High Temperature Electrochemical CO/HC Sensor for Wood Firing Process: Signal Stabilization by Dynamic Electrochemical Methods

Xin Zhang[1,2], Christoph Schwab[2], Binayak Ojha[2], Heinz Kohler[2]

1 LAMTEC Meß- und Regeltechnik für Feuerungen GmbH & Co KG, Walldorf, Germany

2 Institute for Sensor and Information Systems (ISIS), Karlsruhe University of Applied Sciences, Karlsruhe, Germany

Abstract

The stability of a high temperature electrochemical CO/HC sensor (mixed potential type) can be clearly improved by sensitivity check with electrochemical impedance spectroscopy and regeneration by cyclic cathodic polarization under synthetic air conditions. Based on these results, a signal stabilization concept was proposed, and an instrument was built up to improve the quality and stability of automatic control of wood combustion processes. First results showed a clearly more stable sensing behavior and considerable emission reduction of a wood-log fueled fireplace with such control.

1 Introduction

Small scaled wood-log fueled furnaces are widely used and contribute considerably to air pollution and climate problems, especially in winter time [1]. Effective reduction of the emissions of those firing appliances can be achieved if advanced combustion air stream **(CAS)** control concepts are applied. We have experimentally shown that CAS control based only on the measurement of combustion temperature and residual oxygen concentration in the flue gas is not sufficient for optimum control of the combustion process. Only when the CO/HC content in the exhaust gas is also considered, the quality of combustion can be substantially improved. This has been demonstrated to enable a reduction of toxic gas emissions of about 80% compared to the manual operation of the furnace [2].

However, the lack of long-term stable and in-situ applicable CO/HC gas sensors hinders the effectuation of those advanced control systems in the market. In this paper we present a signal stabilization procedure for a commercial mixed potential CO/HC-sensor (LAMTEC GmbH, Germany) by sensitivity check with electrochemical impedance spectroscopy (EIS) and response regeneration by cyclic cathodic polarization (CV). Both procedures can proceed on site of sensor operation at synthetic air conditions [3]. In addition, we report about an achievement of very low emissions of a wood-log fueled fireplace with CAS control complemented by an oxidation catalyst.

2 Experiment

Two different types of commercial CO/HC sensors (Type 1 and Type 2) were studied in this work. Details of these two types of sensors are described elsewhere in [4]. At first, a Type 1 sensor and a Type 2 sensor (1#) were operated at 550 °C in the flue gas of a wood-log fueled fireplace (SF10SK, Brunner GmbH, Eggenfelden). For a first verification of the signal stabilization concept, the Type 1 sensor, which had clearly lost its sensitivity after some operation in the flue gas, was tried to be regenerated by cyclic cathodic polarization. The regeneration was carried out by using a two-electrode configuration (Fig. 1 a blue dashed line) under exposure to synthetic air at 700 °C. During the cathodic polarization, 30 potential sweep cycles between φ_{equ} (equilibrium potential, about 0 mV) and -0.6 V at a scan rate of 50 mV/s were imposed to the Au,Pt,-YSZ|YSZ|Pt solid state electrochemical cell. Further details of this procedure are given in Fig. 1b. In an additional step, another two fresh Type 2 sensor individuals (2# and 3#) were characterized by sensitivity and EIS -measurements, separately, before operation in any batch firing experiment. It has to be noted that the sensitivity characterization and the further operation of these two sensors in flue gas were conducted at a higher temperature (600 °C) compared to that for the Type 1 sensor and the Type 2_1# sensor. One of these two fresh Type 2 sensors (Type 2_2#) at first was pretreated by a cathodic polarization sequence as stated above to verify whether this pretreatment could enhance the signal stability from the very beginning of the operation in flue gas.

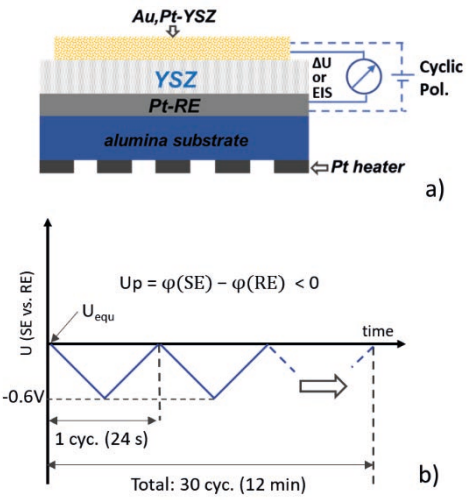

Figure 1 Schematic drawing of the sensor element (details described in [4]) in cross-sectional view (a) and illustration of the electrochemical regeneration process by cyclic cathodic polarization

