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Experimental study of porous tubular catalytic membranes for direct synthesis of hydrogen peroxide

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ABSTRACT

A continuous process for safe direct synthesis of H_2O_2 from H_2 and O_2 over Pd-catalysts in a gas/liquid membrane contactor is proposed. As a prerequisite for the process a method was developed for coating of Pd based catalysts into the fine porous layer on the inside of asymmetric tubular membranes. The method reached uniform distribution and high dispersion of the Pd nano particles with ca. 11 nm size for a range of membrane geometries and lengths and a variety of membrane materials. For the selection of the best catalytic system additional experiments with supported catalysts were performed. They were prepared using the same materials and coating method as for the manufacture of the catalytic membranes. The principle of the membrane contactor was verified with 10 cm long single channel membranes with stable operation of the continuous system for more than 10 h at differential pressures up to 4.5 bar in methanol. Further, the role of key process parameters such as solvent type, system pressure and flow regime were assessed. Productivities up to 1.7 $\text{mol}_{H_2O_2}\ g_{Pd}^{-1}\ h^{-1}$ (6.1 $\text{mol}_{H_2O_2}\ m^{-2}\ h^{-1}$ related to the geometric surface area of the membrane) with a selectivity of 83% towards H_2O_2 were achieved.

1. Introduction

Hydrogen peroxide is a versatile non-polluting oxidizing agent with manifold applications. Nowadays it is mainly consumed for bleaching of paper and textiles and for detoxification of waste water [1,2]. Of growing interest is the use of H_2O_2 as a selective oxidant, e.g., for the manufacture of fine chemicals. Limiting for this application, however, is its relative high price resulting from the complex industrial production route. The dominating multi-step anthraquinone process [1], although safe (prevents the contact of O_2 and H_2 during the reaction), is highly energy consuming and uses an expensive and complex chemical solvent system. It is economically viable only for large-scale production (>40 kt y^{-1}), thus necessitating transportation and storage of concentrated H_2O_2 solutions and causing additional investments for safety precautions. Therefore, the direct synthesis of hydrogen peroxide from O_2 and H_2 over Pd-catalysts is gaining much attention as a green and more efficient alternative to the industrial route, also suitable for small capacity on-site production [2–4]. This process has been investigated for decades already, but it is still not established on a commercial level mainly due to drawbacks related to safety (H_2/O_2 gas mixtures are explosive in a wide concentration range) and selectivity (water is the thermodynamically stable product). An important step towards commercialisation, however, was the start of a demonstration plant for the direct synthesis of hydrogen peroxide at the end of 2006 by Evonik Degussa in Hanau-Wolfgang (Germany) [5], developing the process using a supported Pd/C catalyst in a fixed bed reactor with methanol as solvent.

A possibility to improve the safety of the direct synthesis process is the use of a catalytically active membrane as a multiphase contactor for hydrogen and oxygen, one of them as a gas and the other one dissolved in a liquid. Generally two concepts of such tubular membrane reactors have been studied:

(i) distributor [6–14] – the active component (Pd or PdX, X = Ag, Au, Pt etc.) is in the form of a dense metallic layer coated on the outside surface of the tubular inorganic support. The reaction is performed via a H_2 permeation mechanism with O_2 saturated in the liquid medium on the inside of the membrane.
(ii) contactor [7–10,15,16] – the active component is in the form of highly dispersed metallic nano particles (Pd or Pd/X, X = Ag, Pt) coated into the fine-porous layer of the asymmetric tubular ceramic support, achieving much higher active surface area for reaction and offering better Pd utilization, while keeping the safety benefit of separation of hydrogen and oxygen. The contact between the two reactants takes place by diffusion from opposing sides through a narrow liquid filled region in the membrane where the catalyst is deposited.

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Most of the studies for the distributor type of reactor were performed at very mild conditions – room temperature, H_2 pressures up to 3 bar and O_2 pressure at 1 bar. Further lowering of the temperature to 2–5 °C favours the H_2O_2 synthesis [6] over the decomposition. Only one recent study investigates the performance of such H_2 selective catalytic membranes at higher temperatures (up to 75 °C), reporting increased productivity (from 88 $\mathrm{mmol_{H_2O_2}\,m^{-2}\,h^{-1}}$ at room temperature up to 133 $\mathrm{mmol_{H_2O_2}\,m^{-2}\,h^{-1}}$ at 75 °C), but with somewhat lower selectivity (decreasing from 85% to 35%) due to faster H_2O_2 decomposition [14]. Note that the productivity related to the surface area refers to the geometrical area of the membrane in contact with the liquid. The focus of the research work on the "distributor" lies on catalyst development rather than on reactor optimisation. Pure Pd layers are found to be unstable (due to hydrogen brittleness). Therefore, a further modification with Ag [6,10–12] and the addition of a consecutive Pd layer [6,12] as well as a hydrophobic polymer layer [6] have been performed in order to achieve higher productivity (ca. 28 $\mathrm{mmol_{H_2O_2}\,m^{-2}\,h^{-1}}$ [12], ca. 50 $\mathrm{mmol_{H_2O_2}\,m^{-2}\,h^{-1}}$ [6]) and selectivity (ca. 70% [6]). The combination of Pd with Pt (Pd:Pt = 18:1) increased the membrane performance [9], but this effect is found to be strongly dependent on the support material [10]. Surface morphology (determined from membrane preparation method and conditions) influences also the membrane performance – smooth metal surface with large crystallites [6] and with high uniformity of grains [12] are found to improve catalytic activity. Although expected that the H_2 permeation through the dense Pd layer is the limiting step in the process, some authors claim, that the reaction is kinetically rather than diffusion controlled [12–14] with H_2 permeation rates up to three times higher than the H_2 consumption rates at their experimental conditions [14].

The contactor type multiphase reactor was proposed for direct synthesis of hydrogen peroxide in a project funded by the European Commission [15], and the first studies [7–10] were performed at mild conditions – atmospheric or slightly elevated pressure of the liquid in which O_2 is saturated and H_2 gas pressures are up to 8 bar. Other investigated parameters to improve the performance of the catalytic membranes include the use of bimetallic catalysts (Pd/Ag, Pd/Pt) [9–11], the modification of the ceramic support by coating of a porous carbon layer inside the membrane pores [7–10], the use of methanol as reaction medium [9], and the presence of Br^- as promoter [9]. H_2O_2 formation up to 800 $\mathrm{mg\,L^{-1}}$ H_2O_2 after 5 h with a selectivity up to 28% with Pd/Pt (18/1) catalyst have been observed leading to a productivity of 94.4 $\mathrm{mmol_{H_2O_2}\,m^{-2}\,h^{-1}}$ [9]. Note that the productivity here is also related to the geometrical area of the membrane and not to the surface area of the catalyst nano particles deposited inside the catalytic layer. Therefore, it represents an "effective" value which is influenced, among other factors, by the Pd loading and particle size distribution.

A detailed description of the principle of the membrane contactor and preliminary results for the direct synthesis of hydrogen peroxide with single channel outside coated catalytic membranes in semi-batch experimental mode at elevated pressures (up to 69 bar) can be found in our previous work [16]. Improved productivity up to 16.8 $\mathrm{mol\,m^{-2}\,h^{-1}}$ with very high selectivity between 80% and 90% after optimisation of the reactants feed side have been obtained. The aim of our following work was to further develop the concept and design a compact system for a safe continuous process for the small-scale on-site direct synthesis of hydrogen peroxide with catalytic membranes, operating based on the contactor principle.

