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Continuous and Scale-Up Synthesis of High Purity H_2O_2 by Safe Gas-Phase H_2/O_2 Plasma Reaction

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Significance

A new generation of double dielectric barrier discharge (DDBD) reactor featured by a metal powder (MP) high voltage electrode is presented. The MP high voltage electrode not only has excellent homogeneous discharge performance but also has the advantage of without regular maintenance. Therefore, the MP-DDBD reactor was proved to be suitable for the uninterrupted and safe synthesis of high purity H_2O_2 aqueous solution with up to 65 wt % concentration from the H_2/O_2 mixture. The scale-up synthesis of H_2O_2 was successfully attempted in an integrated device based on the MP-DDBD reactor. The future practical H_2O_2 synthesizer based on the MP-DDBD reactor will be small and movable, and therefore, be convenient to supply high purity H_2O_2 on site for small scale users like semiconductor industry. © 2013 American Institute of Chemical Engineers *AIChE J*, 60: 415–419, 2014

Keywords: high purity H_2O_2, plasma, semiconductors, scale-up, continuous synthesis

Hydrogen peroxide (H_2O_2) is widely used in industry and daily life as an important green-oxidant.[1] Currently, H_2O_2 is almost exclusively manufactured by an indirect and ungreen anthraquinone process (AQ).[2,3] The direct synthesis of H_2O_2 from H_2 and O_2 via electrochemical devices[4,5] and noble metal catalysis[6–13] have been studied. However, due to the use of metal electrode and electrolyte in electrochemical processes and the use of metal catalyst and acid solvents in the catalytic reaction, these ways are difficult to obtain high purity H_2O_2 product without purification.

The semiconductor industry, including microelectronic, display, and photovoltaic sectors, needs electronic grade H_2O_2. This high purity H_2O_2 have to meet the semiconductor equipment and materials international (SEMI) standards (Grades 1–5, Supporting Information Table S1), which has strict requirements about the impurity of oxidizable carbon, anions, and cations.[14] As the development of the semiconductor industry, the consumption of electronic grade H_2O_2 will increase continuously. The manufacture of high purity H_2O_2 from the commercial grade H_2O_2 of AQ process needs a complex and energy-intensive purification techniques, which includes extraction, rectification, ion exchange, and even reverse osmosis operations.[15] The purification is dangerous because of the reactivity of H_2O_2. Currently, the reverse osmosis is considered as a ultrapurification means for H_2O_2,[16,17] but a longer life membrane materials is not available.[18] Therefore, it will be significant to develop a new method for the direct synthesis of high purity H_2O_2.

We have reported the direct synthesis of H_2O_2 with H_2/O_2 plasma.[19–21] It was found that the structure of the dielectric barrier discharge reactor played an important role in the selectivity and safety of the H_2/O_2 plasma reaction. Using a double aqueous electrodes double dielectric barrier discharge (DDBD) reactor, we have carried out safe H_2/O_2 plasma reaction up to 30 mol % O_2 content in the H_2/O_2 mixture, and obtained high purity H_2O_2 with more than 60%

Additional Supporting Information may be found in the online version of this article.

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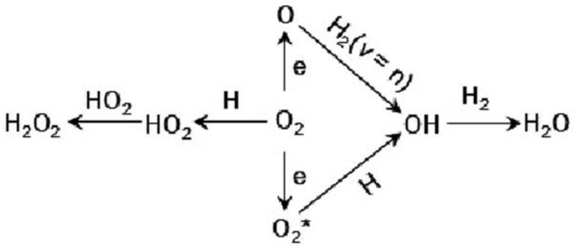

Scheme 1. The main reactions network for formation of H_2O_2 and H_2O in H_2/O_2 nonequilibrium plasma.

