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Original scientific paper

Comparison of H_2O_2 screen-printed sensors with different Prussian blue nanoparticles as electrode material

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Abstract

In order to determine hydrogen peroxide condensing from gaseous and liquid phases screen-printed electrodes with controlled and adjustable thickness, shape and size of the working electrode as well as electrode paste composition were investigated. For this purpose Prussian blue (PB) nanoparticles with a different particle size distribution of 20-30 nm (synthesized) and 60-100 nm (commercially available) were mixed with carbon paste and screen-printed on Al_2O_3 templates to establish H_2O_2-sensitive electrode. These two types of screen-printed sensors were compared to the commercial one during measurements in H_2O_2/water solutions at concentrations between 10^{-5} and 10^{-2} M H_2O_2. The linear signal in the investigated concentration range was found only for the sensor with the commercially available PB particles. Thus, this sensor prepared with PB particles of the size 60-100 nm showed the most reproducible and time-stable response versus the analyte in comparison to the others. This result offers the possibility to create sensors with adjustable design adapted to the concrete functionality. Thin films of collecting electrolytes based on agarose gels were printed on the sensor structures. They showed a distinct response on the application of H_2O_2-containing aerosols and gaseous phase.

Keywords

Hydrogen peroxide; screen printing; carbon paste; agarose; hydrogel

Introduction

The sensitive and selective determination of hydrogen peroxide (H_2O_2) is of great importance for biological, pharmaceutical, ecological and many other fields of application. Especially in the decontamination of surfaces H_2O_2 plays an important role as a sterilant. Depending on the requirements, a highly concentrated H_2O_2 solution is either passed through a vaporizer and then

introduced into the compartment to be sterilized with the aid of a carrier gas [1] or nebulized in the room supported by compressed air [2]. Consequently, H_2O_2 is either only present in the gas phase or additionally solved in aerosol particles. The aim of research is therefore directed to the development of a cost-effective sensor that can reliably detect H_2O_2-amounts in the gas phase as well as in aerosols.

For this purpose, a common method such as the determination of H_2O_2 in solution using electrochemical sensors with the redox mediator Prussian blue (PB) could be modified with regard to the measurement of the analyte in the gas space. PB is known for its excellent catalytic activity and selectivity for the reduction of hydrogen peroxide [3]. PB is usually applied to carbon electrodes by electrochemical deposition [4,5], dip coating [6], inkjet printing [7,8], or immobilization on functionalized surfaces [9,10]. An alternative method suitable for mass production and thus cost-effective is the screen printing of the PB working electrode similar to the procedure described by Benedet *et al.* [11]. By this alternative it is possible to perform specific modifications to the composition of the ingredients of the paste for the working electrode and to tailor the sensor surface and design according to the respective measurement requirements. For the realization, PB nanoparticles were synthesized, freeze-dried and finally mixed with a carbon paste to screen print the working electrode. Based on these electrode structures, preliminary experiments were performed with the PB electrode covered with agarose gel as a supporting electrolyte, and the resulting probe was used for the determination of H_2O_2-amounts in the gas phase.

Experimental

Materials

The following chemicals were used: iron(III) hexacyano-ferrate(II) (Alfa Aesar, Kandel, Germany); hydrochloric acid (1 mol/l), hydrogen peroxide (30 vol.%) and potassium chloride from Carl Roth GmbH + Co. KG, Germany; carbon paste (BQ242 Conductor Paste, DuPont Electronic Materials Ltd., UK); potassium hexacyanoferrate(II) (Fluka Chemie AG, Switzerland); iron(III) chloride (Riedel-de Haën Laborchemikalien GmbH + Co. KG, Germany); Agarose (Biozym LE, Biozym Scientific GmbH, Germany) and hydrogen peroxide (INTEROX SG-50, 49.5 % (w/w), Solvay Chemicals International SA, Belgium).

