Selectivity Control of H_2/O_2 Plasma Reaction for Direct Synthesis of High Purity H_2O_2 with Desired Concentration

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ABSTRACT: Low selectivity is one of the key problems which limit the application of plasma in chemical fields. High selectivity and concentration of H_2O_2 are critical in the direct synthesis of H_2O_2. Herein, we report that the selectivity of the H_2/O_2 plasma reaction can be controlled by specific energy input (SEI), i.e. low SEI leads to high H_2O_2 selectivity. When the SEI was fixed at 2.08 J/ml, the H_2O_2 selectivity reached 91% with 17% O_2 conversion, and a H_2O_2 solution with high concentration (90 wt.%) was achieved. Plasma diagnostics and theoretical calculation results indicate that, low SEI results in low electron density, which leads to high H_2O_2 selectivity but low O_2 conversion. Furthermore, the collision cross sections of H_2 and O_2 molecules with electrons indicate that the H_2/O_2 plasma, with average electron energy of 1~1.5 eV, can synthesize H_2O_2 with high selectivity and high O_2 conversion.

Key Words：Plasma Chemistry; Hydrogen Peroxide; Direct Synthesis; Selectivity Control; Electron Density; Average Electron Energy

1 Introduction

Plasma as the fourth state of natural matter has great potential in chemistry, physics and biomedicine [1-4]. During the 1960~80's, chemical synthesis using plasma chemistry was a hot topic[5-8]. In recent years, non-thermal plasma (NTP) has again been adopted by chemists for chemicals conversion [9-11], materials preparation [12-18], and environmental cleanup[19, 20]. Although NTP shows some unique features in the chemical reaction processes mentioned above, low selectivity to the target product is a critical problem researchers have to face, in particular in the synthesis of chemicals. Until now, only a few simple plasma reactions with only one reactant (e.g., acetylene synthesis) or one product (e.g., ozone synthesis) have been applied on industrial scale.

Hydrogen peroxide (H_2O_2), as one of the 100 most important chemicals in the world, has extensive applications [21], such as in paper manufacturing, environmental protection (treatment of waste water and removal of organic pollutants), metallurgy, chemical synthesis (propylene oxide, cyclohexanone oxime, etc), medical treatment (disinfectant), the electronics industry (as a cleaning agent, corrosion inhibitor and as a photoresist removal agent of semiconductor crystal plates in microelectronics, displays and photovoltaics), as well as aerospace (liquid chemical propellant) [22-25]. Industrially, H_2O_2 is almost exclusively produced by a Palladium-catalyzed anthraquinone (AQ) process, where H_2O_2 is synthesized through sequential hydrogenation and oxidation of alkyl anthraquinone [26]. Thus, the AQ process has high safety regarding the non-direct contact between H_2 and O_2.

However, the emission of exhaust gas (mesitylene isomers), waste water (containing aromatics, 2-ethyl-anthraquinone, tri-octyl phosphate, tert-butyl urea and K_2CO_3 lye) and solid waste (activated alumina) is unacceptable nowadays. In addition, for economic feasibility, the AQ process can only be operated at large-scale, resulting in some security risks in the transportation and storage of concentrated H_2O_2; a strict safety policy must therefore be followed.

During the last two decades, the direct synthesis of hydrogen peroxide (DSHP) from molecular H_2 and O_2 over noble metal catalysts, such as Pd [27-30], Au [31-33], Pd-Au [34-38], Pd-Pt [39-40], Pd-Sn [41] and Pt-Au-Pd [42, 43] has attracted much attention. The DSHP is a green and economic process in comparison to the industrial AQ process, and it has great potential to be applied on a small scale, i.e., operated where needed to produce a desired H_2O_2 concentration [44]. However, due to the usage of metal catalysts and organic solvent, it is difficult to get pure H_2O_2 solution directly via the DSHP process; thus some separation and purification units must be employed, which are unfavorable and impractical for small scale application. Furthermore, the side reaction of H_2O_2 hydrogenation occurs on Pd catalysts, which results in a decrease of H_2O_2 concentration. Currently, the highest H_2O_2 concentration obtained by DSHP is still only around ~10 wt.%, which must be improved to make the process feasible (usually about 30 wt.%).