selectivity (based on O_2) and about 48–67 wt % concentration. In this double aqueous electrodes DDBD reactor, the high voltage electrode was a thin pyrex-tube containing saturated NaCl solution, whereas the grounding electrode was a recycling dilute NaCl solution (0.1 wt %) which also served as a cooling agent. It was observed that the aqueous high voltage electrode was important for realizing weak and homogeneous discharge, which was crucial to make the gas-phase H_2/O_2 plasma reaction proceed along the chain termination reactions ($H + O_2 \rightarrow HO_2$, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, Scheme 1), so as to guarantee the selectivity and safety of the H_2/O_2 plasma reaction.[21] However, the aqueous high voltage electrode suffered from solution evaporation owing to the heat of H_2/O_2 plasma reaction. Consequently, the discharge of the double aqueous electrodes DDBD reactor had to be stopped regularly for the purpose of supplementing the NaCl solution of the high voltage electrode, otherwise the discharge would become heterogeneous, less productivity, and even dangerous.

This letter describes a new generation of DDBD reactor featured by a metal powder (MP) high voltage electrode (Supporting Information Figure S1). The replacement of the aqueous high voltage electrode with a MP high voltage electrode has overcome the shortcomings of the previous reactor completely. In addition, we found that the MP high voltage electrode was very easy to prepare (just pour the fine MP into a thin pyrex-tube). The excellent filling property of the fine MP ensured the MP-DDBD reactor exhibits weak and homogeneous discharge performance (expelling air of the high voltage electrode as completely as possible). Meanwhile, the excellent mobility of the fine MP allowed the metal electrode to expand freely in the glass tube in case of plasma heating. Thus, the broken of the glass tube (served as dielectric), which would easily happen with the pyrex cover-metal wire fusion electrode, could be avoided.

The discharge images (Supporting Information Figure S2) show that the H_2/O_2 mixture in the MP-DDBD reactor could carry out weak and homogeneous discharge. The discharge behavior of the new reactor was almost the same as the double aqueous electrodes DDBD reactor (reference reactor). The weak and homogeneous discharge, very similar to the Townsend discharges, was an indicator of low electron density.[22] Figure 1 shows that the optical emission spectra (OES) of H_2/O_2 plasma in the MP-DDBD reactor was also identical to that of the reference reactor. This means that the new reactor could generate the same H_2/O_2 plasma as the reference reactor. In this H_2/O_2 plasma, the intensity of H line (656.3 nm) was much higher than those of O lines (777.4 and 844.7 nm), which means that the active hydrogen species (ground state and excited H as well as excited H_2*) were main active species. That is, the activation of O_2 in this plasma was limited by the low density of electron, hence most of oxygen existed in the ground state of O_2.[21] At ambient temperature, the rate coefficient of the chain termination reaction, $H + O_2 \rightarrow HO_2$, is about eight orders of magnitude larger than that of the chain branching reaction, $H + O_2 \rightarrow OH + O$,[23,24] thus the reaction of H and ground state of O_2 mainly lead to the production of HO_2 intermediate, which generated H_2O_2 by the reaction of $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (Scheme 1). Therefore, the discharge behavior and OES diagnosis predicted that the performance of the MP-DDBD reactor for H_2O_2 synthesis should be as good as that of the reference reactor.

Fortunately, the H_2O_2 synthesis experiments show that the MP-DDBD reactor and the reference reactor did exhibit same performance in O_2 conversion and H_2O_2 selectivity (Supporting Information Figure S3). In addition, the replacement of the aqueous high-voltage electrode with MP high-voltage electrode not only avoided the evaporation problem of the original aqueous electrode so as to allow a continuous operation, but also did not change the weak and homogeneous discharge properties, which was crucial for the safe synthesis of H_2O_2 with H_2/O_2 mixture of high O_2 content as observed in the reference reactor.[21]

The MP-DDBD reactor was suitable for scale-up synthesis of H_2O_2. Based on the MP-DDBD reactor, a five-reactor integrated device was prepared. As shown in Figure 2, this device included five MP high voltage electrode reaction tubes and a sharing aqueous grounding electrode. The shell of the device was made of polymethyl methacrylate, and the product collector was made of polytetrafluoroethylene (PTFE). The MP high voltage electrode reaction tube was made of pyrex glass, in which an inner pipe filled with 75-μm powdered aluminium as MP high-voltage electrode (Supporting Information Figure S4). All high voltage electrodes were linked to the high-voltage divider. Solution in the aqueous grounding electrode was recycled to remove the reaction heat so as to avoid the thermal decomposition of

