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SiC – FET BASED SO₂ SENSOR FOR POWER PLANT EMISSION APPLICATIONS

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power plant

Abstract

Thermal power plants produce SO_2 during combustion of fuel containing sulfur. One way to decrease the SO_2 emission from power plants is to introduce a sensor as part of the control system of the desulphurization unit. In this study, SiC-FET sensors were studied as one alternative sensor to replace the expensive FTIR (Fourier Transform Infrared) instrument or the inconvenient wet chemical methods. The gas response for the SiC-FET sensors comes from the interaction between the test gas and the catalytic gate metal, which changes the electrical characteristics of the devices. The performance of the sensors depends on the ability of the test gas to be adsorbed, decomposed, and desorbed at the sensor surface. The feature of SO_2 , that it is difficult to desorb from the catalyst surface, makes it known as catalyst poison. It is difficult to quantify the SO_2 with static operation, even at the optimum operation temperature of the sensor due to low response levels and saturation already at low concentration of SO_2 . The challenge of SO_2 desorption can be reduced by introducing dynamic operation in a designed temperature cycle operation (TCO). The intermittent exposure to high temperature can help to desorb SO_2 . Simultaneously, additional features extracted from the sensor data can be used to reduce the influence of sensor drift. The TCO operation, together with pattern recognition, may also reduce the baseline and response variation due to changing concentration of background gases (4-10% O_2 and 0-70% RH), and thus it may improve the overall sensor performance. In addition to the laboratory experiment, testing in the desulphurization pilot unit was performed. Desulphurization pilot unit has less controlled environment compared to the laboratory conditions. Therefore, the risk of influence from the changing concentration of background gas is higher. In this study, Linear Discriminant Analysis (LDA) and Partial Least Square (PLS) were employed as pattern recognition methods. It was demonstrated that using LDA quantification of SO_2 into several groups of concentrations up to 2000 ppm was possible. Additionally, PLS analysis indicated a good agreement between the predicted value from the model and the SO_2 concentration from the reference instrument of the pilot plant.

1. Introduction

SO₂ is one of the major air pollutants because it is a precursor of acid rain, forms acid particulates, and is dangerous for human health. However, in a thermal power plant, SO₂ is generally produced when sulfur containing fuel is combusted. In flue gas cleaning processes, SO₂ is usually removed by absorption with lime (CaOH₂.2H₂O) or other compounds having high alkalinity. State-of-the-art desulphurization can remove more than 98% of the SO₂ from the flue gas. With increasing environmental concerns, the regulation of SO₂ emission from thermal power plants has become stricter. The installation of sensors in the flue gas duct has been proposed as one of the alternatives to improve the efficiency of the desulphurization unit to meet the new regulations.

Due to the nature of the environment where the sensor should be installed, the sensors have to fulfill several requirements. They must be resilient enough to be operated at high temperature, high dust, high humidity (up to 20%), low oxygen (lower than 10%), and corrosive environments. They must be sensitive and selective to SO₂ regardless of changes in the background gas composition. They need to be relatively small and cheaper than conventional analysis systems to make them competitive. These requirements narrow down the possible sensors that can be used. Liquid electrochemical cells cannot operate in high humidity and high temperature conditions [1]. Metal oxide sensors usually are not the best choice in environments with low and changing concentration of oxygen [2,3]. Optical detection such as FTIR is relatively more expensive than chemical sensors [4]. This line of reasoning reduces the options to SiC-FET and solid electrolyte sensors.

Continuous development has been performed since the invention of Si-FET sensors with Pd gate for H₂ sensing in the 1970s [5]. SiC has been utilized as semiconductor material for the sensors due to its stability, inertness, and high temperature properties which are needed for high temperature and harsh environment applications in different industrial areas, including power generation activities [5,6]. More recent developments have shown that Pt-gate SiC-FET sensors can give promising results in industrial monitoring of CO [7] and NH₃ [6,8]. Due to the catalytic nature of the gate, the selectivity and sensitivity of SiC-FET sensors can be tuned by the choice of the gate material and the gate oxide, the morphology of the gate

material, and the operating temperature [5,9]. The sensitivity of SiC-FET sensors towards SO_2 has not been studied before.

