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Optochemical Hydrogen Peroxide Sensor based on Oxygen Detection

H. S. Voraberger, A. Bizzarri, W. Trettnak, V. Ribitsch

JOANNEUM RESEARCH
Forschungsgesellschaft mbH

Institute of
Chemical Process
Development
and Control

Steyrergasse 17
A-8010 Graz, Austria

Tel.: +43 316 876-1228
Fax: +43 316 876-1230

hannes.voraberger@joanneum.at
http://www.joanneum.at/cpk

Introduction

The most important industrial applications of hydrogen peroxide are bleaching processes, chemical oxidation processes in general and sterilisation purposes. The determination of the concentration of hydrogen peroxide in these solutions is of great technological, ecological and economical importance. The methods and instruments for the determination of this substance, which are commercially available, are time consuming, costly, cannot be used for on-line monitoring or are not applicable for hydrogen peroxide concentrations used in the mentioned applications. We describe a hydrogen peroxide sensor based on the principle of a sensor developed by Posch and Wolfbeis [1], which is shown in Figure 1. The aim of this work was to investigate the possibility to make this principle applicable for industrial applications. Therefore the performances of new inorganic catalysts were investigated, additional coatings were tested (to enhance the chemical resistance and to increase oxygen concentration in the sensitive layer) and the influence of oxygen background was determined. Furthermore the measurements were performed with a high performance oxygen probe developed for industrial applications [2].

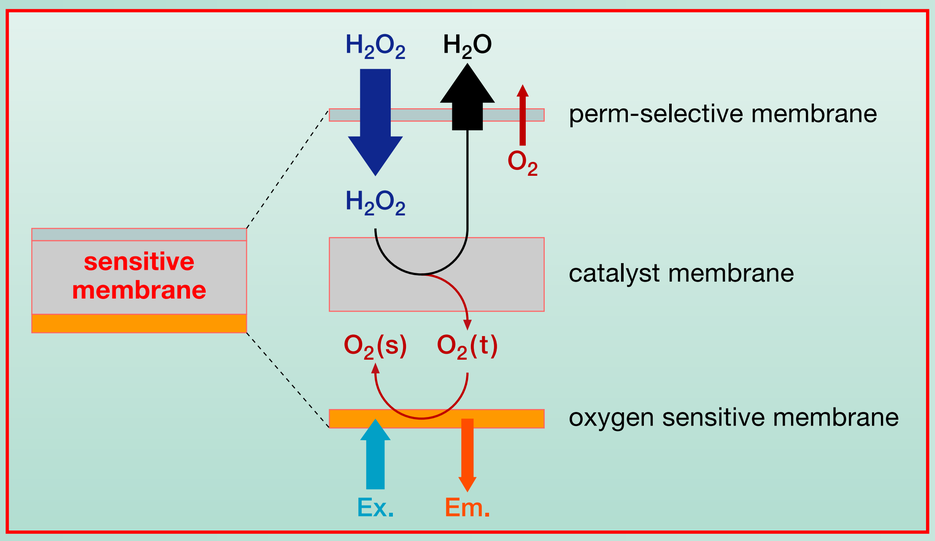

Figure 1. Novel hydrogen peroxide sensitive membrane and principal of hydrogen peroxide detection.

Experimental

Oxygen was measured via the quenching of the luminescence lifetime of a dye (ruthenium(II) diphenylphenanthroline) immobilised in polystyrene. For the production of the catalytic membrane, MnO_2, platinum and silver were mixed with silicone. Polymers, which were used for additional layers, were polysulfone, ethyl cellulose, polystyrene and 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole (Teflon® AF). The lifetime was measured in frequency domain as a phase shift between the excitation and emission light signals. The sensor membrane was mounted at the tip of a glass rod which guides the light. This allows measurements in chemical reactors at high temperatures without damaging the optoelectronic and electronic components at the other end of the rod (Figure 2). Different aqueous hydrogen peroxide concentrations were generated by adding different amounts of hydrogen peroxide stock solution (30 %, Merck, Germany) to a thermostatted vessel containing water, where the measurement was performed. The calibration for oxygen was done with different gas mixtures of oxygen and nitrogen, which were passed in the sample medium.