Our previous research has demonstrated that the DSHP could also be realized through a safe H_2/O_2 plasma reaction in a double dielectric barrier discharge (DDBD) reactor [45, 46]. The plasma DSHP is a green gas-phase radical reaction

process and it does not use any catalysts or solvents, thus high purity H_2O_2 could be obtained directly without any purification operations. We also found out that, in the plasma DSHP process, the dissociation of H_2 (driven by electrons through inelastic collision) induced the H_2/O_2 plasma reaction to synthesize H_2O_2 through a chain termination reaction path (R1-R2). Meanwhile, the activation of O_2 (also driven by electrons through inelastic collision) resulted in the formation of H_2O through a chain branching reaction path (R3-R5). Once the O_2 is activated, the by-product H_2O will be easily produced. The difficulty in achieving high selectivity of H_2O_2 therefore lies in activating the H_2 molecule selectively whilst not activating O_2 molecule. In our previous studies, different kinds of DBD reactors were used, but the activation of O_2 could not be inhibited completely. Thus, the optimized H_2O_2 selectivity was nearly 65 % [45, 47, 48], that is, the concentration of H_2O_2 solution obtained by plasma DSHP was about 65 wt.%.

$$H + O_2 \rightarrow HO_2 \quad \text{R1}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \text{R2}$$

$$H + O_2^* \rightarrow HO + O \quad \text{R3}$$

$$O + H_2 \rightarrow H + OH \quad \text{R4}$$

$$OH + H_2 \rightarrow H_2O + H \quad \text{R5}$$

Herein, we report that, in a double dielectric barrier discharge (DDBD) reactor, the selectivity of H_2O_2 in the H_2/O_2 plasma reaction process can be controlled by adjusting the specific energy density (SEI). Lower SEI is favorable to achieve higher H_2O_2 selectivity.

2 Experimental

2.1 Experimental Setup

The experimental setup is shown in Figure 1. The flow of H_2 and O_2 were controlled by mass flow controllers (H_2 170 ml/min and O_2 10 ml/min), and the composition of H_2/O_2 mixture was controlled so as to be out of the explosion limit (explosion limit 4%-94%). Before discharge, H_2 and O_2 were mixed homogeneously and passed through the DDBD plasma reactor for about 10 minutes to remove O_2 and N_2 to ensure a safe operating procedure. The temperature of the circulating water was maintained at ca. 2 ^{o}C by a refrigeration unit. Then the voltage of the high voltage electrode (HVE) was adjusted to initiate the discharge (High performance computerised plasma and corona discharge experiment generators CTP-2000K). The exhaust gas was analyzed by an on-line gas chromatograph. The H_2O_2 concentration of the collected product solution was determined by iodimetry, then the H_2O_2 selectivity was calculated using formula F2. 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). The optical emission spectra of H_2/O_2 plasma were monitored by a spectrograph (Princeton Instrument SP 2758, 300 G/mm grating, 0.5 s exposure time). When a H_2/O_2 mixture is transformed into a H_2/O_2 DBD plasma, H_2O_2 and H_2O are formed through gas-phase radical reactions and H_2O is the only by-product. The produced H_2O_2 and H_2O will condense on the reactor wall, and then flow into the collector, which is cooled by an ethylene glycol cryogenic

device (-20 ^{o}C).

The conversion of O_2 was defined using formula F1, in which the moles of O_2 converted was detected by the gas chromatograph. The selectivity of H_2O_2 was calculated using formula F2, in which the moles of H_2O_2 produced were measured by iodimetry method. Energy consumption was calculated using formula F3, in which the energy consumed was the mathematical product of SEI and total gas flow rate. The SEI was the discharge power divided by total gas flow rate (180 ml/min = 3 ml/s).

$$C_{O_2} = \frac{moles\ \ of\ \ O_2\ \ converted}{moles\ \ of\ \ initial\ \ O_2} \times 100\% \qquad \text{F1}$$

$$S_{H_2O_2} = \frac{moles\ \ of\ \ H_2O_2\ \ produced}{moles\ \ of\ \ O_2\ \ converted} \times 100\% \qquad \text{F2}$$

$$E_C = \frac{energy\ \ consumed}{mass\ \ of\ \ H_2O_2\ \ p\ r\ o\ d\ u\ c} \qquad \text{F3}$$