This contribution presents the developed experimental set-up for the continuous process, a method for catalyst coating of inorganic membranes with fine porous layer on the inner side of the ceramic tubes and results on catalyst characterisation and the productivity/selectivity of the prepared catalytic membranes including the influence of some crucial parameters on the performance of the membrane contactor in continuous mode such as volumetric flow rate (residence time) and type of flow in the membrane channel.

Table 1
Parameters for the catalyst coating procedure.

Parameter	Single channel membranes 10 cm length	Multi-channel membranes 25 cm length
Pd acetate concentration [$\mathrm{g\,L^{-1}}$]	2–5	2–5
Amount of coating solution used [mL]	4	40
Rotation speed [rpm]	30	30
Air flow for drying [$\mathrm{L\,h^{-1}}$]	150	200
Air direction change [$\mathrm{min^{-1}}$]	6	6
Drying time [min]	30	60
N_2 flow for precursor decomposition [$\mathrm{L\,h^{-1}}$]	15	25

2. Experimental

2.1. Tubular ceramic membranes

Commercially available micro-filtration tubular ceramic membranes with asymmetric structure and fine porous layer on the inner side of the tubes (inside coated membranes) were provided by Inopor GmbH, Hermsdorf, Germany. Because of the relatively large pore sizes (≥100 nm) the membranes are not gas selective and do not show any permselectivity towards H_2 or O_2. They were manufactured from different materials (Al_2O_3, TiO_2, carbon coated Al_2O_3) and were supplied in different geometries – single or multi-channel tubes. Most of the experiments for H_2O_2 synthesis were carried out with single channel membranes (l = 10 cm, $d_{\mathrm{inner}} = 0.7$ cm, $d_{\mathrm{outer}} = 1$ cm, fine porous layer with $d_{\mathrm{pore}} = 100$ nm). Carbon coated Al_2O_3 membranes were prepared by immersing the Al_2O_3 support for 1 min in a phenol resin solution (phenol dissolved in methanol and pyrrolidone), drying for 24 h at room temperature, further polymerisation of the resin for 3 h at 150 °C in air and following carbonisation at 700 °C in N_2 atmosphere. Phenol resin concentrations from 1 to 25 wt% were applied.

2.2. Catalyst preparation

Metallic Pd nano particles were deposited preferably into the fine porous layer on the inner side of the ceramic tubes with the help of an impregnation/decomposition procedure: the membrane for coating is placed in a stainless steel module and sealed with O-rings on both ends. Palladium-II-acetate (≥99 %, Pd content 47%; Merck, Darmstadt, Germany) is used as a precursor for metallic Pd. A coating solution (Pd precursor dissolved in acetone) is filled from the inlets on the outside of the module (from the coarse porous side of the membrane). It wets the membrane, penetrates into the pores and is concentrated into the layer with the finest pores from the inside of the tube. The solvent acetone is constantly evaporated from the inner side with an air stream with changing directions and by constant rotation of the module, in order to obtain an even radial and axial precursor distribution. After complete drying the membrane is placed into a tubular oven and heated up to 250 °C for 3 h in N_2 flow for precursor decomposition. Table 1 summarises important parameters for the coating procedure of single and multi-channel membrane elements with 25 cm length. The method was successfully scaled up by HITK e.V. for multi-channel elements with up to 50 cm length.

The deposition efficiency (DE) of Pd with this method was calculated with Eq. (1), where $m_{(\mathrm{Pd\text{-}exp})}$ is the experimental amount of Pd on the membrane determined gravimetrically and $m_{(\mathrm{Pd\text{-}theory})}$ is the theoretical amount of Pd, calculated from the volume and Pd

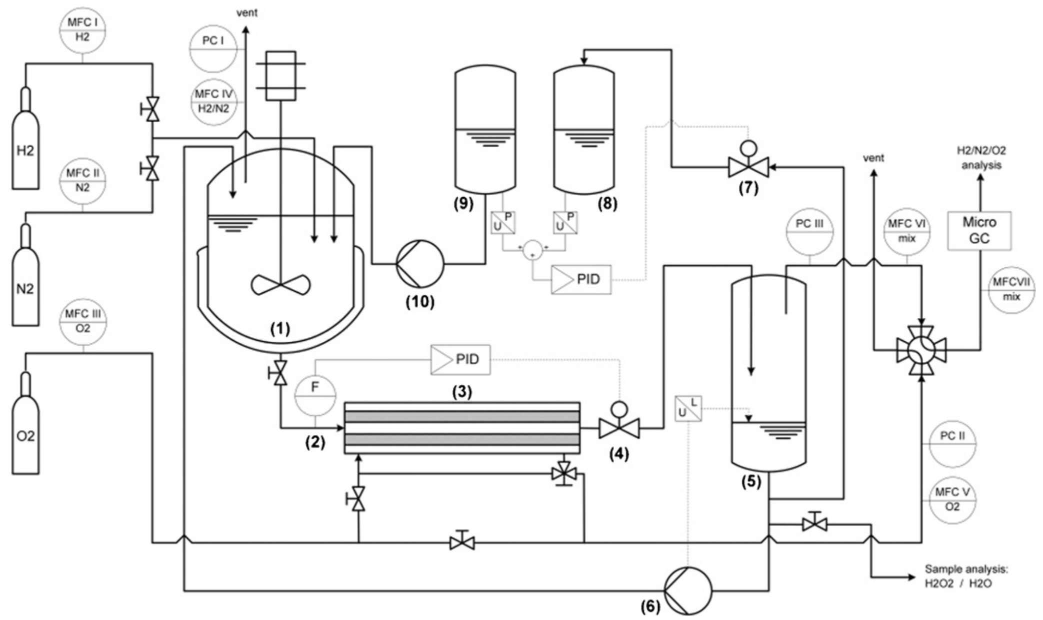

Fig. 1. Experimental set-up for continuous operation of the H_2O_2 direct synthesis process: (1) saturator, (2) flow meter, (3) membrane module, (4) expansion valve, (5) separator, (6) piston pump, (7) control valve, (8) product vessel, (9) fresh solvent vessel, (10) HPLC pump.

concentration of the coating solution used.

$$\mathrm{DE} = \frac{m_{\text{Pd-exp}}}{m_{\text{Pd-theory}}} \qquad (1)$$

The same procedure was used to prepare bimetallic Pd/Au catalysts. Tetra chloroauric acid $HAuCl_4{\cdot}xH_2O$ (Au content 50%, Chempur, Karlsruhe, Germany) was used as Au precursor. For the bimetallic catalyst preparation, a subsequent coating cycle (impregnation, drying, decomposition) at the same conditions but with the Au-precursor, was performed with already Pd coated membranes.

Furthermore, a number of supported catalysts with Pd contents of 0.5 wt%, 1 wt% and 2 wt% and four different types of supports (pure carbon, Al_2O_3, TiO_2 and carbon infiltrated Al_2O_3) were prepared with the same coating procedure (impregnation, drying, decomposition) adapted for powder materials and at the same conditions as for the ceramic membranes.

Several characterisation techniques (described in detail in the Supplementary material section) have been used for assessment of the quality of the catalyst coating.