Methods

PB nanoparticles were synthesized according to Chen *et al*. [9] by mixing 20 ml of a 5 mM potassium hexacyano-ferrate(II) solution with 10 ml 0.1 M potassium chloride and 0.01 M hydrochloric acid. Then 20 ml of 5 mM iron(III) chloride were added and the mixed solution was stirred overnight. In order to dry the PB nanoparticle solution and to obtain a powder, the solution was first frozen for 20 min at a temperature of -80 °C and then dried for 22 h at -50 °C at a pressure of 1 mbar in a freeze dryer (Alpha 1-2 LDplus, Martin Christ Gefriertrocknungsanlagen GmbH, Germany).

Both, the synthesized and the commercially available PB powder (iron(III) hexacyano-ferrate(II)) were mixed with 10 % (w/w) to a carbon paste according to Benedet *et al.* [11]. These mixtures were used to screen print the working electrode with a diameter of 5 mm onto a platinum lead previously applied to an alumina substrate. For the preparation of the screen-printed sensors an electrode arrangement comparable to the electrode arrangement of commercial sensors of the company DropSens (DS710, Spain) was chosen. This enabled a direct comparison of the measurement results of the sensors with each other and provides information about the suitability of the different PB

nanoparticles for electrode fabrication. This is the basis for changing the sensor structure with regard to the intended application.

The electrochemical behavior of the electrodes in solution was studied with a potentiostat/galvanostat (Autolab PGSTAT12, Metrohm AG, The Netherlands). The electrochemical cell was equipped with a three-electrode system, consisting of a PB-carbon working electrode, a screen-printed Pt electrode as counter electrode, and an Ag/AgCl screen-printed electrode as reference electrode (see Figure 1)

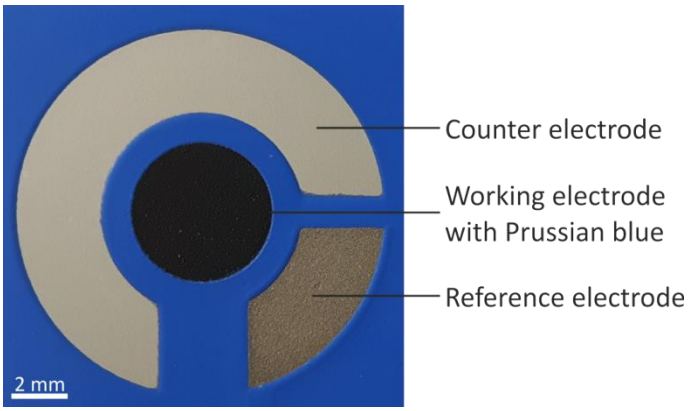

Figure 1. *Design of a screen-printed sensor with three-electrode system*

Before starting an amperometric measurement the electrodes were electrochemically activated. For this purpose, a potential of 0 V *vs.* Ag/AgCl (0.1 M KCl) was applied for 5 min in phosphate buffer solution in absence of hydrogen peroxide. The phosphate buffer had a concentration of 0.1 M with 0.1 M KCl and a pH value of 6.36. This buffer was chosen because it has a sufficiently high concentration of KCl to ensure good conductivity and the pH value is low enough to avoid a signal drop [6,12]. During the amperometric measurements successive volumes of a hydrogen peroxide stock solution (0.1 M) were added into a phosphate buffer solution at a constant potential of 0 V *vs.* Ag/AgCl (0.1 M KCl). For measurements with decreasing hydrogen peroxide concentration, the sensors were removed, rinsed quickly with deionized water and then transferred to separately prepared solutions.

In order to prepare the sensors for measurement of H_2O_2 in the gas phase and aerosols, the sensors were coated with agarose gel based on KCl solution as electrolyte. For this purpose, 0.2 g agarose was dissolved in 10 ml of a 0.2 molar KCl solution at a temperature of 90 °C and heated to 100 °C for 5 min similar to Benedet *et al.* [11]. The gel was then applied by squeegees to the surface of the sensors fixed in a 40 °C-tempered manufactured holder, shown in Figure 2. The reproducible placement of the gel layer directly on the sensor structure was achieved by a hole in the screen. The resulting gel layer had a thickness of 0.3 mm.