2.2 Plasma Reactor

The DDBD reactor consisted of a pair of coaxial glass cylinders and two electrodes (Figure 2). The inner cylinder was made of pyrex with an inner diameter of 8.6 mm and an outer diameter of 11mm. The wall of the inner cylinder served as a dielectric barrier for the discharge. The outer cylinder, which had a liquid inlet at the bottom and a liquid outlet at the top, was also made of glass and was used to form an annular gap in between the inner and outer cylinders. The high-voltage electrode (HVE) was a thin pyrex-tube (2.0 mm inner diameter and 4.0 mm outer diameter) fully filled with Nickel powder (≤ 48 μm). It was installed in the axis of the cylinders

and connected to the high voltage power supply (AC). The grounding electrode (GE) was an 0.1 wt% NaCl 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 grounding electrode was recycled so that it served as a cooling agent at the same time. The HV electrode and the grounding electrode formed a cylindrical discharge space, with a length of 250 mm and a volume of 11.375 ml.

2.3 Measurement of H_2O_2 Concentration and Purity

The concentration of H_2O_2 solution produced was measured using an iodimetry method. Firstly, 0.5 g H_2O_2 product was transferred into a volumetric flask (50 ml) using an electronic balance, and then diluted to 50 ml using distilled water. Then 0.2 ml diluted H_2O_2 solution was transferred into a conical flask, before diluting it with 15 ml deionized water. After that, appropriate dilute H_2SO_4 solution was added, along with excess KI powder and 2 drops ammonium molybdate solution (2 wt.%), into the conical flask. This was shaken up and left to stand for ten minutes. The titration operation was then carried out using 0.01 mol/L sodium thiosulfate solution. The H_2O_2 concentration, moles and mass can be calculated based on the reactions R6 and R7. The purity of the produced H_2O_2 solution, i.e. the content of impurities, was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 2000 DV, Perkin Elmer).

$$2KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + 2H_2O + I_2 \quad \text{R6}$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad \text{R7}$$

2.4 Measurement of Electrical Parameters of the H_2/O_2 DBD Plasma

According to the relative dielectric constant of pyrex material and the geometric dimension of the two layer barrier dielectrics in the DDBD reactor, their capacitors have been calculated to be C_{d1} 9.0265×10^{-11} F and C_{d2} 2.5437×10^{-10} F. Thus, the total dielectrics capacitor (C_d) has been calculated to be 6.65×10^{-11}F using formula F4 (series connection).

$$C_d = \frac{C_{d1} \times C_{d2}}{C_{d1} + C_{d2}} \qquad \text{F4}$$

The electrical parameter of H_2/O_2 DBD plasma has been measured using the method described in the literature [49]. An external capacitor (C_{ext}) with a capacitance value of 2.28×10^{-8} F has been used as shown in Figure 1. The applied voltage (U_a), external capacitor voltage (U_c) and discharge current can be directly detected by a digital oscilloscope. The dielectric voltage (U_d) can then be calculated using the formula F5. The breakdown voltage, i.e., gas voltage (U_g) can be calculated using the formula F6.

$$U_d = \frac{C_{ext} \times U_c}{C_d} \qquad \text{F5}$$

$$U_g = U_a - U_d \qquad \text{F6}$$

3 Modeling

3.1 Descriptions of the Simulations

A 0-dimension time-evaluated model was adopted using the software ZDplaskin [50, 51]. We assumed that no surface reactions and recirculation appeared in our

double dielectric barrier discharge (DDBD) reactor so that all species present in the plasma gas satisfy the conditions for solving the Boltzmann Equation F7.

$$\frac{\partial f}{\partial t} + \upsilon \cdot \nabla f - \frac{e}{m} E \cdot \nabla \mathrm{v}\, f = C[f] \qquad \text{F7}$$

Where E is the electric field, m is the electron mass, f is the electron energy distribution function (EEDF), e is the elementary charge, v is the average electron velocity and $C[f]$ represents the change rate of f. This simulation can be classified into three main blocks; thirty-six electron-neutral/radical reactions, including momentum transfer, excitations/de-excitations, dissociation and ionization reactions; twenty-four neutral-neutral reactions; five ion-neutral/radical/ion reactions. All simulated species are shown in Table 1. Some other data used in this modeling has been summarized in Supporting Information (Table S1, S2 and S3).