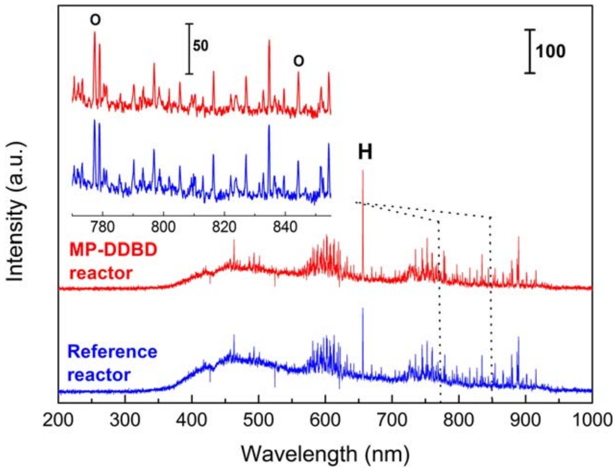

Figure 1. OES of H_2/O_2 plasma in MP-DDBD reactor and reference reactor. (H_2: 95 mL/min, O_2: 5 mL/min, circulating water: 5°C, discharge frequency: 12 kHz, 300 G/mm grating, 0.5 s exposure time.)

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

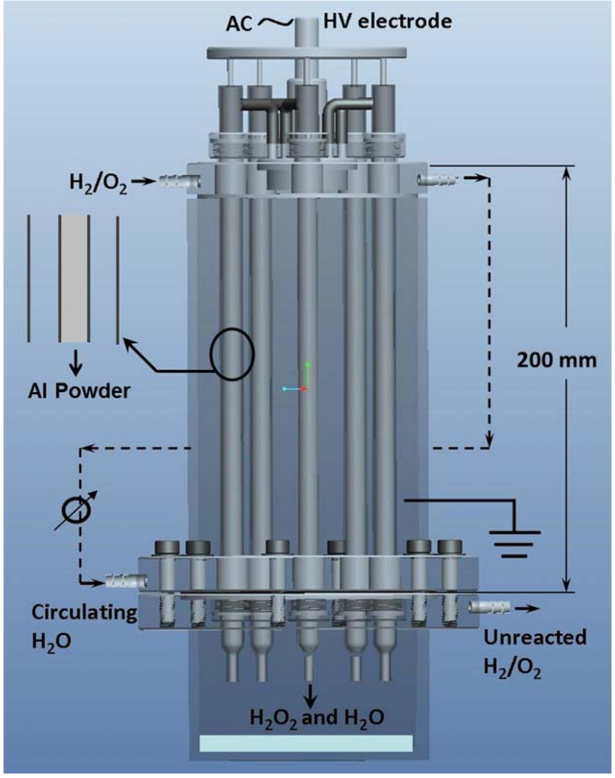

Figure 2. Schematic drawing of the integrated device based on the MP-DDBD reactor for directly synthesizing high purity H2O2 from H2/O2 plasma.

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H_2O_2. Therefore, this five MP high voltage electrode reaction tubes have same high voltage and grounding electrodes, which make sure that every tube of this reactor could be operated identically. H_2O_2 and H_2O produced by the H_2/O_2 plasma reaction in discharge zone were carried by the unreacted H_2 and O_2 into collector which was placed in a cold trap. In the device, the generated H_2O_2 solution contacted only with H_2, O_2, pyrex glass, and PTFE collector, therefore, high purity H_2O_2 solution was guaranteed if only the aforementioned materials were clean. The concentration of the obtained H_2O_2 solution (analyzed by iodometry) should be approximately equal to the value of H_2O_2 selectivity (about 60 wt % based on O_2) in the case of using cold trap for collection. H_2O was formed through the reactions of active oxygen species (O and O_2*) with H_2 and H as shown by Scheme 1. The H_2O_2 concentration was adjustable by absorbing the product with different amount of ultrapure water.