Several types of solid electrolytes sensors with sulfate compounds have been studied [10–12], and showed good sensitivity and selectivity towards SO_2 at high temperature operation. However, these studies did not investigate the behavior of the sensors in the presence of other gases in the background.

The detection of SO_2 is complicated by the fact that it is a catalyst poison [13]. At certain concentrations, the sensor surface becomes saturated and the quantification of SO_2 is not possible anymore. More advanced operating methods will be needed to meet this challenge. Temperature cycled operation (TCO) has shown encouraging results in detecting certain target gases. Previous study on quantification of NO_x with SiC-FET sensors [14] has reported the capability of this method to measure NO_x in a gas mixture with changing background. These features are very beneficial for SO_2 sensing in flue gas, not only to improve the sensor performance against drift and noise, but also to reduce the influence of changing background gas. This is vital because in flue gas, the oxygen concentration and humidity vary depending on the combustion process in the boiler.

The objective of this work was to develop suitable operating methods and data analysis techniques to use SiC-FET sensors as SO_2 sensors in power generation applications. To approach the conditions of a real power plant, performance testing of the SO_2 sensors was also performed in a desulphurization pilot unit in addition to the laboratory testing. The process conditions in the pilot unit offered a more challenging environment for sensor operation as compared to laboratory testing.

2. Material and Methods

2.1. Sensor Deposition, Mounting and Detection mechanism

The sensors were based on commercial SiC Field Effect Transistors produced by SenSiC AB [15]. The schematic diagram of the sensor is presented in Fig. 1(a). The device had a lift off pattern for the gate material to provide more convenience in depositing different catalytic metals as sensing material. The SiC substrate was doped by nitrogen. Ion implantation was performed for the source and drain region. The Ohmic contacts to drain, source and the rear side of the SiC substrate consisted of 50 nm Ni (annealed at 950°C for 5 min in Ar), 5 nm Ti as adhesion layer, and 400 nm Pt as oxygen diffusion barrier for high temperature operation.

Figure 1: SiC-FET sensor; (a) schematic diagram (b) mounted sensor on 16-pin header (c) SEM result of the Pt/SiO₂ surface of a Pt-gate SiC-FET sensor.

The sensing layer was deposited on the SiC transistor by sputter deposition. Porous metal, 25-30 nm, was sputtered on the transistor gate area at an elevated pressure of 50 mTorr to create a porous film. Scanning Electron Microscopy (SEM) was performed on the sensor surface to confirm the porosity, as shown in in Fig. 1(c).

The sensor was mounted on top of a heater in a 16-pin header as shown in Fig.1 (b). Gold wires were bonded to connect the sensor chips to the header. On the same heater, a Pt100 temperature sensor was also attached to enable efficient temperature control of the sensor. The heater and Pt-100 sensor were connected to a PID controller to adjust the operating temperature.

When voltage was applied between drain/gate and source, the current flowed through the n-channel (see Fig.1(a)). The target gas decomposed on the catalytic metal gate and interacted with the oxide/insulator. This surface interaction created a polarized layer of gas related adsorbed species, and the generated electric field changed the conductivity of the n-channel [5].

2.2. Static Operation

As shown in Fig. 2, a preset sequence of gas concentrations was inputted to the gas mixing program, which acted as an interface to the gas mixing system. The gas mixing system had a series of mass flow controllers to vary the concentration of the test and background gases. The test gas flowed to the sensor chamber, and then to the ventilation tube. To simulate the presence of humidity, part of N_2 flow was directed to a humidifier. The humidity was adjusted by changing the flow of N_2 passing the humidifier.

Figure 2: Schematic diagram of the measurement set-up. Gas flow is indicated with solid lines and electrical signal/data flow is indicated with dashed lines. Photos of the mass flow controller, sensor chamber, and data acquisition system are inserted into the figure.

Constant current was supplied to the sensor and the change in the resulting voltage was measured as the sensor signal. The data was recorded by the data acquisition system and was transferred to LabView.