3.2 Physical Model

The time evolution density of species, $N_{i=1\ldots i\max}$, can be written as equation F8. The source terms Q_{ij} describe the contribution from each diverse reaction process, j =1…jmax, defined by user's input file.

$$\frac{d[N_i]}{dt} = \sum_{j=1}^{j_{max}} Q_{ij}(t) \qquad \text{F8}$$

In order to provide a better understanding, an example of the reaction R8 has been provided. The reaction rate can be calculated in equation F9. Therefore, the source terms will be expressed as equation F10, F11and F12.

$$a\mathrm{A} + b\mathrm{B} \rightarrow a'\mathrm{A} + c\mathrm{C} \qquad \text{R8}$$

$$R = k_j [\mathrm{A}]^a [\mathrm{B}]^b \quad \text{F9}$$

$$Q_A = (a' - a)R \quad \text{F10}$$

$$Q_B = -bR \quad \text{F11}$$

$$Q_C = cR \quad \text{F12}$$

However, for some temperature-sensitive reactions, the temperature transport is then important (F13).

$$\frac{N_{gas}}{\gamma - 1}\frac{dT_{gas}}{dt} = \sum_{j=1}^{j_{max}} \pm \delta\varepsilon_j \cdot R_j + P_{elast} \cdot [N_e] \quad \text{F13}$$

Here γ is the specific gas heat ratio, $P_{elast}\cdot[N_e]$ means the joule heating caused by discharge current, and $\delta\varepsilon_j$ is the energy gap between the initial and final diabatic surfaces of the given reaction step. Additionally, calculations of the rate constants, k_j, are different if electrons are taken into account. For the neutral-neutral reactions, the constants can be obtained from the three-parameter Arrhenius form F14.

$$K_j(\mathrm{T}) = A_j T^{Bj} \exp(-E_j \cdot RT^{-1}) \quad \text{F14}$$

The unit of K_j is in m^3/s. T is gas temperature in Kelvin. The three parameters of A_j, B_j and E_j represent pre-exponential factor, temperature factor, and activation energy, respectively. There has been plenty of research conducted into the synthesis of H_2O_2, so all parameters used in this work can be found from NIST database.

However, for the electron-impact reactions, a special range of *E/n* was used to solve the Boltzmann Equation F7 in order to obtain the electron distribution function

and mean electron temperature, while the rate constants for all electron-impact reactions can be calculated by equation F15.

$$k = G\int_0^{\infty} \varepsilon \sigma_k F d\varepsilon \qquad \text{F15}$$

Where σ_k is the cross-section of the target particle, F represents the EEDFs, and ε ($\varepsilon = v/G$) is the electron energy in volt ($G = \sqrt{2e/m}$). The maximum value of E/n is observed around 88 Td.

4 Results and Discussion

4.1 H_2/O_2 Plasma Reaction Results

As shown in Table 2, when the SEI increased from 2.08 to 7.09 J/ml, the O_2 conversion increased gradually from 17 % to 99 %; however, the H_2O_2 selectivity decreased gradually from 91% to 20 % and the concentration of H_2O_2 also showed a similar trend with H_2O_2 selectivity. That is, in the case of low SEI, the H_2O_2 could be synthesized with high selectivity, although the O_2 conversion was low. With the increase of SEI, the energy consumption for the production of unit mass of H_2O_2 (Table 2) also increased. At low SEI of 2.08 J/ml, the energy consumption was reduced to 44 $kW{\cdot}h/kg_{H2O2}$, which was lower than the previous result of 53 $kW{\cdot}h/kg_{H2O2}$ [46]. The energy consumption reduction could be attributed to the improvement in H_2O_2 selectivity. When the SEI was fixed at 2.08 J/ml, a long-run operation with 500 hours continuous synthesis was conducted, the result of which is shown in Figure 3. It can be seen that the O_2 conversion remained relatively stable whilst the volume of H_2O_2 solution obtained (90 wt.%) increased linearly with reaction time. This means that the H_2/O_2 plasma reaction process can be operated with high stability, which is critical for future practical application.

After the 500 hours reaction, the concentration of the H_2O_2 product obtained was measured to be as high as 90 wt%. Furthermore, the content of impurities in the H_2O_2 product obtained was measured using an inductively coupled plasma atomic emission spectroscopy. The results (Table 3) indicate that the content of inorganic ion impurities were at Grade 2 of the equipment and materials international standards (Table 4), hence it can be used in the electronics industry. Our previous paper reported that Grade 1 electronic H_2O_2 solution could be synthesized by a H_2/O_2 plasma reaction. The reason for improvement of purity could be that the SEI has decreased, and lower SEI means fewer impurities (Zn, As, Mg, Ca and B) are sputtered out of dielectrics by DBD. Generally, at ambient temperature, high concentration H_2O_2 solution readily decomposes. Additionally, some metal ions can also catalyze the decomposition of H_2O_2; thus stabilizers are usually used. However, in this experiment, the 90 wt% H_2O_2 solution can be stored stably without using any stabilizers. The reasons might be, firstly, H_2O_2 solution was stored in a collector (Figure 1) cooled at a low temperature (-20 ^{o}C) by an ethylene glycol cryogenic device. Secondly, the content of some metal ions in H_2O_2 solution produced is very low (Table 3) .

