Thin-film calorimetric H$_2$O$_2$ gas sensor for the validation of
germicidal effectivity in aseptic filling processes

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Abstract

A novel thin-film gas sensor was realized to detect the H$_2$O$_2$ concentration up to 10 vol.-% during microbial reduction of carton packages by hydrogen peroxide vapor in aseptic filling processes. The calorimetric sensing device contains two meander-shaped platinum layers as temperature sensing elements, both have been passivated with perfluoralkoxy and one additionally covered with catalytically active manganese oxide particles. First sensor characterizations have shown a sensitivity towards H$_2$O$_2$ of 0.57 °C/vol.-%. In the next step, the calorimetric gas sensor will be coupled on an RFID circuit for in-line detection of H$_2$O$_2$.

Keywords: aseptic filling process; hydrogen peroxide vapor; calorimetric gas sensor; manganese oxide; radio frequency identification

1. Introduction

The microbial reduction of carton packages for food, beverages as well as pharmaceuticals can be accomplished by hydrogen peroxide vapor (HPV). The prevalent application of HPV in aseptic filling processes compared to other chemical sterilization agents, like formaldehyde and ethylene oxide, relies on the decomposition of hydrogen peroxide in environmentally compliant reactants, namely water and oxygen$^1$. For the microbial reduction of packages, an aqueous H$_2$O$_2$ solution (35 wt.-%) is evaporated at a temperature above 200 °C and subsequently streamed into a pre-heated package with a constant gas flow of 2.5 m$^3$/h. The H$_2$O$_2$ concentration of the gas mixture aggregates up to 10 vol.-% and correlates thereby with the germicidal effectivity of the sterilization process$^2-^4$. This points out the requirement of a sensor system for the in-line detection of the H$_2$O$_2$ concentration during the microbial reduction of carton packages.

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In this work, a novel thin-film calorimetric H$_2$O$_2$ gas sensor for the validation of the germicidal effectivity in aseptic filling processes is presented. The calorimetric sensing device is based on a differential set-up of thin-film resistances as temperature sensing elements covered by perfluoralkoxy and one of them catalytically activated by manganese oxide (MnO$_2$) particles. The calorimetric gas sensor will be embedded in a test package and coupled on a passive RFID (radio frequency identification) circuit for the in-line detection of H$_2$O$_2$.

2. Calorimetric H$_2$O$_2$ gas sensor

The calorimetric H$_2$O$_2$ gas sensor has to operate in a chemically aggressive gas mixture at elevated temperatures and has to detect H$_2$O$_2$ concentrations of up to 10 vol.-%. In previous works, the authors have investigated different sensor layouts and materials as chemical transducer, which can be employed for the fabrication of a calorimetric H$_2$O$_2$ gas sensor.$^{5,6}$

As bulk material for the new miniaturized differential set-up, a silicon substrate with an insulating layer of 500 nm SiO$_2$ is used. Two meander-shaped platinum structures have been deposited via physical vapor deposition process on the sensor surface as temperature sensing elements. Both have been covered with perfluoralkoxy (PFA) because of its hydrophobic property and its stability at elevated temperatures of up to 300 °C as well as in reactive atmospheres. The PFA was deposited by spin-coating at 750 rpm for 10 sec to obtain homogenous and closed passivation layers. Afterwards, the PFA was pre-heated at 160 °C for 5 min and subsequently heat-treated at 360 °C for 25 min. Finally, one of the passivated platinum structures was catalytically activated by manganese oxide because of its high sensitivity against H$_2$O$_2$. Therefore, the “active” platinum structure was coated and heat-treated with a mixture of MnO$_2$ particles to achieve a large contact area and primer. The grain size of the MnO$_2$ particles amounts up to 10 µm (Fig. 1(a)). The miniaturized differential set-up has a chip size of 10 x 10 mm$^2$ (Fig. 1(b)).

After the fabrication of the calorimetric H$_2$O$_2$ gas sensor, the meander-shaped resistances have been calibrated at a temperature range between 20 and 130 °C. The temperature-dependent resistances can be calculated as follows:

\[ R_{\text{active}(\nu)} = 1560.8 \ \Omega \cdot (1 + 3.39 \cdot 10^{-3} \ \degree C^{-1} \cdot \nu - 5.89 \cdot 10^{-7} \ \degree C^{-2} \cdot \nu^2) \]  

\[ R_{\text{passive}(\nu)} = 1560.7 \ \Omega \cdot (1 + 3.39 \cdot 10^{-3} \ \degree C^{-1} \cdot \nu - 5.87 \cdot 10^{-7} \ \degree C^{-2} \cdot \nu^2) \]  

If the sensor is provided in H$_2$O$_2$ atmosphere, a temperature difference between the “active” platinum structure and the passivated structure can be detected because of the exothermal decomposition of H$_2$O$_2$ on the MnO$_2$ particles. The theoretical temperature difference can be determined as follows:

\[ \Delta \nu = \Delta H/C_P \]  

Therein, \( \Delta H \) is the change of enthalpy during the decomposition of H$_2$O$_2$ and \( C_P \) is the heat capacity of the gas mixture as summation of the heat capacities of the present gases.

Fig. 1. (a) Scanning electron microscopic picture of manganese oxide particles with primer (magnification: 10.2k); (b) scheme of the fabricated calorimetric H$_2$O$_2$ gas sensor with two meander-shaped resistances covered with passivation layers, where one of them is activated with a catalyst (chip size: 10 x 10 mm$^2$).
For the characterization of the sensor device, a test equipment with measurement chamber was developed, where the sterilization process with HPV of aseptic filling machines can be simulated under real conditions. The calorimetric gas sensor was investigated at various H$_2$O$_2$ concentrations in the measurement chamber (Fig. 2(a)). The sensor has shown a sensitivity of 0.57 °C/vol.-% for H$_2$O$_2$ in a concentration range from 0 to 8 vol.-% H$_2$O$_2$ (Fig. 2(b)) and an accuracy of 0.11 vol.-% H$_2$O$_2$.

3. RFID-based sensor system

In order to read out the calorimetric H$_2$O$_2$ gas sensor wireless and in-line during the aseptic filling process, an RFID transmission system will be developed. The transmission system contains a passive RFID transponder that is inductively coupled to an RFID reader. The transponder, directly connected to the gas sensor, will be realized on chip level with an integrated low power circuit, which includes a microcontroller and a capacitor for energy storage (Fig. 3(a)). The RFID reader is used for the power supply of the transponder and to read out the sensor signal in pulsed mode at an evaluated frequency (Fig. 3(b)). Finally, the calorimetric gas sensor as well as RFID transponder should be embedded in a test package to detect the H$_2$O$_2$ concentration during the microbial reduction by HPV.
4. Conclusions

A thin-film calorimetric H$_2$O$_2$ gas sensor for the validation of the microbial reduction of carton packages by HPV in aseptic filling processes has been realized. The calorimetric sensing device has shown a stable sensor signal in the chemically aggressive gas steam at H$_2$O$_2$ concentrations of up to 10 vol.-% and at elevated temperatures of nearly 250 °C. A sensitivity of 0.57 °C/vol.-% towards H$_2$O$_2$ of the gas sensor was determined in the developed test equipment. In the following step, the calorimetric H$_2$O$_2$ gas sensor will be coupled to a passive RFID transmission system in order to read out the sensor signal in-line during the microbial reduction of packages in aseptic filling processes. Therefore, the thin-film gas sensor and the RFID transponder have to be embedded on a representative position in the test package to detect the H$_2$O$_2$ concentration and send the sensor signal to the outside located RFID reader.

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