Table 1. Direct Synthesis of High Purity H_2O_2 in the Integrated Device with Different Working Volume

Tube Number	1	2	3	4	5
Flow of H_2 (mL/min)	28.4	56.8	85.2	113.6	142.0
Flow of O_2 (mL/min)	5	10	15	20	25
Input power (w)	10	20	30	40	50
Reaction volume (mL)	13.2	26.4	39.6	52.8	66.0
O_2 conversion (%)	63.5	63.5	63.5	63.5	63.5
H_2O_2 selectivity (%)	63.0	65.6	66.0	67.0	67.4
C(H_2O_2) (wt %)	62.0	62.3	63.2	64.2	65.0
Yield (mmol H_2O_2/h)	5.4	11.2	16.8	22.8	28.7

15 mol % O_2 content, circulating water: 5°C, discharge frequency: 12 kHz.)

Although the explosive limits of H_2/O_2 mixture is 6–96 mol % O_2, our previous research[21] has demonstrated that weak and homogeneous discharge could carry out safe H_2/O_2 plasma reaction when O_2 content is lower than 30 mol %. Because the electron density of the weak and homogeneous discharge is very low and most O_2 exist in ground state. The H_2/O_2 plasma reaction was dominated by the chain termination reaction path to synthesize H_2O_2, and the chain branching reaction path as the major cause of H_2/O_2 chain explosion could be avoided (the chain branching reaction could be accelerated by excited O_2 and O as shown in Scheme 1). Therefore, the integrated device has been tested with a H_2/O_2 mixture of 15 mol % O_2 content as feed (in the explosion limits of H_2/O_2 mixture). As it was expected, the safety of the H_2/O_2 mixture discharge was confirmed. Weak and homogeneous discharge was realized from one to five working tubes (Supporting Information Figures S5–S7). In all cases, the discharge went on quietly and smoothly. Table 1 shows that, the increase of the discharge zone volume by increasing the number of reaction tubes from one to five, meanwhile increasing the flow rate of H_2 and O_2 proportionally so as to fix the residence time of the H_2/O_2 reactants in the discharge zone (23.7 s), was accompanied by an linear increase of H_2O_2 yield, and an improvement of H_2O_2 selectivity (based on O_2, the H_2O_2 selectivity based on H_2 was two-thirds of that based on O_2). When five tubes worked together, the concentration and yield of H_2O_2 reached 65 wt % (analyzed by iodometry) and 28.7 mmol h^{-1}, respectively. The integrated device has been continuously operated for 150 h. Figure 3 shows that, during the continuous operation, the conversion of O_2 kept stable and the volume of H_2O_2 product (65 wt %) increased linearly with time. In view of the fact that there was no problems, such as catalyst ageing

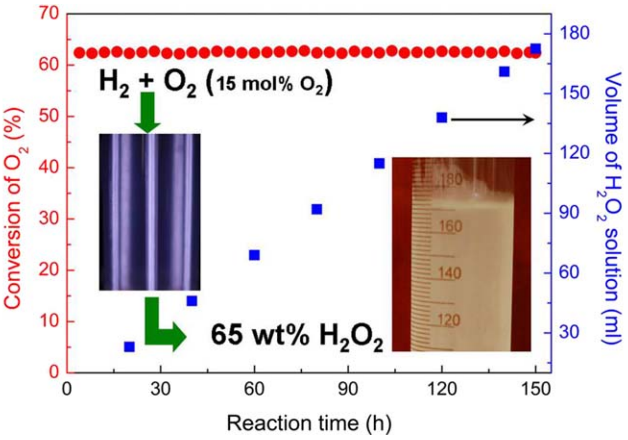

Figure 3. O_2 conversion and H_2O_2 product solution volume vs. reaction time during the direct synthesis of high purity H_2O_2 in the integrated device with 15 mol % O_2 content. (H_2: 142 mL/min, O_2: 25 mL/min, circulating water: 5°C, discharge frequency: 12 kHz.)

