Hydrogen Peroxide Synthesis

DOI: 10.1002/anie.201304134

Safe Direct Synthesis of High Purity H_2O_2 through a H_2/O_2 Plasma Reaction**

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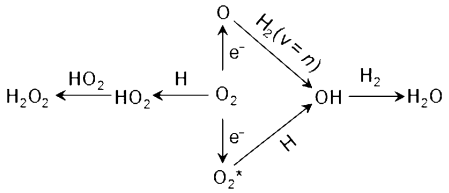
Hydrogen peroxide (H_2O_2), the most desired green oxidant,[1] is almost exclusively produced by an anthraquinone (AQ) process.[2] Direct oxidation of H_2 with O_2 has long been considered an ideal alternative for H_2O_2 production.[3] Extensive studies have been done on direct H_2O_2 synthesis from a H_2/O_2 mixture. To achieve high efficiency, direct H_2O_2 synthesis is generally performed in acidified solvent over supported noble-metal catalysts (Au, Pd, Au–Pd, and Pd–Pt).[4–11] However, the direct synthesis of H_2O_2 from a H_2/O_2 mixture catalyzed by metals is quite hazardous, and it is very difficult to directly obtain high-purity and high-concentration H_2O_2.

Research[12,13] published in the 1960s has demonstrated that H_2O_2 can be generated in H_2/O_2 non-equilibrium plasma through free-radical reactions in the absence of any catalyst or chemical. However, this plasma method has not yet drawn much attention, owing to low H_2O_2 yield (less than ca. 5%) and safety concerns about the discharge-triggered H_2/O_2 reaction.[12,14] The content of O_2 must be strictly controlled below 4 mol% in order to prevent explosion and ignition.[15]

Our previous research[16] showed that the structure of the plasma reactor played an important role in the direct synthesis of H_2O_2. A H_2/O_2 mixture containing 3 mol% of O_2 reaches 100% O_2 conversion, but the H_2O_2 selectivity is only 3.5% (based on O_2) in a single dielectric barrier discharge (SDBD) plasma reactor with a naked metal high-voltage (HV) electrode and an aqueous grounding electrode. On the other hand, 57.8% O_2 conversion and 56.3% H_2O_2 selectivity (based on O_2) can be obtained by using a double dielectric barrier discharge (DDBD) plasma reactor with a pyrex-covered metal HV electrode (the pyrex cover acts as an additional dielectric barrier) and an aqueous grounding electrode. Although the selectivity has been greatly improved, the safety concerns and low efficiency, owing to low O_2 content, are still big challenges.

Herein, we report an experimental realization of controllable H_2/O_2 combustion processes by an optimized plasma reactor. High purity (Grade 1 electronic grade H_2O_2 according to the SEMI standard) and highly concentrated H_2O_2 solution (ca. 60 wt%) can be directly produced from a H_2/O_2 mixture without explosion. These results suggest a different mechanism from conventional H_2/O_2 combustion processes in the H_2/O_2 plasma reaction. As shown in Scheme 1, the electron activation of H_2 into H is responsible for H_2O_2 formation. However, the electron activation of O_2 into O and O_2* (vibrational and electronic excited states) leads to H_2O formation and explosion of the H_2/O_2 mixture. Moreover, low-electron-density H_2/O_2 plasma leads to a low degree of H_2 and O_2 activation, which plays quite a significant role in producing H_2O_2 and controlling H_2/O_2 combustion.



Scheme 1. Main reaction network for formation of H_2O_2 and H_2O in non-equilibrium H_2/O_2 plasma.

The plasma reactor used in our experiments is a double aqueous electrode DDBD reactor (Supporting Information, Figure S1), which has an aqueous grounding electrode and an aqueous HV electrode. When a mixture of H_2/O_2 is transformed into H_2/O_2 plasma, H_2O_2 and H_2O are formed and condense on the reactor wall, then flow into the collector.

