



# 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<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> 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 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> g<sub>pd</sub><sup>-1</sup> h<sup>-1</sup> (6.1 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> related to the geometric surface area of the membrane) with a selectivity of 83% towards H<sub>2</sub>O<sub>2</sub> were achieved.

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## 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> 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<sup>-1</sup>), thus necessitating transportation and storage of concentrated H<sub>2</sub>O<sub>2</sub> solutions and causing additional investments for safety precautions. Therefore, the direct synthesis of hydrogen peroxide from O<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub>/O<sub>2</sub> 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<sub>2</sub> permeation mechanism with O<sub>2</sub> 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<sub>2</sub> pressures up to 3 bar and O<sub>2</sub> pressure at 1 bar. Further lowering of the temperature to 2–5 °C favours the H<sub>2</sub>O<sub>2</sub> synthesis [6] over the decomposition. Only one recent study investigates the performance of such H<sub>2</sub> selective catalytic membranes at higher temperatures (up to 75 °C), reporting increased productivity (from 88 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> at room temperature up to 133 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> at 75 °C), but with somewhat lower selectivity (decreasing from 85% to 35%) due to faster H<sub>2</sub>O<sub>2</sub> 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 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> [12], ca. 50 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> [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<sub>2</sub> 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<sub>2</sub> permeation rates up to three times higher than the H<sub>2</sub> 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<sub>2</sub> is saturated and H<sub>2</sub> 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<sup>-</sup> as promoter [9]. H<sub>2</sub>O<sub>2</sub> formation up to 800 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> 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 mmol<sub>H<sub>2</sub>O<sub>2</sub></sub> m<sup>-2</sup> h<sup>-1</sup> [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 mol m<sup>-2</sup> h<sup>-1</sup> 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

**Table 1**  
Parameters for the catalyst coating procedure.

Parameter	Single channel membranes 10 cm length	Multi-channel membranes 25 cm length
Pd acetate concentration [g L <sup>-1</sup> ]	2–5	2–5
Amount of coating solution used [mL]	4	40
Rotation speed [rpm]	30	30
Air flow for drying [L h <sup>-1</sup> ]	150	200
Air direction change [min <sup>-1</sup> ]	6	6
Drying time [min]	30	60
N <sub>2</sub> flow for precursor decomposition [L h <sup>-1</sup> ]	15	25

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.

## 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<sub>2</sub> or O<sub>2</sub>. They were manufactured from different materials (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, carbon coated Al<sub>2</sub>O<sub>3</sub>) and were supplied in different geometries – single or multi-channel tubes. Most of the experiments for H<sub>2</sub>O<sub>2</sub> synthesis were carried out with single channel membranes (l = 10 cm, d<sub>inner</sub> = 0.7 cm, d<sub>outer</sub> = 1 cm, fine porous layer with d<sub>pore</sub> = 100 nm). Carbon coated Al<sub>2</sub>O<sub>3</sub> membranes were prepared by immersing the Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>(Pd-exp)</sub> is the experimental amount of Pd on the membrane determined gravimetrically and m<sub>(Pd-theory)</sub> is the theoretical amount of Pd, calculated from the volume and Pd

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