2.3. Experimental set-up

Fig. 1 schematically represents the designed experimental set-up for continuous operation of the H_2O_2 direct synthesis process. Key part of it is the membrane contactor (3), where the catalyst coated tubular membrane is mounted. The gaseous reactants are supplied separately. In the saturator (1) (Model 5100, Parr Instruments) H_2 is dissolved at high pressure (up to 70 bar) in the liquid, which is constantly fed through the inner side of the ceramic tube, wetting the membrane from the fine-porous layer side. O_2 is fed as gas from the coarse–porous outer side of the membrane directly into the membrane module (3). By applying a suitable overpressure on the O_2 side, the gas/liquid phase boundary is established inside the membrane close to the transition from the coarse–porous support to the fine-porous catalytic layer, where the reaction takes place. With the help of control valve (4) (RC200, Wagner, Offenbach, Germany) the reaction mixture is expanded into the separator (5), and the liquid phase is recompressed and recycled into the saturator (1) with a piston pump (6) (MTKa 10617, Prominent, Heidelberg, Germany). This sequence comprises the main loop of the process. The recycle is required in order to get to higher concentration of H_2O_2, despite the fact that the amount of H_2O_2 produced per one pass is limited by the concentration of hydrogen in the liquid leaving the saturator. The secondary loop includes a control valve (7), a product vessel (8), a fresh solvent vessel (9) and an HPLC pump (10) (Model 1001, Knuaer). It maintains the continuous operation of the process by compensating the amount of liquid withdrawn from the system and keeping a constant liquid level in the saturator (1). The safety of the process can be guaranteed by monitoring the concentration of dissolved hydrogen at the exit of the membrane contactor and by regulating the flow through the membrane module in a way that all of the hydrogen is consumed within it. Formation of explosive O_2/H_2 mixtures in the saturator (1) is avoided by removing the excess of oxygen from the system in the gas/liquid separator (5).

For a typical experiment with the continuous system 1.4 L methanol (for HPLC, Rotisolv®, Roth, Karlsruhe, Germany) with additives 15–17 $\mathrm{mg\,L^{-1}}$ NaBr (99.995 Suprapur®, Merck) and 0.02–0.03 $\mathrm{mol\,L^{-1}}$ H_2SO_4 (for analysis, 95–97%, Merck), was used as a reaction medium. The system was at first pressurised with H_2/N_2 to the desired total pressure and the membrane contactor (3, Fig. 1) was totally filled with the liquid. The desired system flow was set at the regulated valve (4, Fig. 1) and the continuous mode was started. The O_2 gas pressure in the line was adjusted normally to 2 bars higher than the liquid pressure. Afterwards the O_2 inlet valve was carefully opened (opened and closed several times until the system adjusted) and O_2 was fed into the membrane module, which marked the start of the experiment. The O_2 pressure was slowly further increased to reach the desired pressure difference. The reaction was followed for several hours. Samples were withdrawn from the liquid phase in the separator (5, Fig. 1) in regular time intervals. H_2O formation was determined by Karl–Fischer-Titration (KFT Titrator DL 38, Mettler Toledo, Giessen, Germany). H_2O_2 concentrations were determined by titration with standardized Ce(IV)SO_4 solution (0.1N, TitriPUR®, Merck). Selectivity to H_2O_2 (S) was calculated according to

$$S = \frac{C_{H_2O_2}}{C_{H_2O_2} + C_{H_2O}} \qquad (2)$$

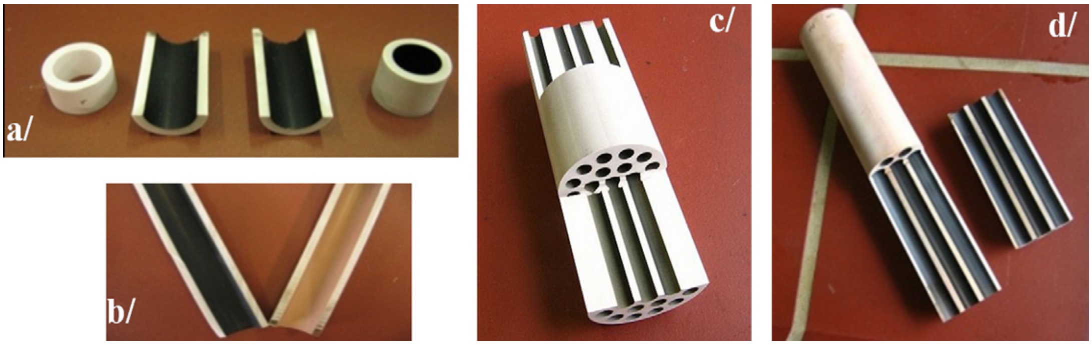

Fig. 2. Asymmetric tubular ceramic membranes coated with the impregnation/decomposition procedure of Pd acetate: (a) single channel Al_2O_3 membrane coated with Pd; (b) single channel TiO_2 membrane with bimetallic coating Pd/Au (left) and pure Au coating (right); (c) 19-channel Al_2O_3 membrane coated with Pd; (d) 7-channel Al_2O_3 membrane coated with Pd.

Additional experiments for the direct synthesis of hydrogen peroxide with supported catalysts were performed both in the saturator of the continuous set-up (1, Fig. 1) in semi-batch mode with continuously fed gas phase and a constant liquid phase, and in a separate high pressure reactor with 600 mL total capacity (Model 4560, Parr Instruments) in batch mode with a constant gas and liquid phase. Experimental conditions:

(i) Semi-batch mode: approx. 1.2 L MeOH with 0.02–0.03 mol L^{-1} H_2SO_4 and 13–15 mg L^{-1} NaBr were supplied into the reactor together with the catalyst powder (ca. 1 g). The system was pressurised with N_2 under stirring (ca. 800 rpm) to the desired total pressure (P_{total} = 60 bar). H_2 and O_2 were mixed in a T-piece in order to have mixture of $H_2/O_2/N_2$ = 8/27/65 vol.% and fed together into the solution. This was marked as a start of the experiment. Samples were withdrawn at certain time intervals and analysed for H_2O_2 and H_2O. The reaction was monitored normally from 4 to 10 h, in some cases even up to 30 h. Selectivity to H_2O_2 was calculated with Eq. (2).

(ii) Batch mode: ca. 300 mL of the solvent (methanol or water with the additives 0.03 mol L^{-1} H_2SO_4 and 15 mg L^{-1} NaBr) were mixed with 500 mg or 1 g powder catalyst in the reactor and pressurised first with 45 bar N_2 then with 12 bar O_2 and afterwards with 3 bar H_2 to obtain the desired gas mixture (e.g., $H_2/O_2/N_2$ = 5/20/75 vol.%) at first without stirring the liquid. After reaching the desired total pressure (60 bar) the gas supply valve was closed and the stirrer was started (1000 rpm), which marked the start of the reaction. During the experiment the total pressure decrease due to the reaction was monitored. The reaction time was set to 1 or 2 h. Afterwards, the measurement was stopped and the liquid was analysed for the products H_2O and H_2O_2. Selectivity to H_2O_2 was calculated with Eq. (2). In case of water as solvent, selectivity was calculated from the pressure drop and the known H_2O_2 concentration, invoking the hydrogen and oxygen material balances for the system assuming no change in the gas and liquid volume.

3. Results and discussion

3.1. Coating and characterisation of catalytic membranes

The described impregnation/decomposition coating procedure was used to prepare catalytically active membranes from different materials and with different geometries. It obtains uniform coatings with Pd concentrated preferably into the layer on the inner side of the membrane tubes (Fig. 2).

Table 2 summarises the theoretical and experimental Pd content, together with the deposition efficiency for a number of different membrane samples with different geometries. Very high deposition efficiencies are observed (above 93%) for the single channel membranes based on pure alumina (entries 1 and 2, Table 2) and titania (entries 5–7, Table 2). A little bit lower values for the carbon infiltrated membranes (entries 3 and 4, Table 2) could be due to an oxidative carbon degradation with traces of O_2 in the heating atmosphere, affecting the determined experimental mass after coating.