As shown in Table 1, using the DDBD reactor with double aqueous electrode, the selectivity and concentration of H_2O_2 are almost more than 60%. The content of O_2 in the feed can be increased by decreasing the flow rate of H_2; by this method, the allowable O_2 content reaches 30 mol% while ensuring the safety of the reaction. With a H_2/O_2 mixture containing 2.0 mol% O_2 at a total flow rate of 500 mL min^{-1}, 57% O_2 conversion and 72% H_2O_2 selectivity can be obtained (based on O_2). The concentration of H_2O_2 is 67 wt% when the space-time yield of H_2O_2 is 26 $g_{H_2O_2}L^{-1}h^{-1}$. As the content of O_2 in the feed was increased to 14.3 mol%, the conversion of O_2 reached 91%, and the selectivity and concentration of H_2O_2 were 64% and 62 wt%, respectively. In addition, the space-time yield of H_2O_2 increased to 37 $g_{H_2O_2}L^{-1}h^{-1}$.

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[**] We acknowledge the financial support from the Natural Science Foundation of China (20233050). We acknowledge some equipment help from Prof. Ma Xuehu and Prof. Zhang Jialiang.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304134.

Table 1: H_2O_2 synthesis with varying O_2 content in the double aqueous electrode DDBD reactor.[a]

O_2 content [V%]	O_2 conv. [%]	H_2O_2 selectivity [%]	$C_{H_2O_2}$ [wt%]	Space-time yield [$g_{H_2O_2} L^{-1} h^{-1}$][b]	Energy consumption [$kW h Kg_{H_2O_2}^{-1}$]
2.0	57	72	67	26	27
4.0	70	70	66	32	23
6.3	79	68	64	35	20
9.1	85	66	63	36	20
14.3	91	64	62	37	19
20.0	96	59	57	37	19
25.0	98	57	54	36	20
30.0	99	50	48	32	22

[a] Aqueous grounding electrode at 5 °C, 1 atm, 10 mL min^{-1} O_2 flow, input power = 10 W, 14.1 mL reactor. [b] The space-time yield of H_2O_2 is counted based on 100 wt%. Experimental error: Conversion ±1%, Selectivity ±1%, $C_{H_2O_2}$ ±1 wt%, Space-time yield ±1 $g_{H_2O_2} L^{-1} h^{-1}$, Energy consumption ±1 $g_{H_2O_2} kW^{-1} h^{-1}$.

Significantly, without any concentration or purification, the H_2O_2 solution is obtained in a concentrated (ca. 60 wt%) form, which complies with the requirements for Grade 1 electronic-grade H_2O_2, according to the SEMI standard (Table S1).[17] The energy consumption for H_2O_2 production is 19.0 $kW h Kg_{H_2O_2}^{-1}$ at 14.3% O_2 (Table 1), which is about a factor of five times higher than for the AQ process. However, the highly energy-consuming concentration and purification processes are avoided, and the equipment investment costs would be dramatically reduced. Therefore, this simple plasma method is attractive for the direct production of concentrated, neutral, and high purity H_2O_2, although the selectivity of H_2O_2 is lower than in AQ process.

Safety is a challenge in the direct synthesis of H_2O_2 by a H_2/O_2 mixture because of the broad composition range that is explosive (6–96 mol% O_2). In the double aqueous electrode DDBD reactor, the H_2/O_2 plasma reaction is safe when the O_2 content is up to 30 mol%. This is in contrast to a SDBD plasma reactor (Figure S2), where explosions would take place immediately after the start of the discharge when the O_2 content was above 10 mol%. To understand why the H_2/O_2 plasma reactions can be safely conducted with such a high O_2 content in the double aqueous electrode DDBD reactor, several comparative in situ diagnostic studies were carried out in the SDBD and double aqueous electrode DDBD reactors.