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Table 2. Impurity Content of the H_2O_2 Solution Obtained in this study (Analyzed by the ICP-AES, Optima 2000 DV, Perkin Elmer, Li can not be measured, Unit: ppb) and the Electronic Grade H_2O_2 of SEMI Standards[14]

Elements	Grade 1	Grade 2	Our H_2O_2	Grade 3
Fe/Mo/Ti/Pd	100	10	<1	1
Au/Pt/Be/Sr	10	10	<1	1
Sn/V/Ga/Ge	10	10	<1	1
Sd	10	5	<1	1
Cd/Mn/Ni	50	10	<1	1
Na	500	5	<1	1
K	200	10	<1	1
Li	–	10	–	1
Ba	100	10	1.8	1
Cr	10	10	3.6	1
Bi	10	10	5.1	1
Co/Cu	10	10	7.2	1
Al	200	10	7.8	1
Pd	50	10	8.5	1
Ag	10	10	9.4	1
Zn	100	10	18	1
As	50	5	22	1
Mg	200	10	20	1
Ca	200	10	45.5	1
B	200	10	185	1

and regeneration, in the plasma method, the reaction of H_2 and O_2 was carried out by the energetic free electrons in the plasma of discharge zone,[21] the reaction heat was taken away by the recycled solution of the aqueous grounding electrode, it is reasonable to believe that the integrated device could work continuously for any long period of time if necessary.

The purity of H_2O_2 solution obtained from the continuous operation experiment was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Table 2 indicates that the content of inorganic ion impurities were between the Grade 1 and Grade 2 of SEMI standards for semiconductor industry.[14] The main impurities of the product were Zn, As, Mg, Ca, and B, they came from the pyrex glass of the reaction tube wall. Obviously, it is possible to obtain higher grade H_2O_2 solution by replacing the pyrex glass with quartz for the preparation of reaction tubes in the future.

The energy consumption of H_2O_2 synthesis (based on input power) in the integrated device was about 52 kW h/Kg H_2O_2 (counted by 100 wt %), which was much higher than the AQ process. Besides, the H_2O_2 selectivity based on H_2 was only about 45%, currently. However, it avoided the highly energy-consuming concentration and purification processes, thus the equipment investment costs for a practical system should be very low. At present, the cost of hydrogen (99%), oxygen (99%), and electricity for the production of 1 Kg 65 wt % high-purity H_2O_2 (Grade 2 at Table 2) is about 85 yuan RMB (9.4% for H_2, 8.2% for O_2, and 82.4% for electricity) based on Chinese market prices. The sale price of the similar high-purity H_2O_2 product in Chinese market is about 150 yuan RMB/Kg. It is estimated that the synthesis cost of the plasma method is still much higher than the traditional process. Obviously, the main chance for the plasma method to further decrease the production cost lies in reducing the electricity consumption.

In summary, the continuous and scale-up synthesis of high purity H_2O_2 by the H_2/O_2 plasma reaction with an integrated device based on the MP-DDBD reactor was proved to be viable. The productivity of H_2O_2 solution could be easily increased by the increase of reaction tubes number, higher grade H_2O_2 solution could be obtained directly using quartz tube discharge reactor. A commercial synthesizer based on the integrated device will be small, movable, and capable of working in switchable mode. It can be used conveniently to supply high quality H_2O_2 on site for special users like electronic industry, medical treatment and public health, scientific research, and fine chemicals areas. Although this plasma method does not have economic advantages currently, it would be attractive because of technique advantages, such as simple synthesis operation and no hazardous transportation process of concentrated H_2O_2 solution. Our future research work will focus on further enhancement of energy efficiency, H_2 utility, purity of H_2O_2, as well as decreasing the discharge voltage of the multitubes discharge system.

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