Important characterisation parameters for the quality of the coating are the radial Pd distribution and Pd penetration depth, investigated with the help of electron probe micro analysis (EPMA). This method is suitable for Pd determination in presence of other metals or non-metals. Fig. 3 shows Pd profiles for a pure alumina single channel membrane (open symbols). All four scans are represented, demonstrating uniform radial Pd distribution in the four directions. Moreover, Pd is concentrated preferably into the fine porous layer from the inner side of the membrane tube with up to ca. 40 μm depth.

In the case of multi-channel membranes with up to 25 cm length for both 7-channel (Fig. 4) and 19-channel elements slightly higher concentrations of Pd in the middle channels as in the outer ones are

Table 2
Properties of coated membranes based on alumina (Pd/Al_2O_3), titania (Pd/TiO_2) and carbon infiltrated alumina ($Pd/C–Al_2O_3$).

No.	Membrane type	Membrane geometry	$m_{Pd\text{-}theory}$ [mg]	$m_{Pd\text{-}exp}$ [mg]	DE [%]
1	Pd/Al_2O_3 (R502_15)	1-channel, 10 cm	9.68	9.70	100
2	Pd/Al_2O_3 (R474_23)	1-channel, 10 cm	12.48	12.23	98
3	$Pd/C–Al_2O_3$ (MC_13)	1-channel, 10 cm	11.21	9.35	85
4	$Pd/C–Al_2O_3$ (MC_0440)	1-channel, 10 cm	9.24	8.80	93
5	Pd/TiO_2 (T_2)	1-channel, 10 cm	18.12	16.90	93
6	Pd/TiO_2 (T_3)	1-channel, 10 cm	17.71	17.70	100
7	Pd/TiO_2 (T_7)	1-channel, 10 cm	8.36	8.40	100
8	Pd/Al_2O_3 (R362_8)	7-channel, 25 cm	57	58	102
9	Pd/Al_2O_3 (R362_3)	7-channel, 25 cm	117	115	98
10	Pd/Al_2O_3 (R402_A9)	19-channel, 25 cm	37	33	89

In brackets is given the indication of the manufacturer HITK.

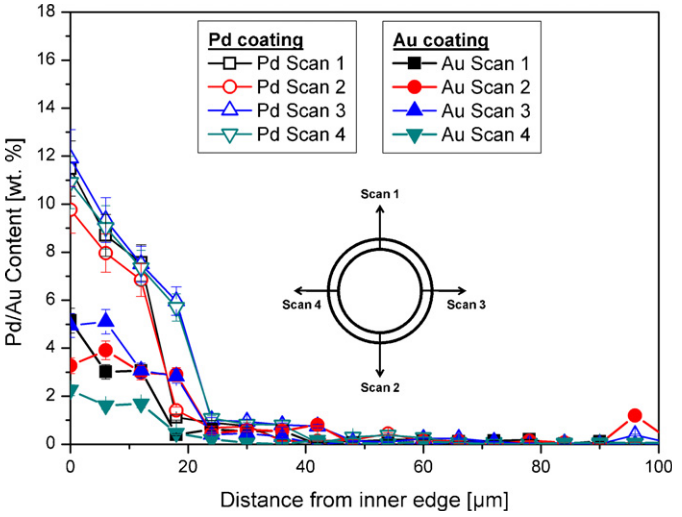

Fig. 3. Electron probe micro analysis characterisation of a single channel pure alumina membrane: opened symbols – Pd profiles from the first coating cycle with $PdAc_2$ as precursor; filled symbols – Au profiles from a second coating cycle with the gold precursor. Performed are four scans (2 times 2 opposite directions) from the inner edge outwards of the membrane piece.

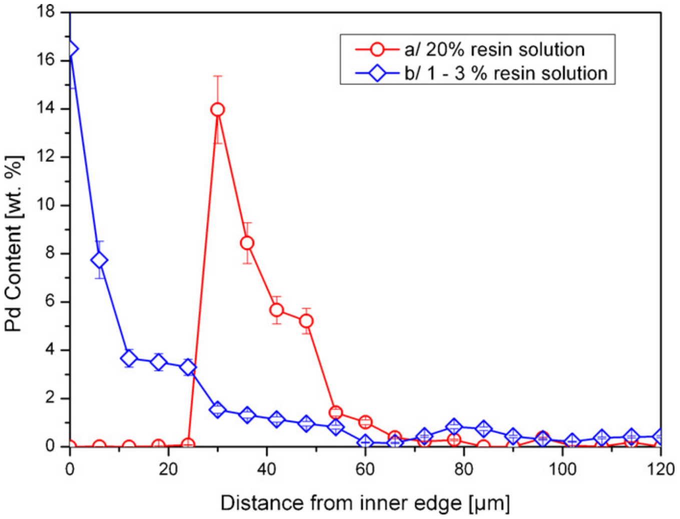

Fig. 5. Electron probe micro analysis Pd profiles of two different carbon infiltrated alumina membranes prepared with: a/concentrated and b/diluted resin solutions.

observed, whereas the discrepancy is stronger for the 7-channel than for the 19-channel membrane, for which not so sharp difference is observed. The reason for this effect was assumed to be the uneven distribution of the air flow in all channels during the drying procedure. This was confirmed by additional laser doppler anemometry measurements of the flow velocity distribution for a 7-channel membrane, showing the highest velocity in the middle channel. More important, however, is the good Pd distribution preferably into the fine porous layer with depths to 30–40 µm from the inner edge of the membrane tube.

First coatings of carbon infiltrated single channel alumina membranes showed poor performance of the method, i.e. an enrichment of the metal particles not in the top layer on the inner side of the tubes but further inside the structure (ca. 20–70 µm) in layers with larger pore sizes (Fig. 5a).

The reason was found to be the blocking of the finest pores of the alumina membrane clearly visible on the SEM image (Fig. 6b), due to highly concentrated resin solutions (20%) used for the carbon infiltration procedure. As a comparison a SEM image of pure alumina (not carbon coated) membrane is represented in Fig. 6a. With more diluted solutions (1–2%), the performance of the Pd-coating method was improved, as can be seen in Fig. 5b, obtaining Pd profiles similar to those typical of Pd deposition in pure alumina membranes (Fig. 3).

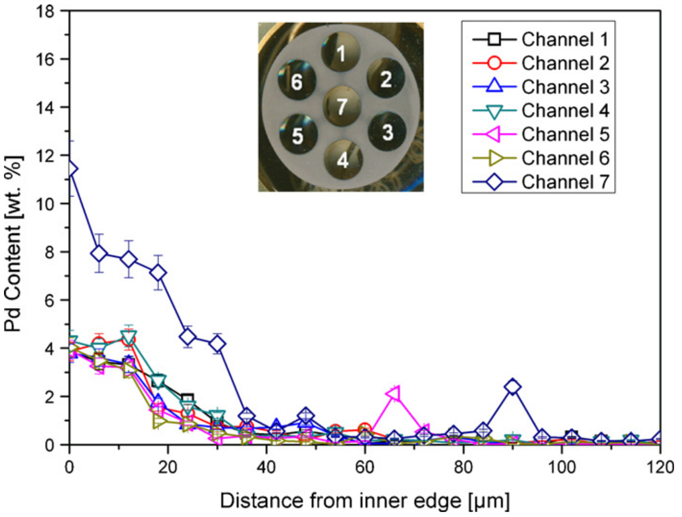

Fig. 4. Electron probe micro analysis characterisation for a 7-channel pure alumina membrane. The signals are mean values from the four scans.

Atomic absorption spectroscopy (AAS) measurements were used to estimate the axial Pd distribution along the membrane tube. For analysis membrane pieces were taken from both ends and from the middle section of a Pd coated carbon infiltrated alumina membrane. An even Pd distribution along the tube was found, somewhat lower than the theoretical Pd content per piece (calculated from weight difference and from the amount of solution used for coating), probably due to loss of carbon throughout the sample preparation procedure.