First, the discharge behavior of the double aqueous electrode DDBD reactor is quite different from that of the SDBD reactor. Briefly, the discharge of the SDBD reactor is from spark filaments (local and highly ionized narrow current pathways; Figure 1a); it is accompanied by strong discharge current pulses (Figure S3) and continuous temperature pulsating (25–50 °C; Figure S4). However, the discharge of the double aqueous electrode DDBD reactor is diffusive and uninterrupted throughout the discharge zone (Figure 1b); it has weak discharge current pulses (Figure S3) and almost unchanged space temperature (ca. 22 °C; Figure S4C). The higher the discharge current, the higher the electron density. These facts suggest that the reaction temperatures in the two reactors are at a low level and the double aqueous electrode DDBD reactor conducts a weak and homogeneous discharge, which has lower electron density.

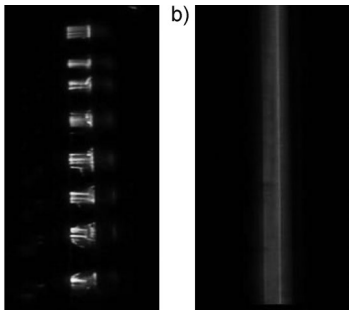

Figure 1. Optical images of H_2/O_2 DBD plasma. a) Optical image in the SDBD reactor. b) Optical image in the double aqueous electrode DDBD reactor. (H_2 152 mL min^{-1}, O_2 8 mL min^{-1}, aqueous grounding electrode at 5 °C, input power 10 W).

Second, when the reactors were used for O_2 discharge, optical emission spectra (OES) show that the plasma generated by the SDBD reactor have more intensive O lines (Figure 2a) and singlet O_2 spectra (Figure 2b) than the double aqueous electrode DDBD reactor. Similarly, when the reactors were used to synthesize H_2O_2 through a H_2/O_2 mixture discharge (Figure 2c), the plasma generated by the SDBD reactor shows much stronger H lines, O lines and H_2 emission bands than those in the double aqueous electrode DDBD reactor. The intensities of the O lines (777.5 nm and 844.7 nm) increases with increasing O_2 content in both reactors (Figure 2d; see also Figures S5A and B), whereas the intensity of the H line shows the reverse trend (Figure S5C). Surprisingly, when an explosion took place in the SDBD reactor and the double aqueous electrode DDBD reactor, the intensities of the O lines (777.5 and 844.7 nm) were near 260 and 150, respectively; the O_2 content was about 10 mol% for the SDBD reactor and 30 mol% for the double aqueous electrode DDBD reactor. The intensities of the O lines are an indicator of the densities of active oxygen (Sections S7 and S8),[18] thus the explosion of H_2/O_2 mixture under non-equilibrium plasma conditions will take place when the density of active oxygen is beyond the critical value. Moreover, the active oxygen also leads to H_2O formation.

It seems puzzling that the yields of H_2O_2 remains at high values for the double aqueous electrode DDBD reactor when the content of O_2 increases from 6.3% to 30% (Table 1), as the amounts of O and excited O_2 increase with increasing O_2 content (Figure 2). However, in terms of the relative intensities of the O lines and the degree of activation of O_2, these values remain constant over the whole range of O_2 content (Figure S7A and B). Furthermore, the degree of activation of O_2 in the double aqueous electrode DDBD reactor is approximately one third of that in the SDBD reactor. Hence, it is reasonable that the degree of activation of O_2 mainly determines the formation efficiency of H_2O_2 when the degree of activation of H_2 (Figure S7C and D) is fixed and sufficient. A low degree of activation of O_2 enhances the formation efficiency of H_2O_2, whereas a high degree of activation of O_2 favors the formation of H_2O. The densities of