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3 Results

The signal development of the type 1 sensor (sensitivity was periodically checked in $CO/O_2/N_2$ model gas mixtures) over time during operation in the flue gas of wood-log combustion processes is represented by star dots in Fig. 2a. The signals of the type 1 sensor clearly declined (Fig. 2a, black star dots) after 12h of operation at 550 in the flue gas. Meanwhile the type 2_1# sensor operated under the same conditions (550 °C) showed a decrease of signal (Fig. 2a, square dots) as well. Even though the signal degradation of the type 2_1# sensor was significantly less than that of the type 1 sensor after 36 h of operation in flue gas, further response reduction of this sensor was again found by additional operation in flue gas for another 50h. The relatively better stability of the type 2_1# sensor was most probably related to the more homogeneous distribution of Au in the Au,Pt-YSZ electrode, as reported in [4].

By application of the cyclic cathodic polarization sequence (Fig. 1b), the signals of the type 1 sensor were found to be raised again (Fig. 2a, red star dots) to values even higher than the ones measured in the very beginning (fresh state). This indicates that reaction sites of the electrode for mixed potential formation were partially blocked by oxidation of the electrode/electrolyte interface (aging effect) and can be reactivated by the cathodic polarization treatment [3]. Surprisingly, it could be shown that this regeneration effect of gas sensitivity leads to a better signal stability for at least 48 hours of further operation in the flue gas.

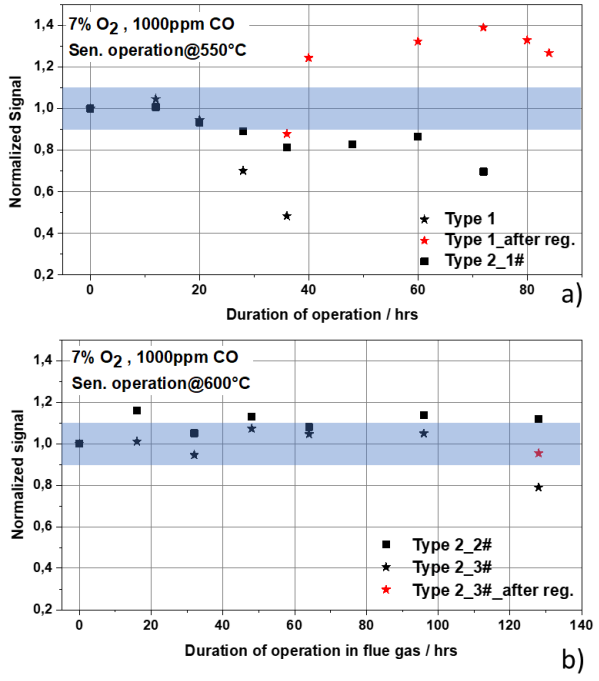

Figure 2 Signals of a Type 1 and a Type 2_1# sensor tested at model gas vs. the duration of operation at 550 °C in flue gas (a) and signal development of another two Type 2 sensors (2# and 3#) over time operated at 600 °C in flue gas (b). The light blue zone marks a margin of ±10% deviation in relation to the fresh sensor response.

Another two individuals (2# and 3#) of the type 2 sensor, which was shown to be relatively more stable than the type 1 sensor operated at 550 °C (before application of the regeneration, Fig. 2a), were tested in the flue gas to study the signal stability at a higher operation temperature (600 °C). Both sensor individuals were found to be evidently more stable compared to the sensors tested at 550 °C (Fig. 2b). Up to 96 h of operation in the flue gas, the type 2_2# sensor with the pre-polarization treatment in general showed a slight increase in the signal with small fluctuations under exposure to $CO/O_2/N_2$ model gas (Fig. 2b, square dots), while the signals of the non-pretreated type 2_3# sensor were found to be lightly fluctuated in the margin of ±10% deviation in relation to the initial response (Fig. 2b, star dots in the half transparent blue zone). The better stability of these two type 2 sensors may be attributed to a slower oxidation process of the electrode/electrolyte interface, which is assumed to be thermo-dynamically less favored at 600 °C compared to the operation at 550 °C [3,5]. Nevertheless, the signal of the type 2_3# sensor without the pre-polarization treatment declined to about 80% of the initial response after 96 h of operation in the flue gas (Fig. 2b, black star dot). This signal degradation could, however, be regenerated by the cyclic cathodic polarization (red star dot) as well. These results suggest that: i) the sensor aging by the oxidation of the electrode/electrolyte interface is retarded at 600 °C, but still leads to some signal degradation; ii) The degraded sensing response at 600 °C could be almost fully regenerated by the cathodic polarization process, which is interpreted as a reactivation of the blocked reaction sites for mixed potential generation formed by sensor aging processes.