The SO₂ concentration was varied from 20-100 ppm to simulate the concentration of SO₂ at the outlet of the desulphurization unit in power generation plants with relatively clean fuels. The operating temperature was adjusted between 200-400°C in order to find the optimum temperature for operation. The minimum temperature limit for the sensor was required to be above the 170°C flue gas temperature in the desulphurization unit in order to allow temperature control. The maximum operating temperature should not exceed 400°C to ensure stability of sensor performance during long term operation. In this set of measurements, the background gas was 10%O₂ in N₂ to represent the average oxygen level in the flue gas. The response was defined as the difference between sensor signal during the test gas injection and the baseline in the background gas. Several different catalytic metals were tested as the sensing layer: Pt, Ir, and Au.

2.3. Dynamic Operation (TCO) and Data Processing

The set-up for this measurement was the same as for static measurements. The measurement was only performed for Pt-gate sensors, which were chosen for their good response time and relative good stability. Different sets of sensor chips were used, which resulted in different baselines and magnitudes of response. The sensor characteristics were, however, still the same. For dynamic operation, the sensors were operated at different operating temperatures in a cycled fashion. The total cycle duration was 45 s divided between 3 different operating temperatures (200°C, 300°C, and 400°C) as described in Fig. 3. The sensors surfaces were relatively large and it required several seconds to stabilize the signal at the new temperature. For this reason the sensor signal was divided into several intervals for data analysis: steady state intervals (2 at 200°C, 4 at 300°C, and 6 at 400°C) and transient intervals when changing from one temperature to the next temperature (1, 3, 5).

Figure 3: Sensor signal and applied temperature in the cycle. The intervals where the features are extracted are marked (1-6).

Both 200°C and 300°C were chosen because of higher sensitivity of Pt sensors to SO₂ around these temperatures, while 400°C was chosen for surface cleaning purposes. The SO₂ test concentration range was set between 20-150 ppm. To study the influence of changes in the background gas, the oxygen concentration was varied between 0-20% and the relative humidity was varied between 0-70%. The humidity was added by bubbling nitrogen through a simple humidifier. It is assumed that the contact between the gas and water was sufficient, and that the outlet gas was saturated with water at room temperature (around 2% at 25°C). The humidity was varied by changing the fraction of the nitrogen passing the humidifier (see Fig. 2).

The sensors generated multidimensional data that required pattern recognition tools [16]. This study employed supervised multivariate data analysis, for which Linear Discriminant Analysis (LDA) [17,18] was chosen. Data from the cycle were treated with a Savitzky-Golay filter [19] to reduce the noise influence and then normalized, by dividing it with the mean value, to reduce the influence of drift. Subsequently, the data were divided into 6 intervals as shown in Fig. 3. From each interval, several features (mean value and best fit line) were extracted as the input for LDA.

2.4. Measurement in Desulphurization Pilot Unit

To achieve a condition close to the real application in power plants, the sensor was installed at the outlet of an operating desulphurization pilot unit. As shown in Fig. 4, the desulphurization unit removed SO_2 from the flue gas by mixing a certain amount of lime (CaOH_2) and dust with the gas [20]. The SO_2 reacted with lime and formed dry rest product. The dust mixture was separated from the gas with a fabric filter. The dust was collected in the bottom area of the filter and recycled into untreated gas. The clean gas flowed to the outlet where the concentration was measured. New reactant was added to the dust mixture if the SO_2 concentration in the outlet became too high. Water could be added to the system if the temperature was too high, due to the exothermal nature of the SO_2 absorption.

Figure 4: Schematic Diagram of Desulphurization Pilot Unit (adapted from[20])

Flue gas was simulated in the desulphurization unit by burning propane and then adding the pollutants under study, such as SO_2 and HCl , into the gas mixture. At the outlet of the unit, the O_2 , CO_2 , and H_2O concentrations, and also the temperature varied depending on the propane combustion and the desulphurization processes. The SO_2 and HCl concentrations

varied based on the injected SO₂ and HCl at the inlet, and also the subsequent absorption process. The overall variation is listed below:

- SO₂: 0-4000 ppm
- O₂: 0-22%
- CO₂: 0-7%
- H₂O (absolute): 0-20%
- HCl: 0-300 ppm
- Gas temperatures: 60-170°C

The SiC-FET sensors were installed at the outlet of a desulphurization pilot unit, as described in Fig. 4. Each sensor was installed in a sensor holder with thread connection and then inserted into the flue gas duct.