Palladium particles sizes were estimated with three different methods: X-ray diffraction (XRD) measurements delivered values between 9 and 16 nm, CO pulse chemisorption analysis estimated Pd particles in the range of 8–13 nm and the transmission electron microscopy (TEM) study gave values between 6 and 14 nm. A mean Pd particle size of 11 ± 2.5 nm was calculated, with the assumption of spherical Pd particles, confirmed from TEM images (Fig. 6c and d). In the case of Pd coatings on pure Al_2O_3 membrane (Fig. 6c), highly symmetric spherical Pd particles are clearly observed anchored on the alumina surface. In the case of carbon infiltrated Al_2O_3 membrane (Fig. 6d) a Pd/C catalyst is formed with Pd particles embedded preferably into the carbon matrix.

Bimetallic catalyst coating was also performed with pure Al_2O_3 single channel membranes. Gold was chosen as a second metal, because of promising results in the literature, i.e. higher productivity and selectivity of the Pd/Au catalysts compared to pure Pd catalysts for the direct synthesis process [17–20]. Fig. 3 (filled symbols) shows the Au electron probe micro analysis profiles, again obtaining optimal metal distribution preferably on the inner side of the membrane channel.

3.2. *Catalyst development/H_2O_2 direct synthesis with supported catalysts*

A number of experiments with self-prepared supported catalysts (powder) were performed, in order to:

(i) verify if the developed catalyst coating procedure leads to active catalysts for the direct synthesis of H_2O_2;

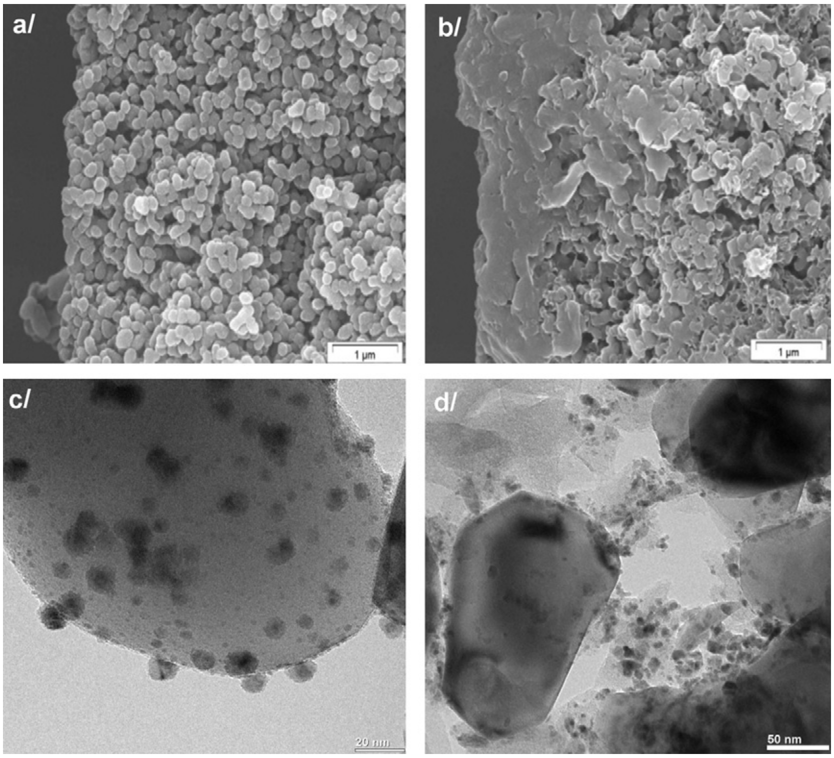

Fig. 6. Scanning electron microscopy (a and b) and transmission electron microscopy (c and d) images of single channel Pd coated membranes from pure Al_2O_3 (a and c) and carbon infiltrated Al_2O_3 (b and d).

(ii) choose the best catalyst type: combination of support material and active metal – mono or bimetallic coating and metal content.

For these reasons the supported catalysts were prepared with the described procedure (impregnation, drying, decomposition) adapted for powder materials and at the same conditions as for the catalytic membranes. Table 3 summarises the prepared supported catalysts with several important properties, type of experiment performed with them, as well as the achieved catalyst productivity and selectivity to H_2O_2.

Different support materials were used – commercial TiO_2 and carbon, Al_2O_3 and carbon infiltrated Al_2O_3 coming from the preparation of the ceramic membranes. The experiments were performed in batch or semi-batch mode as described in the experimental part.

Despite the same preparation procedure many differences in the performance were observed showing the influence of the support material on the catalytic system. For example, the first catalysts based on carbon as support (entry 3, Table 3) showed productivity and selectivity comparable to those published in the literature [3], but the second one (entry 7, Table 3) – performed worse. Surprisingly, the catalyst based on pure alumina 2%Pd/Al_2O_3 (entry 2, Table 3) was totally inactive for H_2O_2 at our experimental conditions and gave only water with low productivity of 0.313 $\mathrm{mol}_{H_2O}\,{g_{pd}}^{-1}\,h^{-1}$. Even the second alumina catalyst with the lower Pd content (entry 2, Table 3) showed low productivity and selectivity. However, Pd coated on carbon infiltrated alumina 0.5%Pd/1%C–Al_2O_3 (entry 8, Table 3) showed one of the best catalytic performances with productivity up to 2.66 $\mathrm{mol}_{H_2O_2}\,{g_{pd}}^{-1}\,h^{-1}$ and selectivity of approx. 50%. Another promising catalytic combination was found to be Pd on TiO_2 (entries 1 and 5, Table 3) with really high productivity and very good selectivity of about 80% for both 1% and 2% Pd loadings.

An example of an experiment with the catalyst 2% Pd/TiO_2 is shown in Fig. 7. Good initial selectivity of ca. 60% is observed. However, with time and advancing water formation it drops down to 30%. Still an H_2O_2 concentration of about 0.14 mol L^{-1} after 23 h reaction time was observed.

The bimetallic catalyst 2%Au2%Pd/TiO_2 (entry 4, Table 3) performed, however, worse than the monometallic 2%Pd/TiO_2. Despite promising results in the literature no improved performance at our experimental conditions was observed. Presumably, the reason was the preparation route of the bimetallic powder. Our choice was to complete two separate coating cycles (impregnation/drying/decomposition) with the Pd-precursor first and the

Table 3
Self-prepared supported catalysts for the direct synthesis of H_2O_2 with characteristic parameters, type of measurement and experimental conditions.

No.	Catalyst type	Support [µm]	BET [$m^2\,g^{-1}$]	Pd particle size [nm]	Productivity [$\mathrm{mol}_{H_2O_2}\,{g_{pd}}^{-1}\,h^{-1}$]	S [%]	Experiment type/solvent
1	2%Pd/TiO_2[a]	<1000	<10	2.5	0.93	79	semi-batch/methanol
2	2%Pd/α-Al_2O_3[b]	315–500	16	2.2	0	0	semi-batch/methanol
3	2%Pd/C[c]	<500	75	19.2	0.78	69	semi-batch/methanol
4	2%Au2%Pd/TiO_2[a]	<1000	<10	22.9 (Au + Pd)	0.06	62	semi-batch/methanol
5	1%Pd/TiO_2[d]	160–250	10.5	1.8	0.90	69	batch/water
6	1%Pd/Al_2O_3[d]	160–250	7.8	1.4	0.26	48	batch/water
7	2%Pd/C[e]	315–500	937	5.3	0.07	19	batch/water
8	0,5%Pd/1%C–Al_2O_3[d]	<100	135	2.44	2.66	49	batch/methanol

[a,b,c,e] commercial; [d] material for membrane preparation supplied by Inopor GmbH.