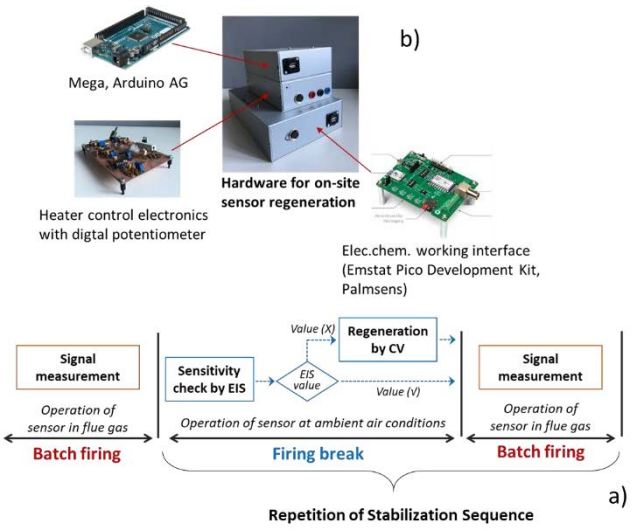

Figure 3 Schematic representation of the signal stabilization concept by repeated electrochemical treatments in flue gas analysis from batch wood-log firing processes (a) and photographs of the hardware (evaluation model) for on-site sensor regeneration ready to be implemented into the CAS control system.

So far, these results are very promising to enable stable CO/HC sensing in the flue gas with an excellent prospect of further stability improvement by the proposed signal stabilization concept. This means at a break between two consecutive batch firing processes, periodic sensitivity checks

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by EIS measurement [3] and if required, on-site regeneration of sensitivity under ambient air conditions are conducted. This is illustrated schematically in Fig. 3a. An electronic device has been already developed in hard- and software and was recently finalized to automate this concept (Fig. 3b).

Thanks to the improved long-term stability of these CO/HC sensors stated above, the system for automated control of the CAS, which was originally reported in [6], did now achieve a much higher level of quality and stability. This system includes not only a CO/HC sensor but also the sensors for combustion temperature, chimney draught, residual oxygen concentration and combustion air flow. In this work, this kind of system was validated at a single room fireplace (HKD7, Brunner GmbH, Eggenfelden) complemented with an oxidation catalyst (EmTechEngineering GmbH, Leipzig). It was demonstrated that, compared to manual operation, this system enables CO emission reductions by about 80%-90% depending on the power, at which the fireplace is operated. The power is determined by amount/weight of wood-logs used in the firing process. In this context, it has to be also noted that not only a considerable decrease of gaseous emissions like CO is achieved, but also a tendency of reduction of particulate matter (PM) emission was indicated under the automated operation. The PM emissions tend to be already moderately decreased under the manual operation when an oxidation catalyst and an electrostatic filter (e-filter) are applied. But, a depression of PM emissions by about 70%- 80% (compared to the value from the fireplace without catalyst and e-filter under manual operation) is only achieved, if the fireplace is complemented by the automated CAS control system introduced above together with the oxidation catalyst and the e-filter. These results will be reported soon [7].

4 Conclusions

The signal stabilization concept for mixed potential CO/HC sensors, consisting of the sensitivity check with EIS and regeneration with CV, has been validated on two different types of mixed potential CO/HC sensors, which are commercially available. It was experimentally shown that a much better level of signal long-term stability could be achieved for both types of sensors when operated in flue gas from wood-log combustion processes. Based on these very stimulating results, an advanced CAS control system, which includes also sensing of combustion temperature, residual oxygen concentration in flue gas, chimney draught and combustion air flow, has been successfully developed. By combination of this novel control system with an oxidation catalyst and an e-filter, a high potential of toxic emission depression (CO reduction by about 80% - 90% and PM reduction by about 70% - 80%) could be demonstrated compared to the manual operation of the fireplace. Details of these recent experimental results will be presented and published in near future [7].

5 Literature

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