Commercially, H_2O_2 is classified by its mass concentration, i.e., 30%, 35%, 50%, 60% and 70%, corresponding to different industrial applications. These commercial H_2O_2 solutions usually contain a small quantity of mechanical impurities, inorganic impurities and organic impurities. However, some high-end applications (electronic industry, medical treatment, food sterilization and aerospace) require a high purity or

high concentration H_2O_2 product. In industry, high purity H_2O_2 (electronic grade or food grade) is produced from the commercial H_2O_2 mentioned above by using a variety of purification methods (distillation, ion exchange resins, membrane separation, supercritical fluid extraction and crystallization). Concentrated H_2O_2 (propellant grade H_2O_2, higher than 90 wt.%) is usually produced from high purity H_2O_2 through some deep enrichment operations (vacuum distillation and recrystallization operations). These purification and enrichment operations have a huge equipment cost, a long production cycle and consume a copious amount of energy. Therefore, the value and price of H_2O_2 products usually increase exponentially with the concentration and purity of the H_2O_2 solution.

The above experimental results indicate that the selectivity of the H_2/O_2 plasma can be controlled to synthesize high purity and high concentration H_2O_2 directly without any purification or concentration operations. More importantly, through either dilution of 90 wt% H_2O_2 solution or adjusting the input energy density, the concentration of H_2O_2 can be controlled to a desired value for many applications, i.e., paper manufacturing, environment protection, metallurgy, chemical synthesis, medical treatment, electronic industry, as well as aerospace, ranging from dilute to concentrated H_2O_2 solutions.

4.2 Diagnostic of the H_2/O_2 Plasma

As mentioned previously, low reaction selectivity is a key problem of plasma chemical processes. The improvement of H_2O_2 selectivity is also an important issue in the field of H_2O_2 synthesis. Therefore, the control of H_2O_2 selectivity by adjusting SEI, as mentioned above, should be paid enormous attention as it may not only shed

new light on the methodology for the control of plasma chemical reactions, but it may also be significant in H_2O_2 synthesis. In order to understand why the H_2O_2 selectivity can be controlled by SEI, on-site diagnostic studies and theoretical calculation were carried out at different SEI.

The discharge behavior of the H_2/O_2 plasma has been recorded by a camera. The optical images (Figure 4) show that all of the H_2/O_2 plasma exhibited similar diffusive and uninterrupted discharge behavior throughout the discharge zone, just like the behavior of the Townsend discharge. That is, the SEI has little influence on the discharge behavior. However, Figure 4 shows that the luminance of the H_2/O_2 plasma was enhanced with the increase of SEI, which indicates that there may be more active and electronic excited species generated in the H_2/O_2 plasma in the case of higher SEI.

On-site optical emission spectroscopy (OES) has been used to diagnose the active and electronic excited species formed in the H_2/O_2 plasma. As shown in Figure 5a, the OES of the H_2/O_2 plasma was quite complex; two main emission bands in the range of 380-550 nm and 580-650 nm, as well as an intensive emission line at 656.3 nm, were detected. Furthermore, the local enlargement (Figure 5b) shows that two weak emission lines at 777.5 and 844.7 nm were also detected. The above detected five emissions correspond to the decay of H_2 molecule ($a^3\sum g^+ \rightarrow b^3\sum u^+$ and $d^3\prod u^+ \rightarrow a^3\sum g^+$), hydrogen atom ($3d^2D \rightarrow 2p^2P^0$) and oxygen atom ($3s^5S^0 \rightarrow 3p^5P$ and $3s^3S^0 \rightarrow 3p^3P$), respectively. It means that both H_2 and O_2 were dissociated in the H_2/O_2 plasma. Figures 5a and 5c show that the emission intensities of the excited H_2,

H and O increase with the increasing of SEI, which indicates more O_2 and H_2 have been activated into active species (H_2*, O_2*, H and O) at higher SEI. Correspondingly, the concentration of active species (H_2*, O_2*, H and O) also increased with SEI. The active oxygen species (O and O_2*) can result in the formation of H_2O through a chain branching reaction path (R3-R5) [45]. This is the reason why the H_2O_2 selectivity decreased with the increasing of SEI.