Dynamic operation of the sensor was performed with settings similar to the laboratory measurements. However, in this part of the experiment, two types of supervised pattern recognition methods were employed: LDA [17,18] and Partial Least Square Regression (PLS) [21]. The calibration and data training measurement values were obtained from a reference instrument (FTIR).

The focus for LDA was to use different features to separate different concentration of SO₂ into several clusters. When the concentration changed from one cluster to another, some warning signals could be generated. The chosen clusters were: 0-65 ppm, 65-100 ppm, 100-150 ppm, and above 300 ppm for low concentrations. For higher concentration the clusters were 0-500 ppm, 500-1000 ppm, 1000-2000, 2000-4000 ppm, and above 4000 ppm.

In PLS, each measurement value from a certain point on the cycle was treated as data from 1 sensor, which made a single sensor operate as 45 sensors in the 45 s cycle. Previous study on with this method was performed successfully for automotive application [22]. This method was performed with the assumption that the SO₂ concentration did not change significantly during 1 cycle (45 s). PLS enabled the linearization of the data and creation of a model to predict the SO₂ concentration based on the training data. The predicted concentration of SO₂ was compared with the results from the reference instruments.

The pilot was run continuously for 4x24h. However the data presented in this study only covered 2 days of measurement due to technical difficulties during the set-up of the equipment.

3. Results and Discussion

3.1. Static Operation

Metals of three kinds were chosen as the gate material for the SiC-FET sensors in this static operation. Platinum and iridium were chosen because they were common catalysts [23,24] and have been proven to be able to detect some other gases [9]. Gold was chosen because it has been reported to be an active catalyst for reactions involving sulfur compounds [25,26]. Previous studies on Au-based sensors [3,27] have also demonstrated the potential of Au as sensing layer for SO₂ sensors.

Figure 5: Response of SiC-FET sensors with different porous catalytic metals on SiO₂ at their optimum operating temperature during exposure to SO₂ in a background of 10% O₂ / N₂ (a) Pt at 300°C, (b) Ir at 300°C, and (c) Au at 350°C

In Figure 5 the sensor signal for the three gate materials are displayed for SO₂ concentrations in the range 20-100 ppm for the optimum operation temperatures. For Pt and Ir, one set of measurements required 1 hour, while in the case of Au, it required 2,5 hour due to the longer recovery time needed by the sensors having Au gates. In addition to that, Au-gate sensors needed longer time to stabilize after the start-up.

For all three catalytic metals, it was possible to determine the presence of SO₂ with normal static operation. However, even in the case of constant concentration of background gases, it was difficult to quantify the concentration of SO₂, especially in the concentration range higher than 40 ppm. In addition to that, drift in the baseline was observed during the measurements.

The response of the SiC-FET sensors is determined by the 3-boundary interaction in the gate region between the gas - catalytic metal – oxide surfaces. In the case of hydrogen containing gas, the gas is adsorbed and decomposed on the gate metal and then spills over to the oxide surface and forms polarized OH groups [6]. For non-hydrogen-containing gas like CO, NO, or SO₂, it has been suggested that the response comes from consumption of adsorbed oxygen on the gate oxide surface [28]. The oxygen on the oxide surface in turn originates from dissociation of oxygen on the metal surface and spillover of oxygen to the oxide. The challenge with SO₂ is that it has strong interaction with the catalyst and the oxide, which causes slow desorption process that saturates the catalytic surface even at low concentrations [13]. The desorption process can be improved by operating the sensor at higher temperature. However, this approach also creates difficulties for the gas to be adsorbed on the sensor surface, which reduces the sensing performance. Exposure to high temperature intermittently, as performed in the TCO, will give the benefit of surface cleaning without reducing the capability of sensor surface and target gas to interact.

From the results of the three catalytic metals, the Pt-gate presented the most promising response. Figure 5 displays that the Ir-gate response was in the opposite direction with shorter response and recovery times as compared to the Pt and Au gate sensors. However, the Ir sensor signal also indicated a complex, or noisy, behavior. The Au gate sensor appeared to saturate already at the lowest concentration of SO₂. Therefore, the subsequent measurements using TCO were only performed with Pt-gate sensors.