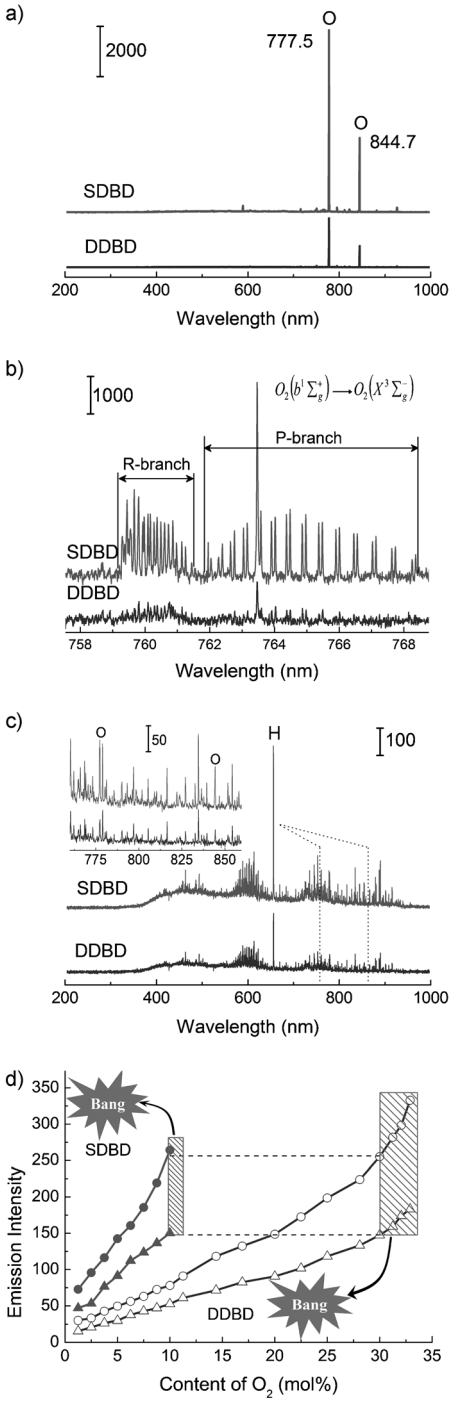

Figure 2. OES of O_2 plasma and H_2/O_2 plasma in the SDBD and double aqueous electrode DDBD reactors (aqueous grounding electrode at 5 °C, 1 atm, input power 10 W). a) 40 mL min^{-1} O_2 flow, 300 G mm^{-1} grating, 0.5 s exposure time. b) 40 mL min^{-1} O_2 flow, 1800 G mm^{-1} grating, 120 s exposure time. c) 152 mL min^{-1} H_2 flow, 8 mL min^{-1} O_2 flow, 300 G mm^{-1} grating, 0.5 s exposure time. d) Intensity of O lines of H_2/O_2 plasma in the SDBD and double aqueous electrode DDBD reactors with different O_2 content (160 mL min^{-1} H_2+O_2 flow, 300 G mm^{-1} grating, 0.5 s exposure time). DDBD-O 777.5 nm (○), DDBD-O 844.7 nm (△), SDBD-O 777.5 nm (●), SDBD-O 844.7 nm (▲).

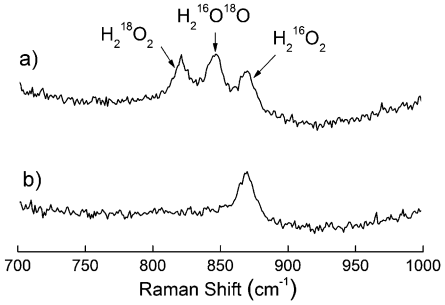

Figure 3. Isotopic product distribution of H_2O_2 synthesized by H_2/O_2 plasma. a) 165 mL min^{-1} H_2 flow, 4 mL min^{-1} $^{16}O_2$ flow, 4 mL min^{-1} $^{18}O_2$ flow. b) 165 mL min^{-1} H_2 flow, 8 mL min^{-1} $^{16}O_2$ flow.

O and excited state O_2 determine whether the explosion of H_2/O_2 takes place.

Third, to understand the mechanism of this H_2O_2 synthesis method, isotope tracing experiments were conducted. Figure 3 shows that the isotopic product distribution of the plasma method is remarkably different from that of the noble-metal-based direct synthesis.[19] It can be deduced that the recombination of HO_2 is the primary path of H_2O_2 formation ($HO_2 + HO_2 \rightarrow H_2O_2 + O_2$; Table S2) and HO_2 radical is a key intermediate. This conclusion is consistent with the experimental results. On the one hand, OES analysis (Figure 2c) shows that hydrogen atoms are the main active atom species, which means that HO_2 can be formed by $H + O_2 \rightarrow HO_2$. On the other hand, H_2O_2 is the principal product in the double aqueous electrode DDBD reactor. However, the isotope tracing experiments provide little insight into the formation of H_2O.