In atmospheric plasma chemical process, the electron density and average electron energy are the two critical parameters, which usually determine the distribution of active species and subsequently determine the final reaction results. However, they are difficult to measure accurately through experimental methodologies (e.g. Langmuir Probe) because of high deviation caused by high gas density. Fortunately, the variation of the electron density and average electron energy are commonly synchronous with the discharge current and breakdown voltage, respectively. Therefore, an on-site digital phosphor oscilloscope has been used to measure the discharge current and breakdown voltage of the H_2/O_2 plasma with different SEI [47]. The SEI was modulated by varying the applied voltage. However, as shown in Table 5, with increasing SEI, the breakdown voltage (U_g) was nearly stable. That is, the electric field intensity in the discharge region was nearly constant with increasing SEI. So, it can be speculated that the average electron energy in the H_2/O_2 plasma also undergoes little change with the variation of SEI. However, the discharge current increased gradually with an increase in SEI (Table 5), which indicates that the electron density increased gradually with increasing SEI.

4.3 Modeling Results of the H_2/O_2 Plasma

In order to corroborate the above experimental results, theoretical simulations on the H_2/O_2 plasma with different SEI have been calculated using the software ZDplaskin [50, 51]. In the modeling, through solving the Boltzmann Equation F7, the average electron energy and electron density can be calculated. Figure 6 shows that, with the increase of SEI from 2.08 to 7.09 J/ml, the average electron energy was nearly constant, but the electron density increased gradually from 1.54×10^{13} to 4.54×10^{14} cm^{-3}. These modeling results (Figure 6) are consistent with the experimental speculation on electron density and average electron energy (Table 5).

The above theoretical simulation results further indicate that the control of H_2O_2 selectivity was achieved through adjusting the electron density of the H_2/O_2 plasma. In plasma chemistry, higher electron density means higher probability of inelastic collisions between an electron and a reactant molecule. At the condition of low SEI, the electron density is low. This means the probability of inelastic collision between the electron and reactant molecule (O_2 and H_2) is also low, which leads to most of O_2 molecules remaining in the ground state. Conversely, at a higher SEI, more O_2 molecules will be activated into active oxygen species (O and O_2*). The active oxygen species (O and O_2*) can result in the formation of H_2O by-product through a chain branching reaction path (R3-R5); however, the ground state oxygen molecule mostly leads to the production of H_2O_2 through a chain termination reaction path (R1-R2) [45]. Therefore, low SEI, i.e., low electron density H_2/O_2 plasma, can synthesize H_2O_2 with high selectivity. However, low electron density will also result

in low O_2 conversion and low H_2O_2 yield.

4.4 Method for Future Improvement

The above results have demonstrated that, in order to get high H_2O_2 selectivity and high H_2O_2 yield simultaneously, the electron density of H_2/O_2 plasma must be increased, but the activation of O_2 must be avoided. The inelastic collision cross sections of H_2 [52-57] and O_2 [58-63] molecules with an electron, summarized in Figure 7 (the detail information is shown in supporting information, Figure S1), are vital for achieving this goal. In plasma, higher collision cross sections have higher probability to induce inelastic collision between particles and electrons, which results in activation of the reactant molecule. Figure 7 shows that, when the electron energy is in the range of 0~10 eV, the electrons can activate the H_2 molecule; however, only the electrons with energy in the range of 0.5~1 or 1.5~10 eV can activate the O_2 molecule. In other words, the electrons with energy between 1~1.5 eV can activate H_2 but cannot activate O_2. This result suggests that further study into the H_2/O_2 plasma reaction for the synthesis of H_2O_2 should be focused on controlling the average electron energy in the range of 1~1.5 eV. However, because the electron energy distribution in plasma is statistical (usually Maxwell distribution), the production of electrons with energy outside the range of 1~1.5 eV is inevitable. So, control of average electron energy may be beneficial for the enhancement of H_2O_2 selectivity but complete inhibition of H_2O formation is not possible. In other words, when the average electron energy is controlled in the range of 1~1.5 eV, the chain branching reaction path (R3-R5) to form H_2O by-product can be inhibited partially,

thus higher H_2O_2 selectivity and higher H_2O_2 yield can be obtained simultaneously at higher SEI.