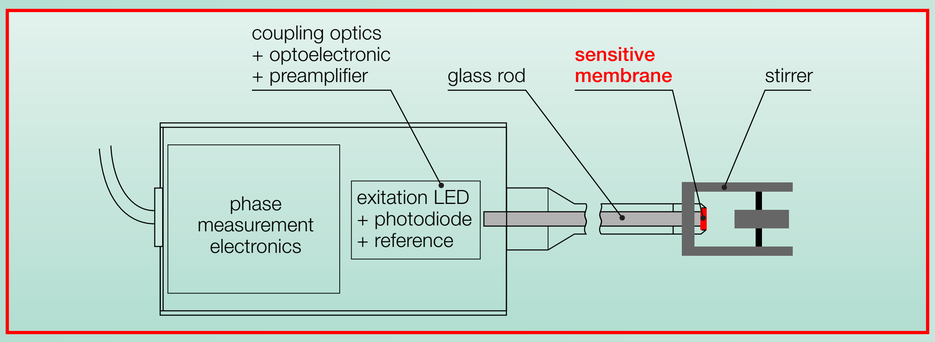

Figure 2. Probe set-up for the measurement of hydrogen peroxide via an optical oxygen sensor.

Results

In Figure 3 the performances of different catalyst materials are compared to the effect resulting from hydrogen peroxide quenching. Pt affected the oxygen concentration most, manganese dioxide showed a similar effect. With respect to the costs, manganese dioxide became the preferred catalyst. Quenching of hydrogen peroxide was less expressed than quenching by molecular oxygen formed by catalytic hydrogen peroxide decomposition.

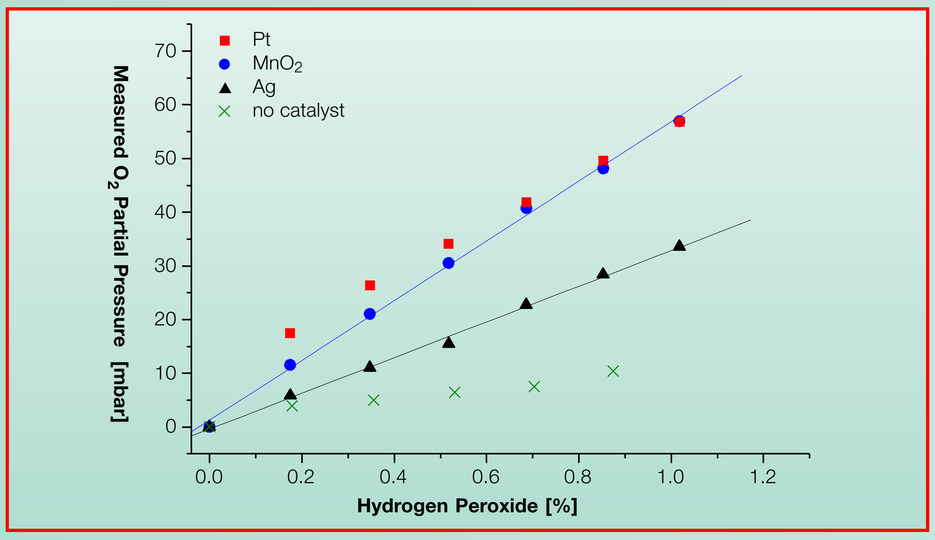

Figure 3. Hydrogen peroxide calibration graphs using different catalysts.

It was shown that by coating the sensor with a proper polymer layer the hydrogen peroxide sensitivity could be improved for up to 5 times compared to an uncoated sensor (see Figure 5 — hydrogen peroxide calibration graphs at different background oxygen concentrations). The investigated polymer layers included materials which are chemically very robust, like polysulfone (PSU) and polyetherimide (PEI). Coatings with these materials improved the chemical resistance of the sensors tremendously.

The major problem of the optochemical hydrogen peroxide sensor becomes obvious by comparing Figure 5a and 5b. The affect of changing the oxygen background from 0 to 21 % oxygen is from the same extent as changing the hydrogen peroxide concentration from 0 to ca. 1 % (depending on the covering layer). This demands for an oxygen compensation.

The response times of the sensor depended on the type of covering layer (see Table) with the shortest response times being similar to that of uncoated sensors (t_{95} was approximately 1 minute for a change from 0 to 0.2 % by weight hydrogen peroxide in water for the best performing sensors).

