# Direct and continuous synthesis of concentrated hydrogen peroxide by the gaseous reaction of $H_2/O_2$ non-equilibrium plasma

**Juncheng Zhou, Hongchen Guo,* Xiangsheng Wang, Mingxing Guo, Jiangli Zhao, Lixing Chen and Weimin Gong**

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**Under ambient conditions, $H_2O_2$ has been synthesized with 32.51% yield and 56.25% selectivity *via* the gas-phase reaction of $H_2/O_2$ non-equilibrium plasma.**

Hydrogen peroxide ($H_2O_2$) is a very important commodity. Currently, it is widely used for pulp bleaching, water treatment and fine chemical production. Highly purified $H_2O_2$ is even used in the electronic industry for etching and purification, and in the cosmetic and pharmaceutical industries for disinfecting purposes. Nowadays, $H_2O_2$ is produced by the anthraquinone (AQ) process on a megaton scale. However, the AQ process involves alkyl anthraquinone and a mixture of organic solvents (work solution); it generates a raw product mixture containing only about 2 wt% $H_2O_2$, and requires a complex process for product recovery. Moreover, the AQ process is not a green process.[1]

In recent years, much effort has been made to develop a direct $H_2O_2$ process from $H_2/O_2$. Noble metals such as Pd and Au have been proved effective for the direct reaction of $H_2/O_2$. Recent studies[2–5] with these catalysts have focused on liquid-phase reaction, using either acidified aqueous solutions or acidified organic solvents. In the presence of solvents, the danger of explosion of $H_2/O_2$ is reduced, but the rate of the reaction can be seriously limited by the diffusion of the gaseous reactants across the gas–liquid interface. This problem, together with the reverse catalysis of the metal catalysts ($H_2O_2$ decomposition), makes it very difficult to increase the yield and concentration of $H_2O_2$.

According to earlier literature,[6] $H_2/O_2$ can be converted into $H_2O_2$ and $H_2O$ under atmospheric pressure if they are activated into a non-equilibrium plasma by silent electric discharge. The plasma method is unique because it does not involve any other chemicals except the $H_2/O_2$ feed, it is performed in the gas-phase, while the stoichiometry of $H_2/O_2$ providing the best selectivity for $H_2O_2$ meets the non-explosive regime of $H_2$–$O_2$ mixtures.[6c] That is to say, the plasma method doesn't have the problem of diffusivity limits, it is a safe and green process which is suitable for the direct synthesis of a pure $H_2O_2$ aqueous solution. However, in the literature the actual $H_2O_2$ yield reported with previous plasmas was very low (*ca.* less than 5%).[6a]

Most recently, we have carried out a study on the direct synthesis of $H_2O_2$ from the gaseous reaction of $H_2/O_2$ plasmas, and obtained quite high $H_2O_2$ yields at room temperature by using an atmospheric pressure dielectric barrier discharge (DBD).

Our discharge reactor (reactor A) mainly consisted of a pair of coaxial glass cylinders and two electrodes. The inner cylinder was made of Pyrex, it had an inner diameter of 9 mm and an outer diameter of 11 mm, it also had a reactant inlet on its upside. The wall of the inner cylinder served as a dielectric barrier for the discharge. The outer cylinder, which had a liquid inlet on its underside and a liquid outlet on its upside, was also made of glass and was used to form an annular gap in between the inner and outer cylinders. The high-voltage (HV) electrode was a thin Pyrex-tube (2 mm inner diameter) covered copper wire, it was installed in the axis of the cylinders and was connected to an alternating current (AC) supply. The grounding electrode was an aqueous solution which filled the annular gap of the glass cylinders, and was linked to the grounding wire through a tungsten connection welded across the wall of the outer cylinder. When the reactor was set to work, the aqueous solution of the liquid electrode was recycled so that it could serve as a cooling agent at the same time. The HV electrode and the grounding electrode formed a cylindrical discharge space, the length of which was 170 mm.

The total flow velocity of the $H_2$–$O_2$ mixture was 10 l $h^{-1}$ (residence time = 3.6 s); the content of $O_2$ in the mixture was fixed at 3% (much smaller than 6%, the lower limit of the explosive regime of $H_2$–$O_2$ mixtures) and monitored by mass flow controllers. 1.4 wt% sodium chloride was used as the aqueous solution of the liquid electrode, its conductance was 4.58 ms $cm^{-1}$ and its temperature was kept at 25 °C during discharge. The voltage of the HV electrode was maintained at 12.8 kV, the discharge frequency was maintained at 12 kHz. The total electric power input into the reactor was measured by a Tektronix TDS3012B digital oscilloscope equiped with a Tektronix TCP 202 current probe and a Tektronix P6015A high voltage probe. The $H_2$–$O_2$ mixture passed through the discharge zone downwards, the gaseous $H_2O_2$ and $H_2O$ produced were taken by the unconverted hydrogen and oxygen into a product collector that contained 10 ml stripping water. In order to calculate the selectivity of $H_2O_2$ and the conversion of $O_2$, the $H_2/O_2$ composition of the feed and effluent was analyzed by on-line gas chromatography, meanwhile the $H_2O_2$ concentration of the collected product solution was determined by iodimetry.