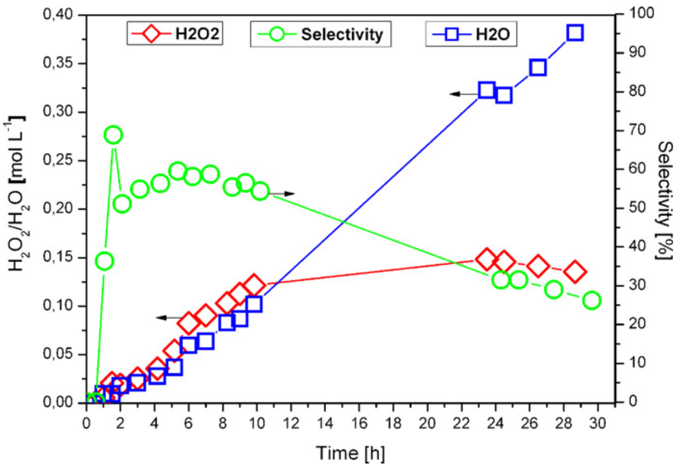

Fig. 7. Semi-batch experiment for H_2O_2 direct synthesis with self-prepared supported catalyst 2%Pd/TiO_2. Experimental conditions: $m_{cat} = 0.97$ g, $P_{total} = 60$ bar, $H_2/O_2/N_2 = 8/27/65$ vol.%, 1.2 L MeOH with additives (13.75 mg L^{-1} NaBr, 0.03 mol L^{-1} H_2SO_4).

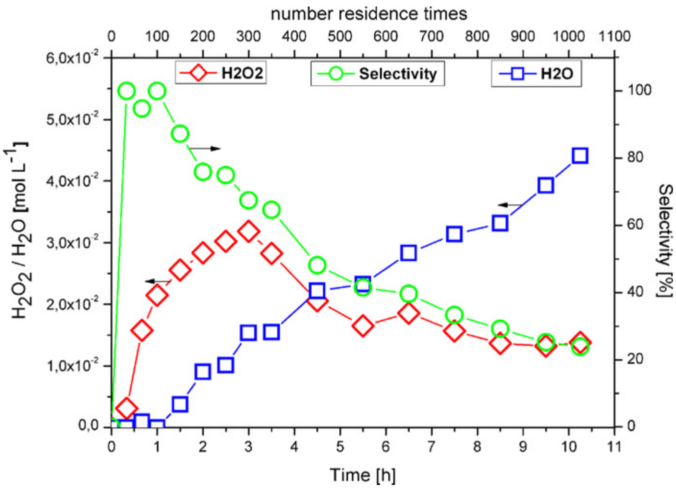

Fig. 8. H_2O_2 direct synthesis in the continuous system with the membrane Pd/TiO_2 (T_7), filled with 0.5 mm inert glass beads. Experimental conditions: solvent methanol with additives (0.03 mol L^{-1} H_2SO_4, 16 mg L^{-1} NaBr), $m_{Pd} = 8.4$ mg, $P_{liq(H_2N_2)} = 50$ bar, $H_2/N_2 = 30/70$ vol.%, $P_{gas(O_2)} = 54.5$ bar, $\Delta P = 4.5$ bar, $F = 5$ mL min^{-1}.

Au-precursor successively, leading probably to formation of separate Pd and Au nano particles, instead of Pd/Au alloying, which was found beneficial for the H_2O_2 direct synthesis process.

The experiments with supported catalysts prove that the coating procedure leads to catalysts active for the direct synthesis of H_2O_2. However, support material and preparation conditions play a crucial role for the catalyst performance. Further on, we were able to identify two promising catalytic combinations with titania (Pd/TiO_2) and carbon infiltrated alumina (Pd/C-Al_2O_3), which were the preferred materials for the preparation of the asymmetric ceramic membranes.

3.3. Performance of the catalytic membranes

Here will be reported only results for direct synthesis of hydrogen peroxide with single channel catalytic membranes ($d_{outer} = 1$ cm, $d_{inner} = 7$ mm, l = 10 cm, $d_{pore} = 100$ nm). Although the operation with multi-channel elements with lengths up to 50 cm was one of our major goals, in order to be able to increase the system's productivity, it was not possible to obtain stable differential pressures (gas side/liquid side) with such membranes. After numerous attempts and observations of the pressure behaviour, this was attributed to persisting sealing problems of the ends and front sides of the membrane channels, therefore, no reliable experimental data could be generated with these membranes so far.

3.3.1. Experiments in continuous mode

The first experiments for the direct synthesis of hydrogen peroxide in the continuous system with catalytically active single channel membranes from TiO_2 and pure Al_2O_3 and methanol as the solvent, however, lead to unexpectedly low H_2O_2 concentrations (lower than 3×10^{-4} mol L^{-1}) with very low selectivity (9%). We assume that this poor initial performance is due to the laminar flow conditions in the empty membrane tube, for which the mass transfer of the reagent (H_2) from the centre to the wall surface, where the reaction takes place, is based on molecular diffusion only. For an empty tube the radial dispersion coefficient (D_{rad}, m^2 s^{-1}), which is a measure of the mass transfer rate in radial direction is merely the diffusion coefficient of the reactant in the liquid medium [24]. Further on, the characteristic time (t_D, s) for diffusive transport over a distance, corresponding to the membrane tube inner radius (r), is found from the relation (Eq. (3))

$$t_D = \frac{r^2}{D_{rad}} \tag{3}$$

For our experimental conditions: solvent methanol, single channel membrane tube (l = 100 mm, $r = 3.5$ mm), $T = 20$ °C, $P_{liq} = 55$ bar ($H_2/N_2 = 20/80$), $P_{gas/O_2} = 58$ bar, $F_{liq} = 20$ mL min^{-1}, $F_{O_2} = 80$ ml min^{-1} and H_2 as the component of interest (diffusion coefficient of hydrogen in methanol $D_{H_2/CH_3OH} = 3.32 \times 10^{-9}$ m^2 s^{-1}), we obtain a value of $t_D = 3676$ s. The comparison of this estimated time of diffusion from the centreline of the tube to the catalytically active wall with the mean residence time at our conditions ($\tau = 9.2$ s) tells that the reaction rate could have been strongly limited by hydrogen transport.

A possibility to minimize the limitation due to mass transfer of hydrogen was to go to much smaller channel diameters in the region of 100 μm and below, which was unfortunately not possible with the existing ceramic membranes. However, the mass transfer rate can be greatly improved by installing an inert packed bed in the membrane tube. In this case the radial dispersion coefficient for the flow through a packed bed (D'_{rad}) is given with Eq. (4) [25], where u is the average fluid velocity [m s^{-1}], d_p is the particle diameter [m], d_m is the membrane channel inner diameter [m] and Pe'_{rad} is the radial Peclet number.

$$D'_{rad} = \frac{u * d_p}{Pe'_{rad}} \left[1 + 19.4 \left(\frac{d_p}{d_m} \right)^2 \right] \tag{4}$$

For glass spheres with a diameter of $d_p = 0.5$ mm and a $Pe'_{rad} = 5.5$ [25], we obtain $D'_{rad} = 7.89 \times 10^{-7}$ m^2 s^{-1} and with Eq. (3) a characteristic time $t'_D = 15.5$ s. This represents an acceleration of the mass transfer rate roughly by a factor of 300. Therefore, all subsequent experiments were performed with membrane tubes filled with glass beads with a mean diameter of ca. 0.5 mm (425–600 μm, unwashed, Sigma, Seelze, Germany). The packed bed was hold by fine meshes installed in the inlet and outlet of the membrane module.