For determinations of H_2O_2 in the gas phase and of the aerosols, a test chamber was used in which a 49.5 % H_2O_2 solution was nebulized using compressed air at a flow rate of 3 ml/min (see Figure 3). The measurement was performed with a potentiostat (Interface 1000, Gamry Instruments, USA) amperometrically at the potential of -0.5 V *vs*. Ag/AgCl reference electrode located on the structure. This reductive condition is considerably more negative than the reduction peak observed in the range between 0.3 V and 0 V. Consequently, all presented PB is converted to its reduced and catalytically active form, the Prussian white (PW) (Equation 1).

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ \rightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \quad (1)$$

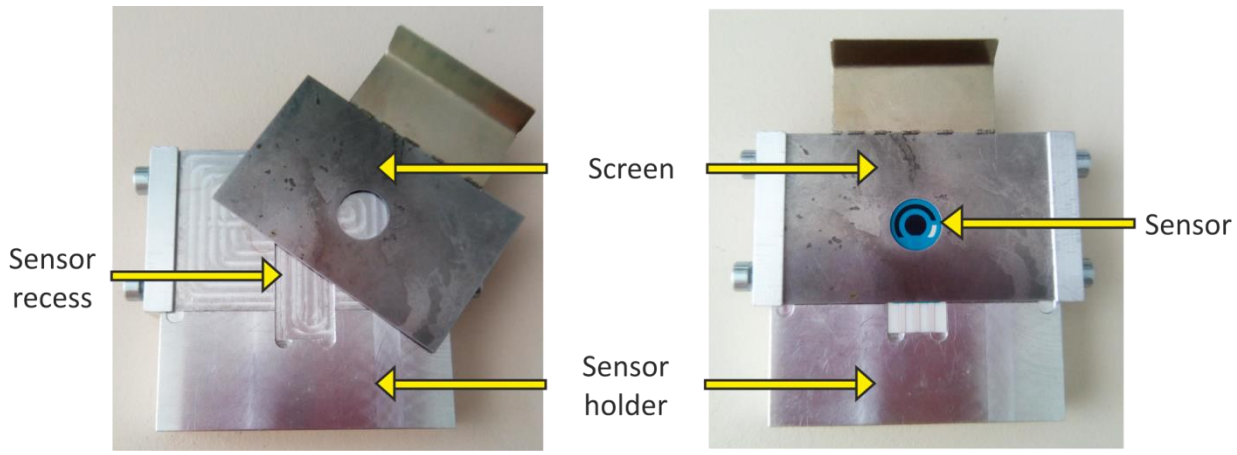

Figure 2. *Manufactured sensor holder for gel coating*

The chamber was also equipped with a sensor for the detection of gaseous H_2O_2 from the company Dräger (Dräger-Sensor H_2O_2 HC, Drägerwerk AG & Co. KGaA, Germany). This sensor measures only gaseous H_2O_2 and served as a reference for monitoring of the beginning and the end of each dosing phase. During a measurement, a permanent airflow was passed through the test chamber to create a constant atmosphere of gaseous H_2O_2 and aerosols.