3.2. Dynamic Operation (TCO) Data Analysis

The dynamic operation (TCO) was performed to improve the sensor response and to reduce the influence of variations in the oxygen concentrations and humidity in the background gas.

3.2.1. Influence of Oxygen Concentration

The quasi-static sensor signal at 200°C, 300°C, and 400°C is shown in Fig. 6. Pulses of SO₂ at different concentrations (20 ppm, 50 ppm, 100 ppm, and 150 ppm) were introduced repeatedly, each in different concentrations of oxygen in the background (0, 4%, 10%, 20%). The quasi-static sensor signal is collected at certain points at the steady-state intervals (see Fig. 3) in the temperature cycle operation.

It can easily be observed that dynamic operation gave more information about the sensor response to different concentrations of SO_2 as compared to the static operation. The surface cleaning step at 400°C accelerated the desorption of sulfur containing species from the sensor surface.

Figure 6: Quasi static (Pt gate) sensor signal during the exposure to different concentration of SO_2 with changing oxygen background concentration.

Figure 6 also shows that changes in oxygen background concentration from 10% to 20% did not significantly influence the baseline level of the sensor signal. However, both the baseline and the size of the response changed slightly when the oxygen concentration decreased to 4%. The change became significant when oxygen was not present in the background gas. This is something that needs to be considered because in large combustion power plants, the oxygen concentration might vary between 4-10%.

Figure 7: Oxygen influence to the differentiation of SO_2 concentrations. SO_2 concentration given in ppm, the center points in each concentration cluster are marked (crosses). Data extracted from Fig. 6 from the intervals indicated in Fig. 3.

Figure 7 shows the SO_2 discrimination using LDA when the oxygen concentration was constant at four different levels, 0, 4, 10, 20%. SO_2 data were grouped into different clusters for different concentrations. The cluster boundaries and the center points were added for better visualization. The values of the Discriminants were adjusted so that all four LDAs could have the same axis for easier observation of oxygen influence on the SO_2 clusters.

It was observed in Fig. 7 that higher oxygen concentrations improve the possibility to identify the presence of SO_2 in the gas mixture. Despite the scatter in the data, LDA could be employed to perform quantification of SO_2 at constant oxygen concentration. As expected, quantification of SO_2 at higher concentrations (100 ppm and 150 ppm) was more challenging. This phenomenon took place because of the limited storage capacity of sulfur related compounds at the sensor surface. Saturation of the sensor surface was faster during exposure to higher concentrations of SO_2 . This might be caused by the increased rate of SO_2 oxidation to SO_3 or SO_4 , which enhance the uptake of the sulfur containing gas by the oxide surface [29] and the difficulty to release the molecules.

Figure 8: LDA plot of the influence of oxygen (in-%) on (a) the baseline and (b) the 100 ppm SO₂ measurement. Data extracted from Fig. 6.

Figure 8 shows the comparison, between the LDA of the baseline (see Fig. 8(a)) and the LDA when 100 ppm of SO₂ was introduced into the gas mixture (see Fig. 8(b)), at different oxygen concentrations. It shows how the sensor response was quite strongly influenced by the oxygen concentration. The drift and noise in the sensor signal introduced scattering in the direction of the 2nd Discriminant Function, most pronounced for the baseline of the sensor (compare Fig. 8(a) and (b)). In the LDA plot in Fig.8 (a), overlap between 10% and 20% oxygen can be observed, which signifies the similarity in the baseline level. When 100 ppm of SO₂ was introduced (see Fig. 8(b)), the results with 20% oxygen in the background were different as compared to those of 10% and 4%. This suggests a shift in the equilibrium of the chemical reactions when SO₂ interacted with oxygen on the sensor surface. Overlap was observed in the LDA plot for the sensor response to 100 ppm SO₂ with 10% and 4% oxygen in the background. Although there was a noticeable shift in the baseline in Fig. 6, the difference of the sensor response with 10% and 4% oxygen in the background was not large enough.

