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Direct hydrogen peroxide synthesis using glass microfabricated reactor – Paralleled packed bed operation

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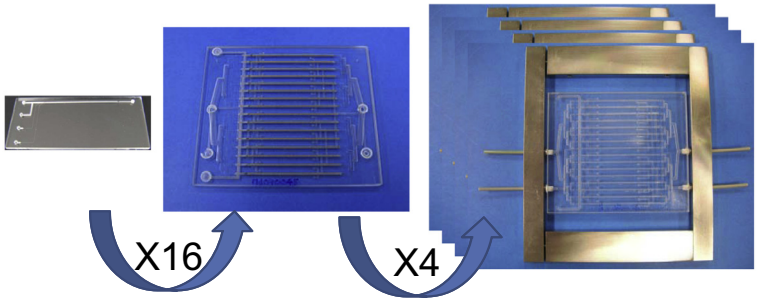
HIGHLIGHTS

- We prepared microreactor with parallel packed beds for H_2–O_2 reaction to H_2O_2.
- Maldistribution of reaction fluid was overcome to promote reaction performance.
- We were also successful in parallel reactor operation to promote productivity.

GRAPHICAL ABSTRACT



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ABSTRACT

We designed and fabricated a microreactor with paralleled packed beds suitable for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. The reactor is based on microfluidic design for equal distribution of reaction fluids to each catalyst packed bed, which was validated by the reactor performance and gas- and liquid flow regime visualization. We extended the concept to parallel operation so that 1 kg/day of 4 wt% of hydrogen peroxide was produced by 4-reactor parallel operation. Our strategy gives an alternative opportunity to the scaling-up strategy of flow chemical process technology, by overcoming the fluid maldistribution problem in a gas–liquid and solid multiphase system.

1. Introduction

Hydrogen peroxide is one of the basic chemicals having various kinds of applications [1]. It is currently produced in petrochemical complexes, but a small scale production system could also be economical for some applications. In this case, an alternative process is preferred to the anthraquinone process, by which hydrogen peroxide is currently produced, for it relies on an energy source supplied by the petrochemical complex [1,2].

The direct synthesis of hydrogen peroxide, from hydrogen and oxygen, is considered to be favorable for its simplicity as a chemical process. It is a three phase, gas (hydrogen and oxygen) – liquid (aqueous and/or alcohol solution to store hydrogen peroxide stably) – solid (catalyst), reaction. Both hydrogen and oxygen dissolved in the reaction solution react over the catalyst, and hydrogen peroxide produced is stored in the reaction solution with water as a byproduct. The reaction has been known for decades, and much effort has been paid to commercialize the process [2]. Still, such effort has been challenged by the risk of handling a hydrogen and oxygen mixture, and low productivity.

In recent decades, the microreactor technology has offered an alternative opportunity to enable safe handling of potential

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hazards in chemical processes [3–8]. The applications include a controlled reaction of a hydrogen and oxygen mixture having explosive risk [9,10], and the direct synthesis of hydrogen peroxide using the mixture; we demonstrated that hydrogen peroxide could be produced, even from the hydrogen–oxygen mixture of potentially explosive content [7,11–15].

Recently, we showed that hydrogen peroxide could be efficiently produced by a glass fabricated microreactor with a catalyst packed bed specifically designed for gas- and liquid reactions: a steady gas- and liquid flows were as achieved by the reactor design [16,17]. Combined with catalyst development, we also demonstrated that more than 10 wt% of hydrogen peroxide can be produced under low pressure (ca. 1 MPa), and at room temperature, without cooling effort [18–20].

For chemical processes based on the microreactor technology, both scaling-up and scaling-out techniques have been developed, and the former one has already been commercially demonstrated [21,22]. The scaling-up technique relies on enlarged reactor while the scaling-out depends on parallel operation of microchannels. The direct synthesis of hydrogen peroxide process is, as mentioned before, based on the catalyst packed bed reactor with both gases and liquid phases flowing through. As we showed previously, the catalyst packed bed microchannel prevented explosion and it offered effective mass transfer from gas to liquid phase [12]. Considering that both hydrogen and oxygen are sparse solutes to water, retaining such effective mass transfer as well as preventing the explosion are imperative for the reaction, hence we opted for the scaling-out strategy with maintaining microchannel size dimensions.

In this paper, we focus on establishing the scaling-out technique within one microreactor and its parallel operation. In order to run the scaling-out reactor successfully, equal reaction fluids distribution is crucial and it is reasonable to apply proper pressure drops to fluid distributors [23–28], which we also applied to design the parallel packed bed reactors [18,20,29]. We conduct flow regime studies for our microreactors. We also validated the equal flow distributions by using the reaction itself as a probe.