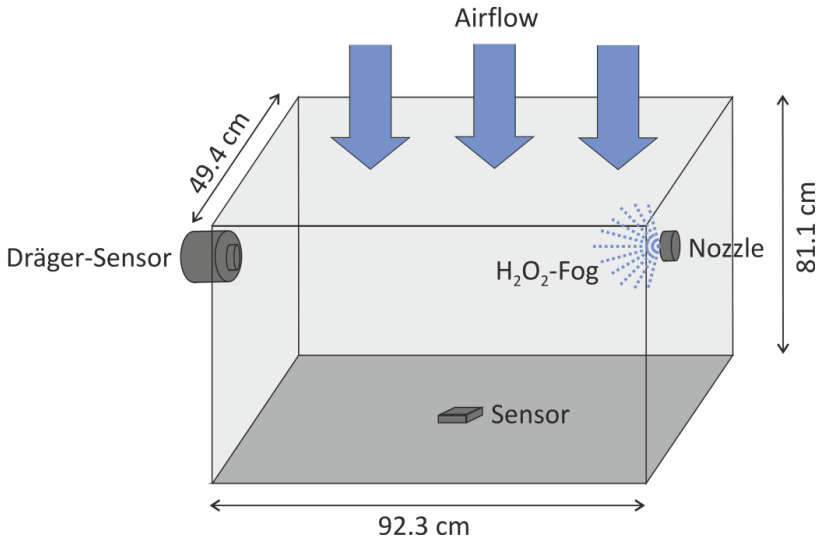

Figure 3. *Test chamber for the measurement of gaseous H_2O_2 and aerosols*

Results and discussion

The synthesis of PB yielded sphere shaped nanoparticles. According to the SEM images, the PB nanoparticles had a particle size of 20-30 nm, shown in Figure 4A. Therefore, they were smaller than the commercially available PB particles with a size of 60-100 nm (Figure 4B).

Both, the synthesized nanoparticles and the commercially available PB powder could be mixed without agglomeration into the carbon screen printing paste. The surfaces of the printed electrodes were comparable to those of a commercial screen-printed Prussian blue/carbon electrode of the company DropSens, see Figure 4C-E. The PB nanoparticles mostly covered the surfaces of the electrodes, so that the large slate-like particles of carbon paste were only visible in a few places. The images of the breaking edges of the working electrodes in Figures 4F-H show that the particles are evenly distributed in the carbon paste over the entire layer thickness. The sensors only differed in the thickness of the printed carbon PB layer, approximately 25 µm for the sensors with synthesized and commercially available PB and 20 µm for the commercial sensor.