Generally, the chain-termination reaction ($H + O_2 \rightarrow HO_2$) leads to H_2O_2 formation, whereas the chain-branching reactions ($H + O_2 \rightarrow OH + O$ and $O + H_2 \rightarrow OH + H$) result in H_2O formation.[20,21] 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, $H + O_2 \rightarrow OH + O$, owing to the energy barrier of the latter reaction.[22,23] However, the rate coefficient of $H + O_2 \rightarrow OH + O$ will dramatically increase when the oxygen molecule is in an excited state, because the barriers of the reaction decrease for excited-state O_2.[24,25] Hence, the rate ratio of $H + O_2 \rightarrow OH + O$ to $H + O_2 \rightarrow HO_2$ increases with an increase of the ratio of excited O_2 molecules to ground-state O_2 molecules, which results in an increase in the OH/HO_2 ratio. Furthermore, OH can also be produced by $O + H_2 \rightarrow OH + H$, and the O atoms are mainly produced by the electron impact dissociation of O_2 and $H + O_2^* \rightarrow OH + O$. The rate coefficient of $O + H_2 \rightarrow OH + H$ is small, but it can be remarkably enhanced by vibrational excited electronic ground-state H_2.[26] The high concentration of vibrational H_2 in the H_2/O_2 plasma makes this path important for OH formation (Scheme 1).

It is easy for an explosion to take place in the SDBD reactor. This is because the high electron density results in a high density of H_2 ($v = n$) and active oxygen species (Figure 2), which favors chain-branching reactions (Scheme 1). In the double aqueous electrode DDBD reactor,

the discharge (Figure 1b) is very similar to the Townsend discharges characterized by low current density and low electron density,[27] which favors the chain termination reaction and thus results in a low degree of activation of oxygen (Section S9, Figure S7B and D), enhanced safety of the H_2/O_2 discharge, and the higher selectivity for H_2O_2 (Scheme 1).

In summary, gaseous H_2/O_2 plasma reactions have been demonstrated to be controllable for the direct synthesis of H_2O_2 when using a double aqueous electrode DDBD reactor. In this method, low electron density favors the generation of H_2O_2 by a chain termination path. This plasma method is promising for the direct synthesis of neutral, high concentration (ca. 60 wt%) and high purity (electronic grade) H_2O_2. It has also been successfully integrated with a titanium silicate molecular sieve catalyst for propene epoxidation.[28]

On the other hand, the selectivity of H_2O_2 should be improved further, because it is still much lower than that of the AQ process (above 95%); moreover, more energy efficient means of triggering the H_2/O_2 plasma reaction should be studied in the future. Significantly, the mechanism of the control process sheds new light on plasma chemistry,[29] radical chemistry,[30,31] and material treatment by plasma.[32] This control process could be helpful for other chemical reactions, especially for certain selective redox reactions.

Experimental Section

The flow velocities of H_2 and O_2 were monitored by a mass flow controller and mixed homogeneously to pass through the plasma reactor. The temperature of circulating water was maintained at ca. 5°C by a refrigeration unit. After about 10 min (remove O_2 and N_2 to ensure safety), the voltage of the HV electrode was adjusted by controlling the plasma power (high performance computerized plasma and corona discharge experiment generators CTP-2000K) to initiate the DBD discharge. The H_2/O_2 composition of the feed and effluent was analyzed by an on-line gas chromatograph. The H_2O_2 concentration of the collected product solution was determined by iodometry, then the H_2O_2 selectivity was calculated. In the process, the discharge voltage, discharge current, and power were measured on site by a digital oscilloscope (Tektronix DPO 3012, HV probe Tektronix P6015A, current probe Pearson 6585). The discharge images were taken by a camera (Nikon D50).

Received: May 14, 2013
Published online: June 26, 2013

Keywords: green chemistry · hydrogen peroxide · plasma chemistry · radical chemistry · synthetic methods

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