_3/NO_x sensors in the literature have involved semiconductor metal oxide sensors and mixed potential sensors using conductivity, amperometry, or voltammetry as sensing parameters [6–9]. Currently there is no commercially available automotive sensor which is capable of measuring the NH_3/NO_x concentration simultaneously in exhaust gases. Cross interference between the signals in the presence of both NO_x and NH_3 have driven a substantial amount of research towards sensors which are strongly selective towards either NO_x or NH_3. These methods include measuring the conductivity of zeolites engineered to be sensitive towards the target gas [10] and coating a sensor with a catalytic layer to filter out unwanted gas species [11].

* Corresponding author. 1001 University Blvd SE, Center for MicroEngineered Materials, Albuqerque, NM, 87106, USA.
E-mail address: lktsui@unm.edu (L.-k. Tsui).

https://doi.org/10.1016/j.electacta.2018.06.133
0013-4686/

Arrays of metal oxide sensor elements have also been studied where each element is to be sensitive to a specific gas by changing the noble metal doping and substrate [12].

Mixed potential electrochemical sensors are one of the most promising technologies for use in automotive emissions control because of their high stability in the environment, fast response, and tunable selectivity to a broad range of target gases by materials selection or current biasing. The mixed potential on each electrode is determined by the balance between the reduction and oxidation reactions of the gases present in the atmosphere. A difference in mixed potentials due to the different catalytic activities of the electrode materials can then be used as a sensing parameter on oxidizable (HC, CO, NH_3) or reducible gases (NO_x) [13,14]. Au/YSZ/Pt sensors have been identified as effective for detection of NH_3, while $La_{0.8}Sr_{0.2}CrO_3$ (LSCO)/YSZ/Pt sensors are sensitive to hydrocarbons under open circuit and sensitive to NO_x under an applied bias [15,16]. We have designed a three-electrode mixed potential sensor incorporating LSCO, $Au_{0.5}Pd_{0.5}$ (Au/Pd) alloy, and Pt electrodes with an over layer of porous YSZ electrolyte. The sensor has an integrated Pt thin film heater on the back, which controls the temperature by an applied bias.

Quantitative decoding of the sensor responses of mixed potential electrochemical sensors to NO_x/NH_3 in the presence of cross interference remains an unsolved challenge. Tsitron et al. and Ramaiyan et al. have pursued a Bayesian approach to quantify the ratio of concentrations in a binary mixtures of NO_x, C_3H_8, and NH_3 [17,18]. This approach started with linear and logarithmic functional relationships between concentration and voltage and Bayesian inference was used to obtain the fitting parameters. We have previously explored an alternative approach involving artificial neural networks (ANNs) to quantify binary and ternary concentrations of NO, C_3H_8, and CO [19,20], and in this report we extend this work to quantification of NH_3 and NO_x. A major advantage of ANNs is that they do not require specification of functional forms in advance as these structures can take advantage of their ability to automatically learn the relationships between sensor responses and species concentrations from a training dataset. This feature allows the network to easily scale the automatic analysis with an increasing number of signal inputs and cross-interference effects that are introduced with the addition of more gases into the mixture. The application of this technique to a new set of gas mixtures also demonstrates its versatility and shows that the same sensor can be used to analyze gas species at different stages of the exhaust treatment pipeline.

We report the extraction of concentrations of NH_3 and NO_x from sensor signals automatically using an artificial neural network. By operating the sensor in unbiased mode, we are able to increase sensitivity to NH_3, while operating in biased mode provides sensitivity to NO_x. As a result, we are able to achieve a total peak error of 5% in the concentration of NO_x and NH_3 with 90% of test data points confined to less than 15% error. The stability of the sensor is also monitored for over 3 months and impedance spectroscopy was used to track changes in the resistance of the YSZ and resistance associated with the electrochemical reactions at the three-phase interface.