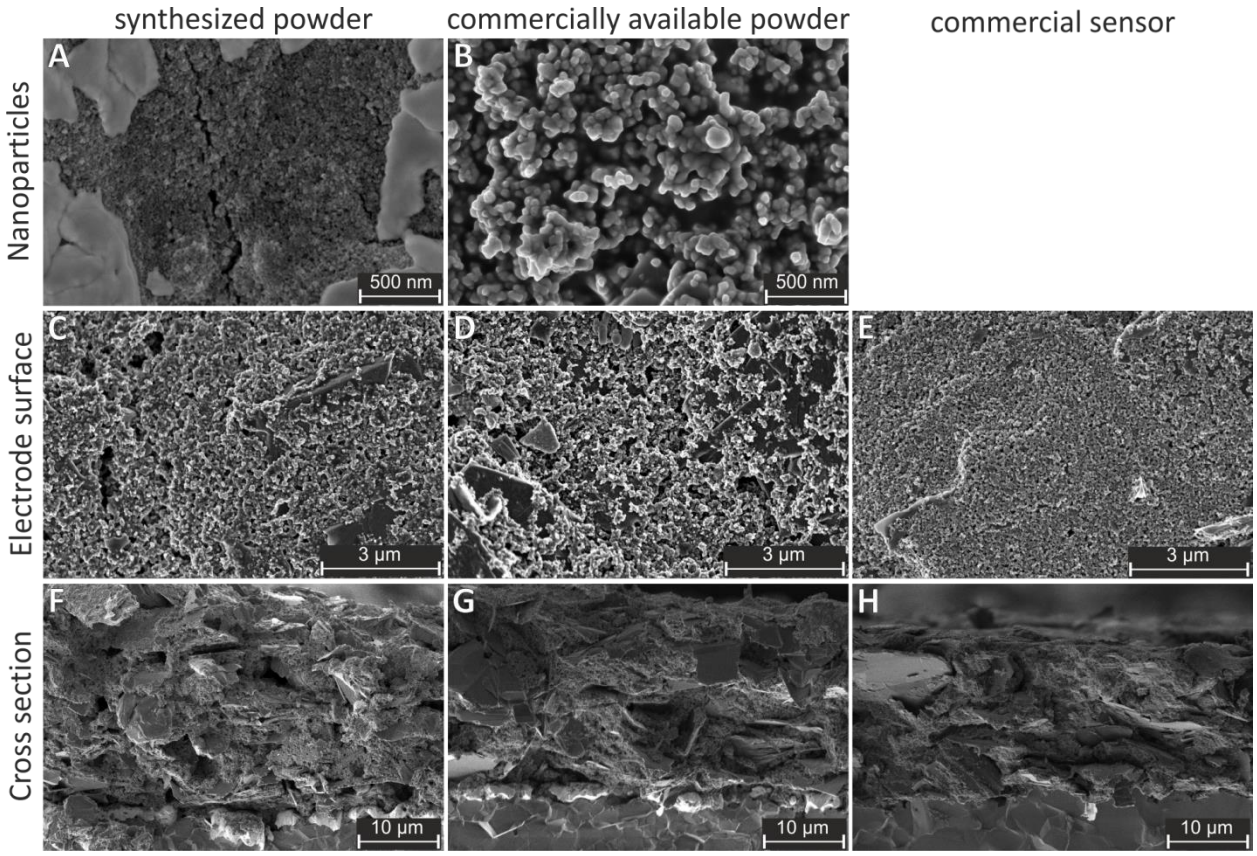

***Figure 4**. SEM images of **(A)** synthesized PB-powder. **(B)** Commercially available PB-powder. **(C)** Electrode surface screen-printed with synthesized PB-powder. **(D)** Electrode surface screen-printed with commercially available PB-powder. **(E)** Electrode surface from a commercial sensor. **(F)** Cross section of an electrode printed with synthesized PB. **(G)** Cross section of an electrode printed with commercially available PB. **(H)** Cross section of a commercial sensor*

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In Figure 5 the current densities of the sensors during the amperometric determination of hydrogen peroxide in different concentrations are monitored as a function of time. It must be noted that all measurements were carried out in unstirred media. Therefore, all processes were diffusion controlled and the response times were extended. Although this was rather unusual for amperometric measurements, the investigations were performed in this way to compare them with additional planned measurements, in which H_2O_2 was detected after diffusion from the gas phase into a thin electrolyte layer. All three sensor types show a clear response to the different H_2O_2 concentrations. The sensor printed with the commercially available PB powder and the commercial sensors had almost identical measurement curves and showed comparable current densities.

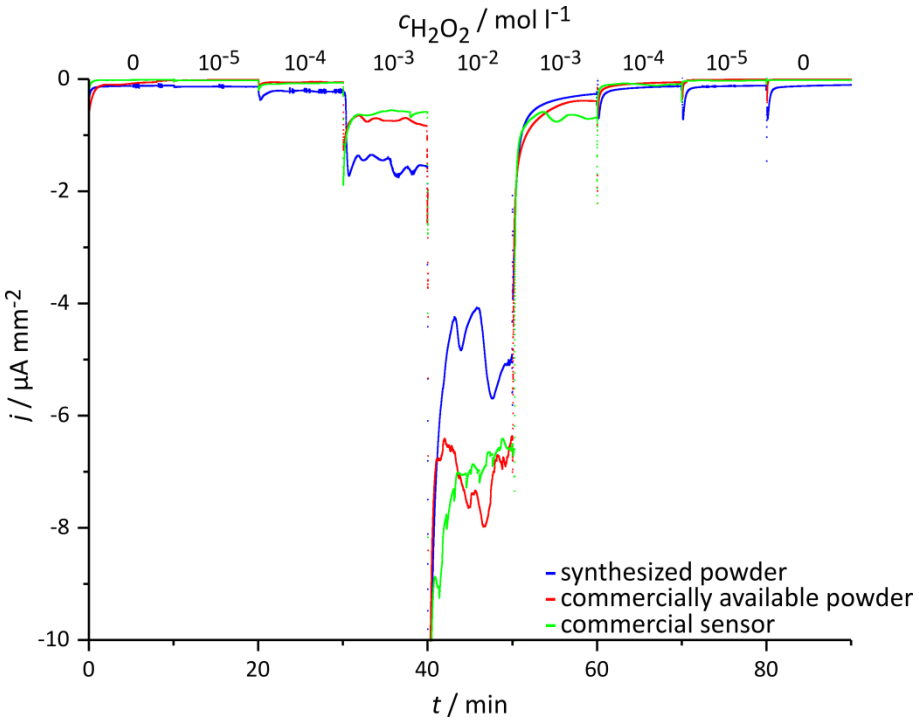

***Figure 5**. Amperometric measurements of sensors with synthesized PB and commercially available PB as well as a commercial sensor in 0.1 M phosphate buffer with 0.1 M KCl (pH 6.36) and different H_2O_2 concentrations at a polarization voltage of 0 V* vs. *Ag/AgCl, 0.1 M KCl*

