Proceedings

Electrochemical Multisensor System for Monitoring the Hydrogen Peroxide Direct Synthesis in Microreactors [†]

Sebastian Urban [1,*], Andreas Weltin [1], Hubert Flamm [1], Jochen Kieninger [1], Benedikt J. Deschner [2], Manfred Kraut [2], Roland Dittmeyer [2] and Gerald A. Urban [1]

[1] Laboratory for Sensors, IMTEK—Department of Microsystems Engineering, University of Freiburg, Freiburg, Germany; weltin@imtek.de (A.W.); flamm@imtek.de (H.F.); jochen.kieninger@imtek.uni-freiburg.de (J.K.); urban@imtek.de (G.A.U.)

[2] Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology, Karlsruhe, Germany; benedikt.deschner@kit.edu (B.J.D.); manfred.kraut@kit.edu (M.K.); roland.dittmeyer@kit.edu (R.D.)

[*] Correspondence: sebastian.urban@imtek.de; Tel.: +49-761-203-7277

[†] Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 8 August 2017

Abstract: We present an electrochemical sensor system for the detection of hydrogen peroxide inside a direct synthesis microreactor. The setup allows the online, in situ measurement of high reactant concentrations by amperometric detection across the micro channel width and length. The robust integration of the electrochemical cell in the microreactor was demonstrated. Hydrogen peroxide was detected under reaction conditions (pH 3–4, presence of bromide) showing linear behaviour up to 2 mM with high sensitivity and excellent stability. The linear range was increased up to 10 mM by applying a diffusion limiting pHEMA layer to the electrode surface.

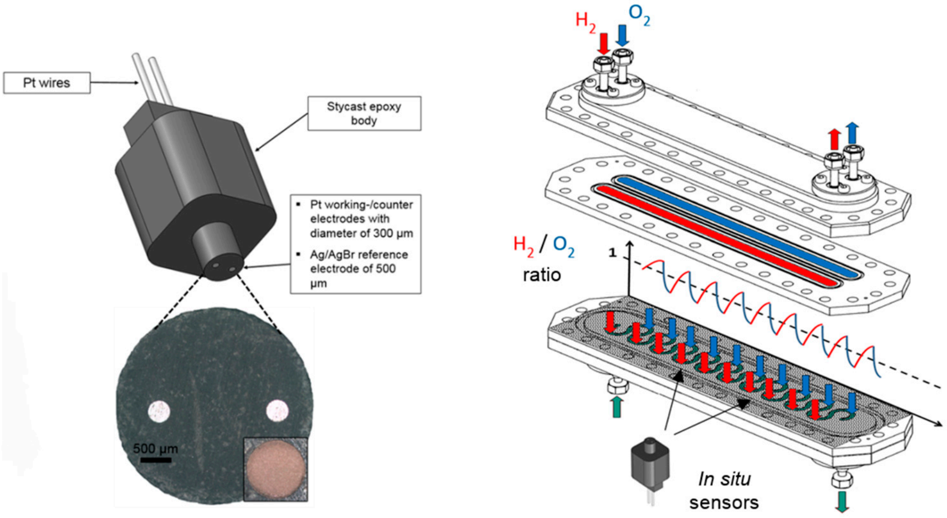
Keywords: hydrogen peroxide; microreactor; microsensor; amperometry; electrochemistry

1. Introduction

Hydrogen peroxide (H_2O_2) with its use as ecofriendly, strong oxidizing agent is one of the key parts of a more sustainable chemical industry. The heterogeneous catalytic direct synthesis of H_2O_2 from the elements H_2 and O_2 provides an attractive alternative for the decentralized production in comparison to the established anthraquinone method [1]. Conventional reactor designs are not fit to yield the full potential of the direct synthesis process, as the mass transport resistances in the liquid reaction medium are production limiting factors. A way to overcome these challenges is the use of microreactors [2]. However, defining and optimizing the process parameters for these microreactors is challenging as commercially available analytic systems only allow the concentration measurement of the reactants H_2, O_2 and H_2O_2 at the outlets of the microreactor. To measure the concentration distribution of the reactants inside the microchannels with a high spatial and temporal resolution, for the first time we developed a measurement setup of miniaturized electrochemical sensors.