2. Materials and methods

Sensors were constructed by ESL ElectroScience on laminated tapes of YSZ substrates coated with an insulating ceramic layer. A serpentine thin film Pt heater element on the rear and dense electrodes made of Pt, $Au_{0.5}Pd_{0.5}$, LSCO with a porous YSZ electrolyte on the front were deposited by screen printing. The electrodes are evenly spaced and the Au/Pd electrode is located between the Pt and LSCO electrodes. The sintering temperatures for Pt electrodes and heater path, LSCO electrodes, Au/Pd electrode, and YSZ electrolytes are 1450 °C, 1200 °C, 1100 °C, and 1100 °C respectively.

Contacts to the elements were made by Ag-Sn soldering Ag wires to the electrode elements and Cu wires to the rear heater unit. The wires were threaded through alumina tubes and JB Weld epoxy was used to reinforce the connections against mechanical stress. Two sensors were inserted into 1" glass tubes. The sensors are heated from two of the outputs of an HP 6627A quad-output power supply to 530 °C by applying a voltage of 14V. Gas mixing is controlled by an Environics 2000 gas mixing system, and a schematic of the gas mixing and test system is available in Ref. [20]. Voltages across each of the electrode pairs are recorded by two Keithley 2400 digital sourcemeters, a Fluke 8842A digital multimeter, and three HP 34401A digital multimeters with the following polarity convention: Au/Pd(+) and Pt(−), LSCO(+) and Pt(−), Au/Pd(+) and LSCO(−). One sensor is left at open circuit while the second sensor is held at an applied current bias of −0.6 μA to the LSCO/Pt pair.

The sensors were exposed to a gas mixture consisting of a base gas of 10% O_2, 2.5% CO_2, and balance nitrogen. Binary mixtures of NH_3 with NO or NO_2 were obtained in concentration windows of 50–200 ppm. Ternary mixtures of NH_3 with NO_x (NO and NO_2) were obtained in concentration windows of 50–150 ppm. The flow rate from the gas mixer was set to 220 SCCM and split to 110 SCCM per sensor. The sensors were exposed to alternating 10 min intervals of base gas only and base gas with test gas.

We trained artificial neural networks to take the voltage readings from the biased and unbiased sensor as inputs and output the NO_x/NH_3 concentrations. A Python 2.7.3 neural network library Keras with the Theano back-end in CPU mode was used for building artificial neural networks [21]. Fully connected, feed-forward artificial neural networks were constructed using the architecture in Fig. 1 with 6 input neurons, 16 hidden layer neurons, and two output neurons. The voltages were provided to the input side of the neural network, and the normalized concentrations were obtained from the output of the neural network. The activation function used was sigmoidal with bias. Prior to analysis, voltage readings were normalized to 100 mV and concentrations were normalized to 200 ppm. The voltage input was then stretched so that the variance of the training data was unity. A total of 159 data points was collected for binary mixtures of NH_3 and NO or NO_2 and 215 data points were collected from ternary mixtures of NH_3 and varying ratios of NO:NO_2 in NO_x. A total of 10^4 iterations of training were performed with the Keras's built-in ADAM training algorithm with a runtime of 20–70 s on a desktop PC with an Intel i5-6500 processor. To assess how well the artificial neural network generalizes, the datasets were processed with 10 iterations of randomly partitioning into test-training splits at a ratio of 80% training data and 20% test data.

Contour plots of the behavior of the neural networks were generated by principle component analysis (PCA) following the process outlined in Ref. [20] using the method of covariance matrices and singular value decomposition. The 6D sensor signal data points are projected down into a 2D plane in order to be represented in an image. The contour plots are generated by sampling the 2D plane, determining the equivalent 6D sensor reading, and obtaining a prediction of concentration from the neural network. This allows us to visualize whether the predicted concentrations qualitatively match with trends as one moves around in 2D PCA space.

Additional electrochemical measurements were collected using a PAR 2273 potentiostat to assess the robustness of the sensor over time and examine the behavior of the 3-electrode sensor under applied current bias. Electrochemical impedance spectroscopy was collected at open circuit between 2 MHz and 0.1 Hz with an applied