5 Conclusions

In summary, the selectivity of H_2O_2 in the H_2/O_2 plasma reaction process can be effectively controlled by controlling the SEI: The higher the SEI, the lower the H_2O_2 selectivity. Plasma diagnostics and theoretical calculation results indicate that low electron density H_2/O_2 plasma is the critical factor for obtaining high selectivity. When the SEI was fixed at 2.08 J/ml, 500 hours continuous operation was carried out with high stability. The H_2O_2 selectivity reached 91 % and the H_2O_2 product obtained was high purity (electronic grade), producing concentrated H_2O_2 solution (90 wt%). However, low SEI leads to low O_2 conversion and low H_2O_2 yield. In the future, if the average electron energy of H_2/O_2 plasma could be controlled in the range of 1~1.5 eV, higher H_2O_2 selectivity and higher H_2O_2 yield could be achieved simultaneously at higher SEI.

These results provide the idea that, by combining a H_2/O_2 plasma experimental setup with a water electrolysis device, a H_2O_2 generator can be designed to produce high purity H_2O_2 directly from H_2O. Furthermore, only consuming electrical energy, this H_2O_2 generator can synthesize H_2O_2 with a desired concentration ranging from dilute to concentrated H_2O_2 solution, which has broad applications, i.e., paper manufacturing, environment protection, metallurgy, chemical synthesis, medical treatment, electronic industry, as well as aerospace. However, more studies need to be done to improve H_2O_2 productivity and decrease the energy consumption.

In addition, through analyzing the collision cross section of reactants with an electron and adjusting the electron energy distribution, the selectivity of some complex plasma reaction systems (various reactants and products) could be controlled in theory and practical applications.

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Notation

SEI = specific energy input

NTP = non-thermal plasma

H_2O_2 = hydrogen peroxide

AQ = anthraquinone

DSHP = direct synthesis of hydrogen peroxide

DDBD = double dielectric barrier discharge

DBD = dielectric barrier discharge

HVE = high voltage electrode

AC = alternating current

GE = grounding electrode

C_d = dielectrics capacitor

U_a = applied voltage

U_c = external capacitor voltage

U_d = dielectric voltage

U_g = gas voltage = breakdown voltage

BE = boltzmann equation

EEDF = electron energy distribution function

OES = optical emission spectroscopy

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Figure Captions

Fig. 1 – Schematic diagram of experimental setup for direct synthesis of H_2O_2 through H_2/O_2 plasma

Fig. 2 – Schematic structure of the DDBD reactor

Fig. 3 – O_2 conversion and H_2O_2 product solution volume VS. reaction time during the 500 h continuous operation. The left inset is the discharge photo and the right inset is the photo of the H_2O_2 production. (2.08 J/ml SEI, 12 kHz discharge frequency, 1 atm, 10 ml/min O_2, 170 ml/min H_2)

Fig. 4 – Optical images of the H_2/O_2 DBD plasma at different specific energy input. (0.5 s exposure time, 12 kHz discharge frequency, 1 atm, 10 ml/min O_2, 170 ml/min H_2).

Fig. 5 – a) OES of the H_2/O_2 DBD plasma with different specific energy input; b) the local enlargement of a); c) OES intensity of H and O atomic lines in the H_2/O_2 DBD plasma with different specific energy input. (300 g/mm grating, 0.5 s exposure time, 12 kHz discharge frequency, 1 atm, 10 ml/min O_2, 170 ml/min H_2)

Fig. 6 – Electron density and average electron energy of H_2/O_2 plasma as a function of specific energy input simulated using ZDplaskin software.

Fig. 7 – Inelastic collision cross sections of H_2 and O_2 molecule with electron in the energy range of 0~10 eV.

Table 1 – Summary of all ground-state species included in the model.

Table 2 – H_2O_2 synthesis with varying specific energy input in a DDBD reactor.

Table 3 – Impurity content of the H_2O_2 solution obtained in the 500 h continuous operation and the electronic grade H_2O_2 of SEMI Standards (Unite: ppb).

Table 4 – Requirements for electronic grade hydrogen peroxide according to SEMI Standards (SEMI Document C30-1110, 2010).

Table 5 – Electrical parameters of the H_2/O_2 DBD plasma with different specific energy input.