Figure 9: Processed data from Fig. 6 of SO₂ with combination of 4% and 10% O₂ concentration in the background (a) LDA plot (b) Correlation between SO₂ concentration and 1st Discriminant Function

In Fig. 9(a), data with the same SO₂ concentration but with different oxygen level, 4% and 10%, were assigned to one group. The data were quite scattered since the sensor response was strongly dependent of O₂ concentration. However, it was still possible to derive a correlation between SO₂ concentration and the center point of the 1st Discriminant Function as shown in Fig. 9(b).

3.2.2. Influence of Humidity

The influence of humidity is described in Fig. 10. Pulses of SO₂ at different concentrations (20 ppm, 50 ppm, 100 ppm, and 150 ppm) were supplied to the sensor repeatedly, for different relative humidity level in the background (0, 20%, 50%, and 70%).

Figure 10: Quasi-static measurement of Pt gate sensor during exposure to different concentrations of SO₂ at different humidity levels

As shown in Fig.10, humidity did not influence the sensor response and baseline as strongly as oxygen. However, there was still a pronounced difference in the baseline between dry gas and humid gas. There was also a difference in the size of the response since humidity increased the size of the response to SO₂. Most likely this was caused by a surface reaction between SO₂ and water forming HSO₃⁻ [30,31], which might adsorb on the sensor surface and thereby contribute to the response of by the sensor. In Figure 10(b) shows a close up of the sensor signal. The humidity is set to zero before switching to another level, which is seen as an increase of the baseline level. The quasi-static sensor signals at different temperature are extracted from a certain point (see Fig. 3) at the steady-state intervals in Fig. 10.

Figure 11: Relative humidity influence to the differentiation of SO₂ concentrations. SO₂ concentration given in ppm, the center points in each concentration cluster are marked (crosses). Data extracted from Fig. 10 from the intervals indicated in Fig. 3.

Fig. 11 shows the SO₂ discrimination with LDA when the humidity was constant, which gives four LDA plots. SO₂ data were grouped into different clusters for different concentrations and the cluster boundaries were added for better visualization. It was observed from the four LDA plots that the difference in the values of the 1st Discriminant Functions and 2nd Discriminant

Functions were not significant for different humidity levels (20, 50, 70% RH). This confirms that humidity had less of an effect as compared to oxygen (see Fig. 7).

Data pre-processing removed many imperfections from the raw data. The noise in the raw data was reduced by a Savitzky-Golay smoothing process. The drift in the sensor signal, and also the shift in the baseline due to humidity, decreased when data normalization was applied. The main features extracted from the raw data were the mean value from interval 2, 4, and 6 in Fig. 3, and also best-fit—line from all the 6 intervals. Figure 12 shows the results after the features were extracted and the data processed by LDA.

Figure 11: Processed data from Fig. 10 for SO₂ with 0% to 70% relative humidity (a) LDA plot (b) Correlation between SO₂ concentration and 1st Discriminant Function

In Figure 12, it is shown that the SO₂ concentrations at different humidity levels could be discriminated using both the 1st and 2nd Discriminant Function. The change in the response due to the changing humidity made it harder to differentiate different SO₂ concentrations. For example 20 ppm of SO₂ is differentiated from 50 ppm of SO₂ in the 1st Discriminant (x-axis), but not in the 2nd Discriminant (y-axis), while the vice versa is true for 50 and 100 ppm of SO₂. Subsequently, the center point of the 1st Discriminant function was plotted against SO₂ concentration in Fig. 12 (b) for better visualization. This shows that the correlation is not completely linear, compare to Fig. 9 for varying oxygen concentration. Fitting with 2nd order polynomial might perform better in this case.

3.3. Measurement in Desulphurization Pilot Unit

Due to mechanical and data acquisition problems, only data from 2 days of the 4 day test can be presented in this study. Figure 13, shows the quasi-static signal of the Pt-gate sensor at different temperatures compared to the data from the reference instrument. These data were chosen because they represented both lower and higher concentration ranges. The first measurement in Fig.13 (a) covers a concentration range below 800 ppm on day 1, while higher concentrations (up to 4000 ppm) on day 2 is shown in Fig. 13 (b). The difference in the concentration range was due to different stages of the desulphurization experiment in the pilot unit, and these phenomena could be explored to check also the measurement limit of the sensor. The detection limit for the reference instrument was adjusted after about 350 minutes during Day 1 to a higher detection limit of SO₂, which resulted in the observed step in the signal.