Both, for measurements with increasing and decreasing concentrations, a linear correlation between H_2O_2 concentration and the sensor signal at concentrations between 10^{-4} M and 10^{-2} M could be determined for all sensors with the exception of sensors with synthesized PB during measurement with decreasing concentration. For the sensor with commercially available PB, the linear correlation could even be extended to the concentration of 10^{-5} M. This can be seen in the calibration plots in Figure 6. The mean values were calculated for data obtained after 10 min of measuring time per hydrogen peroxide solution.

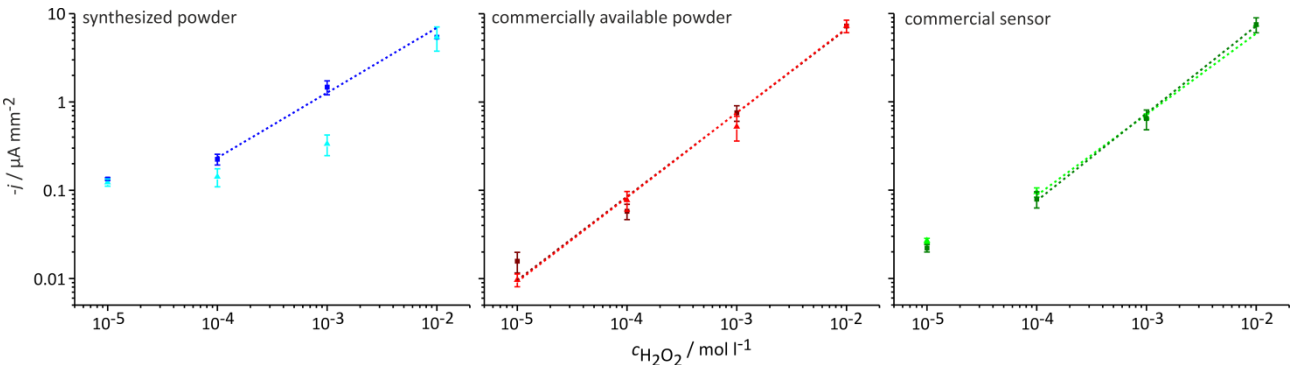

***Figure 6.** Mean current densities with the associated standard deviations for different concentrations of H_2O_2 (■ increasing concentration, ▲ decreasing concentration) for n = 3*

The sensor, which was manufactured with synthesized PB powder, initially showed a comparable sensitivity to the other two sensor types. However, from a concentration of 10^{-2} M H_2O_2, the sensor increasingly lost its sensitivity and the remaining sensitivity dropped clearly. This is an indication that changes have occurred on the surface of the working electrode during the measurement. This could be due to impurities caused by KCl, a by-product of PB synthesis. EDX studies of the synthesized and commercially available PB nanoparticles by an accelerating voltage of 20 keV

showed an increased presence of KCl in the synthesized PB powder. KCl could be identified as plate-shaped structures in the SEM images in Figure 4A, which was confirmed by EDX studies (Figure 7). CN (yellow-green) has been chosen for the detection of PB, because the iron ions were apparent through all other layers and therefore could not be assigned correctly. In the figure the potassium ions are marked blue and the chloride ions red. From this, it could be concluded that the lilac colored areas represent potassium chloride.