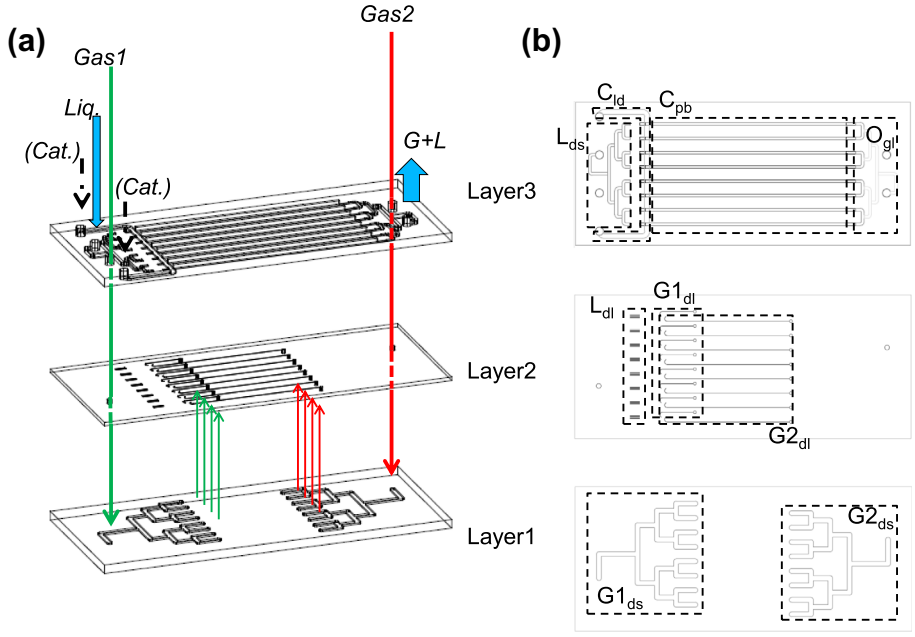
2. Experimental

2.1. Reactor fabrication

We already published fabrication procedures for the microreactor we designed [20,30]. Briefly, our microreactor is a fluidic device of a thermally bonded stack of glass substrates with microchannels and holes. The channel fabrication processes are chemical isotropic etching using HF solution for thin channels (width is ca. 0.05 mm and the line depth is 0.02 mm) and a numerically controlled end-milling for channels with larger size dimensions and through holes. After channel fabrications, each glass sheet was sonicated to remove small debris from the machining process, followed by cleaning in H_2SO_4–H_2O_2 mixture (piranha process) [31]. Finally, a glass sheet stack was formed, followed by the thermal bonding process in a furnace.

Scheme 1 shows the detailed structure of the reactor with 8 parallel packed beds (8ch reactor) and the fluid delivering scheme. In Scheme 1(a), we show how glass sheets with microchannels stacked to form the reactor, with reaction fluids pathways. The parallel packed bed channel reactor we designed consists of three glass sheets. The layer 1 has gas distributing channels ($G1_{ds}$ and $G2_{ds}$), which distribute two types of gases (in our case, G1 for oxygen and G2 for hydrogen, respectively) into 8 parallel locations. The layer 2 has gases and liquid delivering channels ($G1_{dl}$, $G2_{dl}$, and L_{dl}), which deliver two types of gases and liquid into each catalyst packed bed. The bonding between the layer 1 and the layer 2 connects $G1_{ds}$ and $G1_{dl}$, and $G2_{ds}$ and $G2_{dl}$, respectively, via through holes fabricated in the layer 2. The layer 3 has a liquid distribution channel (L_{ds}), a catalyst loading channel (C_{ld}), catalyst packed beds (C_{pd}), and a gas–liquid outlet channel (O_{gl}). The bonding between the layer 1 and layer 2 connects $G1_{dl}$, $G2_{dl}$, and L_{dl} enabling gases and a liquid supply into each packed bed channel.

The reactors we used are shown in Fig. 1, all of which contain catalyst. After the reactor fabrication was completed, the catalyst was loaded as an aqueous suspension. For the single packed bed reactor (1ch reactor), it was loaded from the port C with closing



Scheme 1. (a) The 8ch reactor structure with layered representation with fluids (*Gas1*, *Gas2*, Liquid (*Liq.*)), and an aqueous catalyst slurry before the reaction (*Cat.*) delivery procedure. (b) Layers representation with functions description in the 8ch reactor. Layer 1 consists of channel networks distributing gas1 and gas2 ($G1_{ds}$ and $G2_{ds}$). Layer 2 consists of liquid delivering channels (L_{dl}), gas1 delivering channels ($G1_{dl}$), and gas2 delivering channels ($G2_{dl}$). Layer 3 consists of networks distributing liquid (L_{ds}), gas and liquid outlet (O_{gl}), a catalyst loading channel (C_{ld}), and catalyst packed beds (C_{pb}).