Fig. 8 represents an experiment with one of the best performing catalytic membranes – Pd/TiO_2(T_7) in continuous mode with a membrane channel filled with glass beads. The measurement was performed as described in the experimental part. The reaction was followed for more than 10 h with a differential transmem-

Table 4

Results summary for H_2O_2 direct synthesis experiments in single pass mode with membrane channel filled with glass beads (d = 0.5 mm) and water as solvent (+0.03 mol L^{-1} H_2SO_4 + 15 mg L^{-1} NaBr) at different liquid flow rates, transmembrane differential pressures (ΔP) and total system pressures (P_{sys}).

No.	Catalytic membrane	Pressure [bar]	Liq. flow rate [mL min^{-1}]	H_2O_2 [mol L^{-1}]	Productivity [$mol_{H_2O_2}$ $g_{pd}{}^{-1}$ h^{-1}]	Productivity [$mol_{H_2O_2}$ m^{-2} h^{-1}]
1	Pd/TiO_2 (T_7); m(Pd) = 8.4 mg	$P_{sys} = 50$ (H_2/N_2 = 30/70) $\Delta P = 7$	10	3.63×10^{-3}	0.24	1.14
2	Pd/TiO_2 (T_7); m(Pd) = 8.4 mg	$P_{sys} = 50$ (H_2/N_2 = 10/90) $\Delta P = 6$	1	0.00	0.00	0.0
3	Pd/TiO_2 (T_2); m(Pd) = 16.9 mg	$P_{sys} = 30$ (H_2/N_2 = 33/67) $\Delta P = 5$	35	7.35×10^{-4}	0.09	0.88
4	Pd/Al_2O_3 (R104_5); m(Pd) = 15.7 mg	$P_{sys} = 30$ (H_2/N_2 = 33/67) $\Delta P = 5$	35	7.25×10^{-4}	0.10	0.88

brane pressure of 4.5 bar. The maximal concentration of H_2O_2 after ca. 3 h reached 3.18×10^{-2} mol L^{-1} (0.14 wt%) with selectivity at about 60%. This ca. 100 times improved performance compared to the experiments with an empty membrane channel clearly confirmed our theoretical considerations. The maximal productivity of the membrane in this experiment was calculated to be 1.27 $mol_{H_2O_2}$ $g_{pd}{}^{-1}$ h^{-1}, and per area membrane available – 6.06 $mol_{H_2O_2}$ m^{-2} h^{-1}. These results are close to values reported in our previous work for outside coated catalytic membranes used for the direct synthesis of hydrogen peroxide in batch experimental mode [16] (1.65 $mol_{H_2O_2}$ $g_{pd}{}^{-1}$ h^{-1} and 1.68 $mol_{H_2O_2}$ m^{-2} h^{-1}).

However, after 3 h reaction time a decrease of the H_2O_2 concentration and, respectively, selectivity was observed, and after ca. 10 h the concentration settled down to 1.38×10^{-2} mol L^{-1} with ca. 20% selectivity. On one side this effect could be caused by uncontrolled further decomposition of the synthesised H_2O_2 inside the experimental set-up. Therefore, a series of additional experiments with known initial H_2O_2 concentration at different conditions – with or without the presence of catalyst, up to 50 bar system pressure with different gas mixtures (pure N_2 or H_2/N_2 and O_2/N_2) were performed, in order to assess the decomposition activity of the experimental set-up. The obtained decomposition rate constants were not extraordinarily high and varied between 1.8×10^{-5} and 21×10^{-5} min^{-1}, similar to those measured in previous work [16] and much lower than the values cited in literature [9,23], suggesting that following H_2O_2 decomposition inside the set-up might be ruled out as a reason for the observed sharp concentration decrease.

On the other side, the effect of H_2O_2 concentration decrease might be caused by catalyst deactivation phenomena through out the process caused by different factors. To find out whether Pd leaching was one of them atomic absorption spectroscopy (AAS) analysis of the liquid reaction medium in the separator was performed. No dissolved Pd was found.

A possibility for the decrease of catalytic activity might also be the change of the oxidation state of Pd throughout the process. As a result of the developed coating procedure we obtain metallic nano particles with Pd in its reduced state, confirmed by X-ray diffraction (XRD) analysis (see Supplementary data), beneficial for a good catalytic performance [21,22]. In an oxygen-rich system such as ours, where at least a twofold excess of O_2 over H_2 is granted for higher selectivity to H_2O_2, a partial change of the Pd oxidation state might occur, leading to formation of oxidized palladium (PdO) and loss in activity. XRD examinations were performed with one of the unused Pd/TiO_2 membranes in fresh state (T_6) and with another Pd/TiO_2 membrane (T_3) used for several experiments in continuous operation. The results gave no evidence of the presence of PdO, but only showed the patterns for metallic Pd. However, XRD is not sensitive enough to detect a thin layer of PdO on the surface of the Pd particles. Therefore, a partial change of the oxidation state cannot be completely ruled out.

Surprisingly, the CO pulse chemisorption behaviour of the same two samples, Pd/TiO_2(T_6) and Pd/TiO_2(T_3), was completely different despite the same sample preparation procedure. The CO pulse chemisorption analysis is used for determining the available active surface area of Pd and for estimation of the Pd particle size, respectively the dispersion. Whereas the fresh sample Pd/TiO_2(T_6) showed the expected pulse profile (see Supplementary data), no CO uptake at all was observed for the membrane Pd/TiO_2(T_3), indicating a reduction of the available active surface area, which is a clear sign of deactivation of the catalyst after being mounted in the system and used several times. This deactivation behaviour could explain the concentration profile observed in continuous mode of operation (Fig. 8). Still, additional experiments are needed in order to be able to clarify the exact reasons for it.

A strategy for catalyst regeneration will depend very much on the reasons of the deactivation. In the case of suspected partial oxidation of the catalyst surface a treatment of the catalyst in a reducing atmosphere (H_2/N_2) at high temperature (250–300 °C) for several hours might be applicable in order to turn Pd into its more active metallic state.

3.3.2. *Experiments in single pass mode*

In order to be able to estimate the net performance of a catalytic membrane without the effect of concentration decrease observed, a series of experiments in single pass mode were performed with the experimental set-up shown in Fig. 1. Unlike in continuous mode, the reaction mixture was expanded into a separate vessel after passing through the membrane module just once and was not recompressed back into the saturator. Samples were withdrawn directly at the exit of the membrane module. The membrane channel was again filled with 0.5 mm glass beads.

With this simplified mode of operation the influence of several parameters on the performance of the membrane contactor was investigated. Table 4 summarises the results for three different membranes at different experimental conditions with water as solvent.

The positive effect of the inert packed bed is also clearly visible for the single pass mode of operation. Almost 10 times higher concentrations of H_2O_2 in water (up to 3.63×10^{-3} mol L^{-1}) with the membrane Pd/TiO_2(T_7) were reached (entry 1, Table 4) compared to the first experiments without glass beads performed in methanol (3×10^{-4} mol L^{-1}), although methanol is the better solvent, because of the higher solubility of H_2 and O_2 in it than in water (ca. a factor of 5 for H_2).