2. Materials and Methods

The sensor setup, which is based on platinum electrochemistry, allows the amperometric measurement of H_2O_2 through direct oxidation on the electrode surface [3]. By changing the applied electrode potential it is possible to also selectively measure the concentrations of the dissolved process gases O_2 [3] and H_2. For the robust integration of the sensors and to achieve a packaging compatible with the microreactor layout and its harsh environmental conditions, platinum electrodes with a diameter of 300 µm were encapsulated into an Stycast epoxy housing, including an electrodeposited Ag/AgBr reference electrode. As shown in Figure 1a, each prepared sensor plug contains two platinum electrodes as working (WE)/counter electrode (CE) or alternatively the reference electrode (RE). Depending on the chosen setup, several of these plugs can be mounted in the microreactor as schematically shown in Figure 1b, allowing the determination of the reactants gradient over the channel length. All amperometric measurements were performed in a 3-electrode-setup, inside a test microreactor with an electrolyte containing 0.15 mM H_2SO_4 and 4 mM NaBr at a flowrate of the electrolyte of 1.5 mL min^{-1} if not stated otherwise.

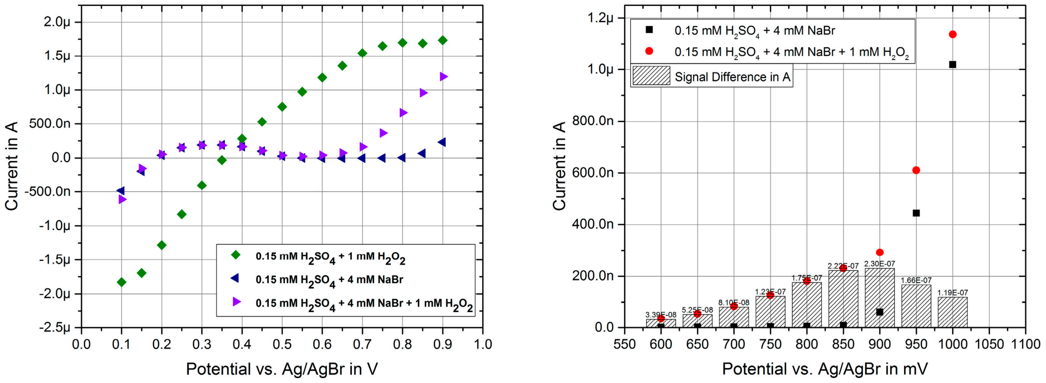


(**a**) (**b**)

Figure 1. (**a**) Schematic depiction and photograph of the electrode plug design used in the reactor, including Pt microelectrodes and Ag/AgBr reference electrode (inset); (**b**) Schematic of the membrane micro reactor with electrochemical in situ sensors in the microchannel.

3. Results and Discussion

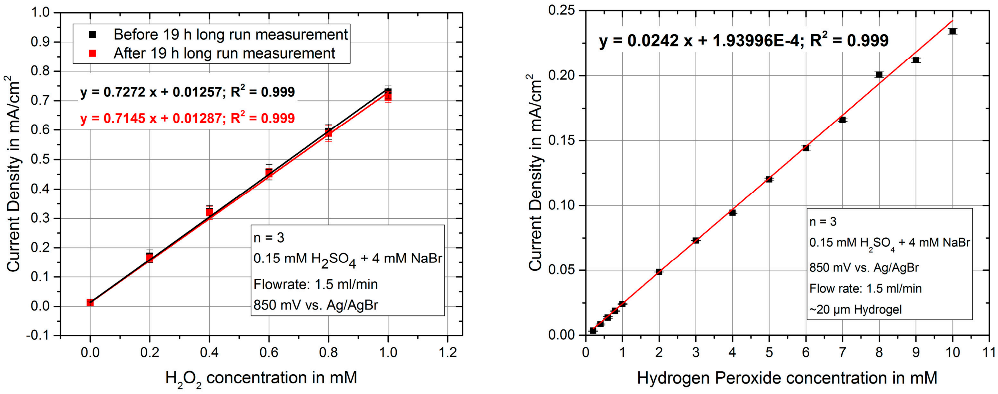
One of the main challenges for the sensor setup to overcome is the sulfuric acid electrolyte (PH 3–4) also containing a NaBr as catalytic promoter. As shown in Figure 2a, the bromide ions inhibit oxidation of H_2O_2 in the potential range of 400 to 700 mV vs. Ag/AgBr, which makes it necessary to shift to higher detection potentials for the selective amperometric detection of hydrogen peroxide.