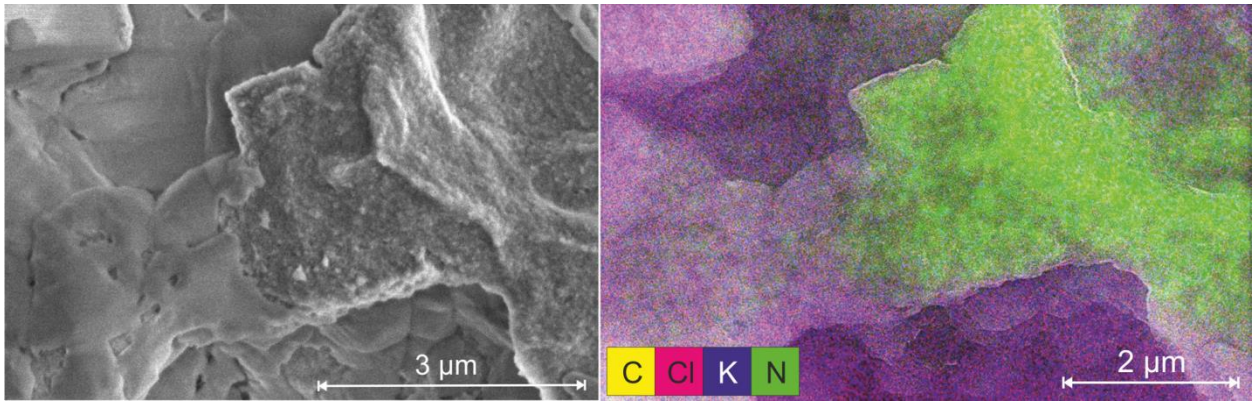

Figure 7. *SEM image (left) with EDX analysis (right) of synthesized PB powder*

This KCl becomes detached from the surface of the electrode during the measurement and may carry along PB nanoparticles or reduce the stability of the PB paste composite. This could explain the reduction in selectivity as the measurement progresses. Further investigations will show whether purification of the synthesized PB powder will reduce this process and whether these nanoparticles are suitable for the manufacture of screen-printed electrodes. The EDX studies of the commercially available PB powder indicated reasons for this assumption. Table 1 shows the standardized weight percentages of Fe as a representative of PB and of K and Cl within the different powders.

Table 1. *Chemical composition (EDX) of samples in standardized wt.%.*

Element	Content of synthesized powder, wt.%.	Content in commercially available powder, wt.%.
K	29.91	0.1
Cl	22.29	0.06
Fe	16.90	35.32

Consequently, using the commercially available PB powder, screen-printed sensors could be created that show a larger linear range than the commercial sensors while measurement in solution.

The next step for sensor development was the integration of a suitable electrolyte which, in addition to the typical electrolyte properties, also showed chemical resistance against higher concentrations of H_2O_2, good permeability for H_2O_2, low evaporation rate and could be reproducibly applied to the electrode surface in thin layers. Investigations showed that a polymer system known from sensor technology, agarose, fulfills these properties. Therefore, an agarose hydrogel based on KCl solution could be suitable for the use as electrolyte for detection of H_2O_2 in the gas phase and aerosols [11].

The amperometric measurements of sensors coated with a 0.3 mm thick agarose layer in the test chamber when exposed to gaseous H_2O_2 and aerosols are shown in Figure 8. The current density is monitored in dependency from the introduced gaseous H_2O_2-phase and aerosol particles (49.5 %

H_2O_2). The introduction of the gaseous H_2O_2 was controlled by a Dräger-sensor (dotted line) and served as a monitoring tool for the start and end of the dosing phase.