The effect of the liquid flow rate on the membrane performance is also represented in Table 4 (entries 1 and 2). The liquid flow rate determines the residence time in the membrane contactor. For one and the same membrane Pd/TiO_2(T_7) experiments at 10 mL min^{-1} and 1 mL min^{-1} system flow were performed at very similar other experimental conditions. It can be seen that for 1 mL min^{-1} the residence time of 3.85 min in the system is too long, and the synthesised H_2O_2 is completely decomposed to water within the membrane contactor resulting in no detectable H_2O_2 concentrations at the exit. This, however, is not the case for 10 mL min^{-1} liquid flow, resulting in a maximum H_2O_2 concentration of 3.63×10^{-3} mol L^{-1}.

The effect of the system pressure (P_{sys}) on the membrane performance is also visible from the results summary in Table 4 (entries 1, 3 and 4). The increase of pressure increases the solubility of both reactants in the liquid medium. At 30 bar and similar other reaction conditions both membranes Pd/TiO_2 (T_2) and Pd/Al_2O_3 (R104_5)

Table 5
Results summary for H_2O_2 direct synthesis experiments in single pass mode with built in glass beads (d = 0.5 mm) and methanol as solvent (+0.03 mol L^{-1} H_2SO_4 + 15 mg L^{-1} NaBr). P_{sys} – total system pressure, ΔP – transmembrane differential pressure, F – liquid flow rate.

No.	Catalytic membrane	Reaction conditions	H_2O_2 [mol L^{-1}]	Productivity [$mol_{H_2O_2}$ $g_{pd}{}^{-1}$ h^{-1}]	Productivity [$mol_{H_2O_2}$ m^{-2} h^{-1}]	S [%]
1	Pd/TiO_2 (T_7) m(Pd) = 8.4 mg	P_{sys} = 50 bar H_2/N_2 = 30/70 ΔP = 4 bar F = 13.5 mL/min	1.73×10^{-2}	1.69	6.11	83
2	$Pd/C–Al_2O_3$ (MC_0442) m(Pd) = 6.9 mg	P_{sys} = 50 bar H_2/N_2 = 30/70 ΔP = 4 bar F = 8.0 mL/min	2.35×10^{-2}	1.63	6.41	75

Table 6
Results summary for the membranes Pd/TiO_2(T_7) and $Pd/C–Al_2O_3$ (MC_0442) in single pass mode with methanol as solvent compared to literature data for the performance of different catalytic membranes operating on both principles.

No.	Catalytic membrane	Reactor principle	Productivity [$mol_{H_2O_2}$ $g_{pd}{}^{-1}$ h^{-1}]	Productivity [$mol_{H_2O_2}$ m^{-2} h^{-1}]	S [%]
1	Pd/TiO_2 (T_7)[a]	contactor	1.69	6.11	83
2	$Pd/C–Al_2O_3$ (MC_0442)[a]	contactor	1.63	6.41	75
3	Pd/Al_2O_3 [16]	contactor	1.65	16.8	80
4	$PdPt(18:1)/Al_2O_3$ [9]	contactor	–	0.09	12
5	Pd/ZrO_2 [14]	distributor	–	0.09	85
6	Pd/Al_2O_3 [12]	distributor	–	0.03	-
7	Pd/Al_2O_3 [6]	distributor	–	0.5	70

[a] This work; in brackets is given the indication of the manufacturer HITK.

(entries 3 and 4) showed very similar performance. The increase of 30–50 bar in the system leads to ca. 5 times higher H_2O_2 concentrations up to 3.63×10^{-3} mol L^{-1} for the membrane Pd/TiO_2 (T_7) (entry 1, Table 4).

In order to be able to use the benefits of the organic solvent several experiments in single pass mode in methanol were performed. The results for the two catalytic membranes Pd/TiO_2(T_7) and $Pd/C-Al_2O_3$(MC_0442) in methanol at similar conditions, both filled with 0.5 mm glass beads, are summarised in Table 5.

Hydrogen peroxide concentrations up to 2.35×10^{-2} mol L^{-1} were observed with very high selectivity of ca. 80% with the carbon infiltrated membrane giving a slightly better performance. This is a 6 fold increase compared to the membrane performance in water as solvent.

Although the reported absolute hydrogen peroxide concentrations with our system and the self-prepared catalytic membranes are still rather low for most technical H_2O_2 applications, a possibility for use in UV combined waste water treatment seems to exist, where low H_2O_2 concentrations are needed, normally in the range of 5 mmol L^{-1} with molar ratio H_2O_2/pollutant of 1 or lower [26–28]. Note also that, having in mind the literature data on the dense Pd membrane distributor concept (entries 5–7, Table 6), our catalyst productivity for the porous membrane contactor is up to 12 times higher (with high selectivity of 83%). Moreover, the performance of the distributor concept per g Pd and hour is even lower due to the higher amount of Pd needed for a dense Pd layer.

4. Conclusions

Experimental results on preparation, characterisation and performance of catalytically active asymmetric tubular ceramic membranes in a continuous process for the direct synthesis of hydrogen peroxide at elevated pressures, based on the principle of the "membrane contactor" were presented. Our achievements together with the experienced difficulties in the course of the work are summarised below:

(1) As a prerequisite for the continuous process a method was developed for coating of Pd based catalysts preferably into the fine porous layer on the inside of the ceramic membrane tubes. The method reached uniform distribution and high dispersion of the Pd nano particles with ca. 11 nm size for different membrane geometries (single and multi-channel elements) and lengths (10–50 cm) as well as different membrane materials (pure Al_2O_3, carbon infiltrated Al_2O_3, TiO_2). A series of experiments in batch mode with powder supported catalysts verified that the developed method produces active catalysts for the direct synthesis of hydrogen peroxide and helped to identify promising catalytic combinations – Pd supported on TiO_2 or carbon infiltrated Al_2O_3, which were further investigated in the form of catalytic membranes.

(2) The principle of operation of the membrane contactor was successfully verified with 10 cm long single channel membranes with very stable performance of the continuous system for more than 10 h at differential pressures up to 4.5 bar in methanol (up to 7 bar in water). The application of the multichannel elements in the continuous experimental set-up could not be achieved due to persistent sealing problems with the ends and front sides of the membrane channels.

(3) Crucial for the performance of the membrane contactor proved to be the sufficient diffusive transport of the reactants to the catalytically active zone, situated on the inner walls of the membrane channel. This was found to be a major problem under the conditions of pure laminar flow in an empty membrane channel. Therefore, additional measures had to be undertaken to guarantee more turbulent flow, to shorten diffusion pathways and increase radial mixing in the system. In our case filling the membrane channel with inert material (0.5 mm glass beads) was one of the investigated possibilities, leading to a significant (ca. 100 fold) increase of the synthesised H_2O_2 concentration.

(4) Catalyst deactivation problems in continuous mode of operation with the single channel membranes were observed. This was attributed to a loss of active surface area during the process, due presumably to partial change of the Pd oxidation state. Further experiments are needed to find out the exact reasons for this effect. No evidence of Pd leaching was found.

(5) As a consequence, experiments in single pass mode were used to characterise the system and explore the net performance of the catalytic membranes at different conditions. In this case no catalyst deactivation was detected after observing the reaction for several hours. The results demonstrated the benefit of organic solvents (methanol) and higher pressures on the direct synthesis reaction with productivities up to $1.69\,\mathrm{mol}_{H_2O_2}\,g_{pd}{}^{-1}\,h^{-1}$ ($6.11\,\mathrm{mol}_{H_2O_2}\,m^{-2}\,h^{-1}$) and selectivity of 83% for the membrane based on TiO_2.

In conclusion we may state that our current work helped to gain further insight into the performance of the "porous membrane contactor" and to determine crucial parameters for its improvement, indicating that this type of reactor might be well suited for local H_2O_2 production for certain applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.10.011.

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