Fig. 1 indicates that the $H_2O_2$ concentration of the product solution collected from reactor A increased linearly with discharge time. After one hour's discharge, the $H_2O_2$ concentration reached 1.46 wt%; it increased to 4.12 wt% and 14.28 wt% after the discharge time extended to 3 and 11 hours, respectively. This phenomenon indicates that the $H_2O_2$ yield of the discharge reactor was stable during continuous discharge. The average total electric power input into the reactor was approximately 11.9 W. From these results, as well as the $H_2$–$O_2$ mixture feed velocity (10 l $h^{-1}$)

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*hongchenguo@163.com

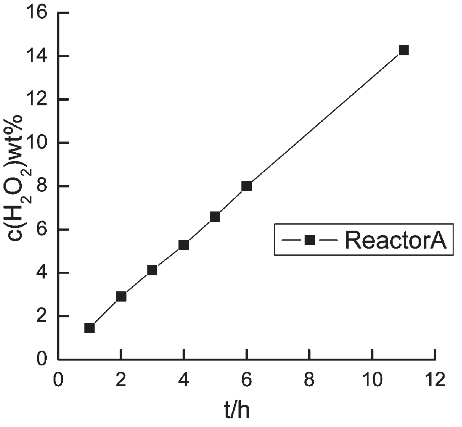

**Fig. 1** Hydrogen peroxide concentration profile *versus* time along the direct reaction of hydrogen and oxygen by discharge reactor A.

and the volume of the product solution collected (nomallized to 10 ml before iodimetry), the $H_2O_2$ formation efficiency was estimated to be 14.8 g $H_2O_2$ per $Nm^3$ $H_2$–$O_2$ mixture fed, and the average total energy consumption of reactor A was estimated to be 80 kW h $kg^{-1}$ $H_2O_2$. These data are comparable to those reported for the synthesis of $O_3$ from air *via* the plasma method.[7]

In order to better understand the effect of reactor A on the synthesis of $H_2O_2$, the same experiment was repeated with another two reference reactors, *i.e.*, reactor B and reactor C. Reactor B differed from reactor A by using a naked copper wire (with the same diameter) as its HV electrode; while reactor C differed from reactor A by using not only a naked copper wire as its HV electrode, but also a single pyrex cylinder (the size was the same as that of the inner cylinder in reactors A and B) as its main body and a copper foil wrapped on the surface of the pyrex cylinder as its grounding electrode.

Fig. 2 indicates that the performances of reactor B and C are quite different from that of reactor A. That is, after one hour's discharge, only 0.18 wt% $H_2O_2$ solution was collected from reactor B, and only a trace amount of $H_2O_2$ was detected in the solution collected from reactor C. Over extended time, the $H_2O_2$ concentration in the collector of reactor B increased linearly, however, it was just 0.47 wt% after 3 hours' discharge. With reactor C, on the other hand, the $H_2O_2$ concentration did not increase with the discharge time.

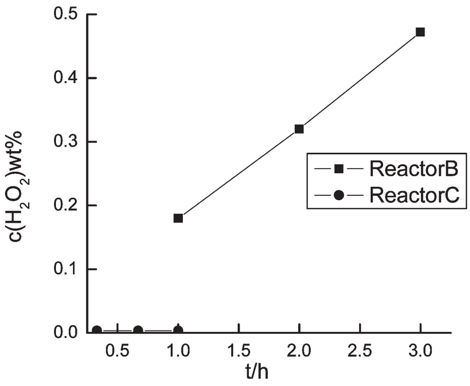

**Fig. 2** Hydrogen peroxide concentration profile *versus* time along the direct reaction of hydrogen and oxygen by discharge reactor B and reactor C.

Fig. 3 indictes that, the remarkable difference in the efficiency of $H_2O_2$ synthesis between the three reactors was a consequence of their different selectivity towards $H_2O_2$ formation. Reactor C had 100% $O_2$ conversion, whereas its $H_2O_2$ selectivity was only 0.04% (not shown). Reactor B also had 100% $O_2$ conversion, its $H_2O_2$ selectivity was 3.50%, much higher than reactor C. In the case of reactor A, the $O_2$ conversion decreased to 57.80%, approximately half of the value of reactor C and B, however, the $H_2O_2$ selectivity of reactor A was as high as 56.25%, one order of magnitude higher than that of reactor B, three orders of magnitude higher than that of reactor C. So the hydrogen consumption decreased from more than 6% in reactors B and C to 1.82% in reactor A, but the $H_2O_2$ yield of reactor A had reached 32.51%, almost one order of magnitude higher than that reported in the earlier study.[6a] These results show that the use of a Pyrex-tube covered copper wire as the HV electrode and the use of an aqueous solution as the grounding electrode play important roles in improving the selectivity of $H_2O_2$.