Polymer of covering layer	t_{90} [sec]	t_{95} [sec]	t_{99} [sec]
None	60	105	105
PSU	440	525	673
PEI	797	967	1261
PS	315	378	459
Teflon AF	60	60	60
ethyl cellulose	42	60	294

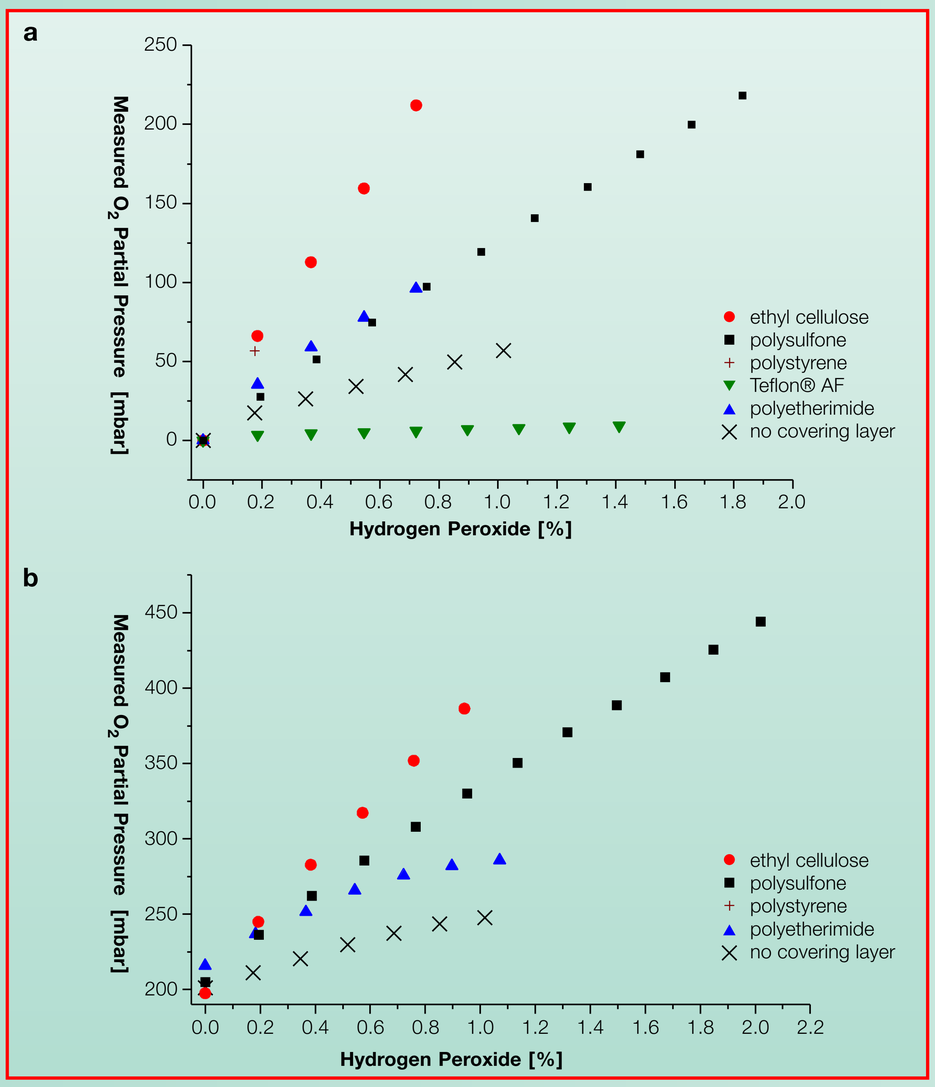

Figure 4. Hydrogen peroxide calibration graphs obtained with sensor membranes using different covering layers. The measurements were taken by passing 100% nitrogen (a) and 21% oxygen in nitrogen (b) into the sample solution.

Conclusion

The optochemical sensor measures reversibly hydrogen peroxide concentrations from 0.1 to 2 %. Measuring lower and higher concentrations of hydrogen peroxide should be possible, but were not tested so far. The sensor membrane can be covered with chemically resistant membranes, which enhance the oxygen concentration in the oxygen sensitive layer and protect the underlying membranes from being chemically attacked by the sample medium. By varying the covering membrane the sensor can be tailored for many applications. But each application demands for sensor optimisation. To be able to use this sensor in practical applications such as process control, a method to compensate for the background oxygen concentration and the temperature of the sample solution has to be developed.

References

[1]

Posch H. E., Wolfbeis O. S., Optical Sensor for Hydrogen Peroxide, *Microchim. Acta* **1** (1989) 41–50

[2]

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