Figure 12: Quasi-static measurement at the desulphurization pilot unit (a) Day 1 (b) Day 2. Pt gate SiC-FET sensor.

Data from Day 1 and Day 2 were treated differently because of the different concentration ranges. The processed data are shown in the form of LDA plot in Fig. 14 (a) and (b). Due to the variation in the data, they were divided into several groups. For Day 1, the data were divided into three groups, all below 150 ppm, and one group above 300 ppm. On Day 2, the data were divided into three groups up to 2000 ppm and two groups above 2000 ppm (2000-4000 ppm and above 4000 ppm). However, Fig. 14(b) shows that for the SO₂ concentration above 2000 ppm, the sensor could not differentiate between different SO₂ concentrations. This might have been caused by the continuous high SO₂ surface loading that made the sensor reach saturated response as in static operation. For such high SO₂ concentration, it seemed

like the dynamic operation and intermittent exposure to high temperature of 400°C did not help. However, this may not preclude acceptable operation because in most power plants, the SO₂ concentration normally does not exceed 2000 ppm at the outlet of the desulphurization system.

Figure 13: LDA plot of the SO₂ concentration (ppm) in the desulphurization pilot unit on (a) Day 1 (b) Day 2. Data extracted from Fig. 13.

Besides LDA, the data from the pilot measurement were also treated with PLS, for which it was possible to plot the predicted value over time. The predicted value and the reference instruments value was compared directly as shown in Fig. 15 (a) and (b). PLS results from the measurement data showed a fairly good agreement with the reference instrument.

Figure 14: PLS model of the SO₂ concentration in the desulphurization pilot unit on (a) Day 1 (b) Day 2. Data extracted from Fig. 13.

As in other controlled multivariate data analysis methods, the data used for training and calibration play an important role in the utility of the model and the accuracy of the predicted values. The more comprehensive the training data, the better the model will be. In this case, less than 0,5% of the data were used for training, which is enough as long as they cover all concentrations necessary to make a proper model. It has to be noted that the training and calibration for Day 1 could not be used for Day 2, and vice versa, due to the differences in the SO₂ concentration ranges.

The weakness of this method is that it needs significant amount of data points to train the model. In this case, the data for training were taken from the same data set. To apply this method in a real application, extensive data training with different scenarios involving numerous changes in the background gases, would be needed to obtain good calibration of the system. The other method that might be applicable is 2-step LDA [32], which will be investigated in a continuation of this study. More advanced data processing such as linearization of the data will also be considered as pre-processing before feeding it to a linear model like PLS.

4. Conclusions

In this study SiC-FET sensors were studied as one alternative sensor technology enabling the usage of several sensors for control of the SO₂ emissions from power plants. However, the SiC-FET sensor response depends on the chemical reactions on the catalytic metal gate, while on the other hand SO₂ is a catalyst poison. Measurement with Pt, Au, and Ir-gate SiC-FET sensors at different temperature in static operation has failed to perform SO₂ quantification. A more advanced method using temperature cycle operation (TCO) was therefore tested. It was observed that the intermittent exposure to high temperature can help the desorption of sulfur containing adsorbates. Data pre-processing helped to reduce the influence of sensor drift and baseline and response level shift due to the changing concentration of background gases (4-10% O₂ and 0-70% RH). Additional features extracted from the measurement data also improved the overall sensor performance for SO₂ concentration between 20-150 ppm. In addition to the testing in the laboratory, additional testing in a desulphurization pilot unit was also performed to simulate the sensor behavior in an environment closer to the real application. In the pilot unit, the influence from the changing concentration of background gas was higher. The results show that it was possible to quantify SO₂ into several groups of concentrations with LDA up to a concentration of 2000 ppm. Moreover, PLS was also performed and showed promising agreement between the predicted value from the model and the SO₂ concentration from the reference instrument.

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