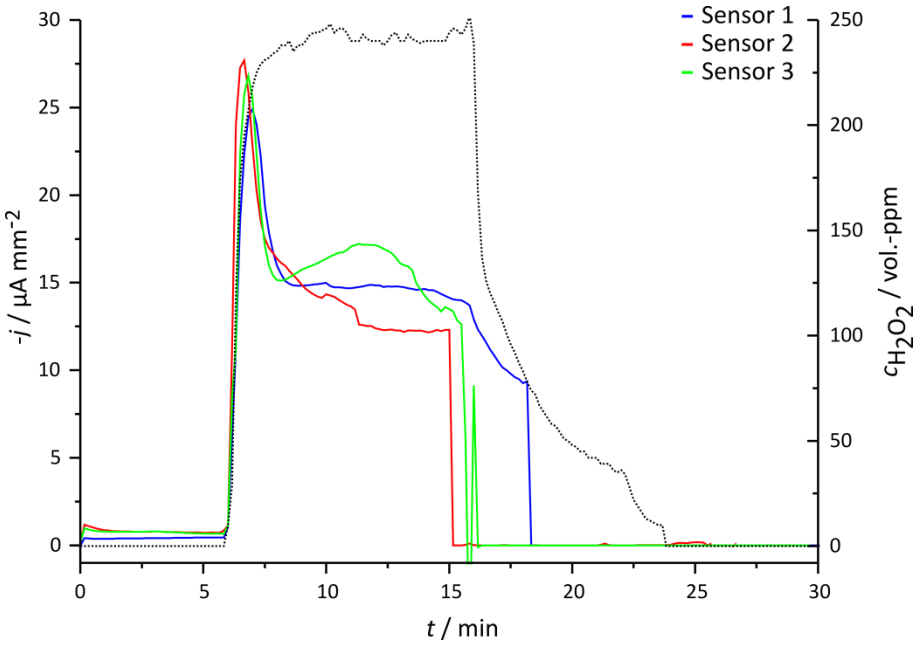

Figure 8. *Amperometric measurements of gaseous H_2O_2 and aerosols with three screen-printed PB-sensors coated with agarose gel in the same way*

The Dräger-sensor showed that a constant concentration of gaseous H_2O_2 of about 240 vol.-ppm was maintained over the dosing phase. In contrast, the screen-printed sensors covered with agarose showed a rapid signal increase after start of the introduction of H_2O_2. This sensor response pointed to a fast reaction from PW with H_2O_2 on the electrode surface (Equation 2).

$$K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 + 2H_2O_2 \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4K^+ + 4OH^- \quad (2)$$

After the first minute the sensor signal insignificantly decreased, forming a plateau. This plateau indicated that the detection process was limited either by the kinetic of electron transfer for the electrochemical regeneration of PW or structural transformations of PB paste layer, or changes within the electrolyte during the lasting measurement process. The experiment showed that not all incoming H_2O_2 reacts with PW at the electrode. A considerable amount was decomposed at the sensor surface, creating O_2 accumulating in the agarose gel. After oxygen saturation of the gel, bubbles are formed between the electrode surface and the gel layer. These cavities caused a detachment of the gel membrane resulting in a signal interruption.

Since the sensors coated with agarose showed promising results except for the formation of bubbles, it would be useful in further investigations to reduce the formation of the undesirable cavities by constructive changes or to simplify the gas escape from the electrolyte.

Conclusions

With both, the synthesized and the commercially available PB powder, screen-printed electrodes could be successfully realized which respond sensitively to varying H_2O_2 concentrations comparable to a purchasable product. With the commercially available PB powder it was even possible to produce electrodes which show a linear response at H_2O_2 concentrations between 10^{-5} and 10^{-2} M that is a larger linear measuring range than of the commercial sensor. In the case of sensors with synthesized PB nanoparticles, a change at the working electrode occurred during the investigation,

whereby the sensitivity decreased with continuing measurement. A reproducible determination of H_2O_2 over a longer period of time is currently not possible with this PB paste. Further investigations will clarify what causes the changes on the surface of the working electrode in the sensors with synthesized PB powder. Therefore, the synthesized PB powder will be purified from KCl.

Based on the research of the sensors with commercial Prussian blue crystals covered with a KCl including agarose gel as the supporting electrolyte, it was shown that the determination of high concentrated gaseous H_2O_2 amounts and aerosol particles was possible with this sensor setup. Further improvements have to be directed on the phase boundary electrode surface / gel electrolyte to avoid the formation of O_2-bubbles by catalytic decomposition of hydrogen peroxide and to establish a rapid exchange of the solved analyte with PW particles. Furthermore, changes in the electrode structure with the tested PB nanoparticles, as well as variations of the gel composition will be executed. This would allow an adaption of the sensor layout to the requirements for an aspired measuring of condensed H_2O_2 within a thin electrolyte film to monitor hydrogen peroxide in the gaseous phase.

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