We believe that the cooling function of the liquid grounding electrode of reactor A in removing electric heat and the reaction heat of $H_2/O_2$ (to $H_2O$ and $H_2O_2$) was helpful in preventing the $H_2O_2$ product from being decomposed at higher temperatures, and therefore contributed to the $H_2O_2$ selectivity. Fundamentally, the role of the DBD in the present synthesis system was to activate the $H_2$–$O_2$ mixture into a state of non-equilibrium plasma which would spontaneously form $H_2O_2$ and $H_2O$ *via* radical reaction. The activation energy of the reaction of $H_2$ and $O_2$ to $H_2O_2$ by the plasma method is only 5 kJ $mol^{-1}$,[6c] which means that 0.04 kW h electric energy would be enough to activate the reactants to produce 1 kg $H_2O_2$, providing the reaction proceeded with 100% selectivity. It is then easy to understand that the total electric energy input into reactor A during discharge (80 kW h $kg^{-1}$ $H_2O_2$) was mostly consumed in the form of electric heat. On the other hand, thermodynamic calculation indicated that the total heat given by the reactions to both $H_2O$ and $H_2O_2$ was approximately 8872 kJ $kg^{-1}$ $H_2O_2$ at 60% $O_2$ conversion and 60% $H_2O_2$ selectivity. Taking only this reaction heat under consideration, it

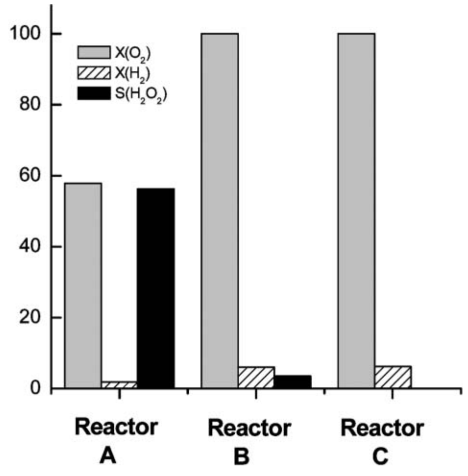

**Fig. 3** Effect of different discharge reactors on the conversion of $O_2$ ($X(O_2)$), the conversion of $H_2$ ($X(H_2)$) and the selectivity to $H_2O_2$ based on $O_2$ ($S(H_2O_2)$) ($t$ = 2 h).

would make the temperature of the gas mixture to increase to as high as 195 °C under adiabatic condition. In reactor A, both electric heat and reaction heat could be removed as soon as possible by the liquid electrode, so that it could be operated under 25 °C.

Besides, we also found that the liquid grounding electrode had an addtional function in improving the discharge behavior of the atmospheric pressure discharge.[8] That is, it decreased the spark filaments (local and highly ionized narrow pathways for the conduction of current) in the discharge space and made the discharge more homogenous and stable. In addition, the Pyrex-covered copper HV electrode in reactor A is believed to be superior to the naked metal electrode in preventing both $O_2$ and $H_2O_2$ from being consumed by the surface of the metal electrode. It might also favor the formation of OH radicals according to Luo *et al.*[9] OH radicals are supposed to be one of the key intermediates leading to $H_2O_2$ in the non-equilibrium plasma of $H_2/O_2$.[10] These factors also contributed to the $H_2O_2$ selectivity.

In conclusion, the gaseous synthesis of $H_2O_2$ *via* the direct reaction of $H_2/O_2$ non-equilibrium plasma seems promising. By using the plasma method, it is possible to continuously generate $H_2O_2$ aqueous solutions with different concentrations if the time course of pre-discharge is properly selected and then the flow rate of the stripping water (in) and the $H_2O_2$ product solution (out) is precisely controlled. If the work volume of the discharge reactor could be scaled up to 1 $m^3$ with the same performance, aqueous solutions of 30 wt% $H_2O_2$ could be produced continuously at a rate of 48 kg $h^{-1}$ $m^{-3}$. Compared with other known methods, the merits of the plasma method might include mild conditions, good safety, environmentally friendly, virtually no separation/purification process is needed, and being able to continuously generate $H_2O_2$ with high concentration and purity. It may be developed as a convenient and flexible $H_2O_2$-production process. The primary issue concerning the plasma method is the electric energy utilization. Although the actual electric energy consumption by the discharge reactor is very high (80 kW h $kg^{-1}$ $H_2O_2$) currently, the low activation energy of the plasma method for $H_2O_2$ synthesis, and the exothermic nature of the $H_2O_2$ forming reaction indicate a fairly low theoretical electric energy consumption (0.04 kW h $kg^{-1}$ $H_2O_2$). Therefore, a big improvement in energy utilization could be anticipated in future work. Now, work has been carried out in our laboratory to enhance the formation efficiency of $H_2O_2$, and to increase the electric energy utilization by optimizing the discharge conditions and the structure of the discharge reactor.

**Juncheng Zhou, Hongchen Guo,* Xiangsheng Wang, Mingxing Guo, Jiangli Zhao, Lixing Chen and Weimin Gong**
*Department of Catalytic Chemistry and Engineering & National Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116012, P. R. China. E-mail: hongchenguo@163.com;*
*Fax: (+86) 411-8368-9065*

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