(**a**) (**b**)

Figure 2. (**a**) Results for chrono amperometric measurements to determine the influence of the bromide ions in the electrolyte solution. The presence of bromide inhibits the direct oxidation of hydrogen peroxide in the potential range of 400 mV to 700 mV vs. Ag/AgBr; (**b**) Due to the oxidation of bromide ions, a trade-off between high detection and low background signal has to be made. To obtain selective results for the amperometric measurement of H_2O_2, a potential of 850 mV was chosen.

Furthermore, by increasing the measurement potential, an increase in background signal in the absence of hydrogen peroxide is visible. This effect is caused by the oxidation of the bromide ions to bromine at these potentials. For the selective detection of hydrogen peroxide it is therefore necessary to make a trade-off between very high detection and low background signals as shown in Figure 2b. For the following experiments a measurement potential of 850 mV vs. Ag/AgBr was chosen. By applying a measurement potential of 850 mV vs. Ag/AgBr we were able to detect H_2O_2 concentration linearly up to 2 mM inside the reactor ($R^2 = 0.997$) with an excellent sensitivity of 727 µA cm^{-2} mM^{-1}. As shown in Figure 3a even after constantly measuring for 19 h the sensitivity for the detection concentrations up to 1 mM of hydrogen peroxide showed no loss in sensitivity (727 µA cm^{-2} mM^{-1} vs. 715 µA cm^{-2} mM^{-1}; both with $R^2 = 0.999$). Due to the nature of the direct synthesis process of H_2O_2, the expected concentrations which can be obtained inside the microreactor setup exceed these concentrations more than tenfold. Therefore, the linear range for the amperometric detection of hydrogen peroxide was significantly increased up to a concentration of 10 mM ($R^2 = 0.999$) by applying a 20 µm thick layer of pHEMA hydrogel on the platinum electrode (Figure 3b) [3]. However, the sensitivity of the measurement was decreased due to the mass transport limiting effect of the hydrogel to a value of 24 µA cm^{-2} mM^{-1}. A further increase in linear response might be obtainable by increasing the size of the pHEMA hydrogel layer. However, that will also decrease the sensitivity for the H_2O_2 detection further.



(**a**) (**b**)

Figure 3. (**a**) Calibration curves for the detection of H_2O_2 for concentrations up to 1 mM show excellent linearity ($R^2 = 0.999$) and high sensitivity (727 µA cm^{-2} mM^{-1}). Continuous long-term measurements showed no loss of sensitivity over a measurement time of 19 h; (**b**) Calibration curve for the amperometric detection of H_2O_2 with 20 µm pHEMA-based hydrogel applied to the electrode increasing the linear range tenfold.

4. Conclusions

In this work, we present the first results for the electrochemical measurements of H_2O_2 with the described microreactor setup. The influence of the presence of bromide ions in the electrolyte on the detection process was examined. Furthermore, the overall sensitivity, linearity and stability of the amperometric H_2O_2 detection was evaluated. By applying a pHEMA-based hydrogel to the surface of the electrode a tenfold increase in linear range was achieved. Hereby we successfully showed the measurement of H_2O_2 under reaction conditions inside a microreactor.

Acknowledgments: This work was funded by German Research Foundation (DFG) within research unit "Erfassung und Steuerung dynamischerlokaler Prozesszustände in Mikroreaktoren mittels neuer in situ-Sensorik (ProMiSe)" (FOR 2383).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Campos-Martin, J.M.; Blanco-Brieva, G.; Fierro, J.L.G. Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. *Angew. Chem. Int. Ed.* **2006**, *45*, 6962–6984.
2. Dittmeyer, R.; Grunwaldt, J.-D.; Pashkova, A. A review of catalyst performance and novel reaction engineering concepts in direct synthesis of hydrogen peroxide. *Catal. Today* **2015**, *248*, 149–159.
3. Weltin, A.; Enderle, B.; Kieninger, J.; Urban, G.A. Multiparametric, Flexible Microsensor Platform for Metabolic Monitoring In Vivo. *IEEE Sens. J.* **2014**, *14*, 3345–3351.