

Synthesis of ozone from air via a polymer-electrolyte-membrane cell with a doped tin oxide anode.

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The generation of ozone from air using an electrochemical cell consisting of an air cathode, a polymer-electrolyte-membrane (PEM), and a doped tin oxide anode is reported. This synthesis is green compared to the conventional high-voltage corona discharge process since NO_x formation is eliminated; a higher ozone concentration is generated; and lower energy may be required.

Introduction

Ozone is a powerful oxidant in advanced oxidation processes for treating water and solids. Ozone is a green oxidant since it self decomposes in time, leaving no residual effects. It can also oxidize persistent pathogens and contaminants more effectively than chlorine [1,2]. The conventional route to synthesize ozone is through high voltage corona discharge (CD) in air producing a 2 to 3% concentration of ozone [3]. The overall energy consumption of the CD process is high since cooling and drying of air are needed in addition to the electrical energy. This process can produce NO_x as a by-product unless pure oxygen is supplied, which will require additional energy. The energy required to purify air to oxygen is at least two times that of making ozone from oxygen [4].

The alternative route of ozone generation via water electrolysis is attractive since no NO_x could be generated and only a low voltage source is needed. If dissolved ozone is the desired product, then the water electrolysis route is more direct and effective. Some losses of ozone to oxygen are expected in the slow dissolution of gaseous ozone generated by the CD process due to self-decomposition. The electrochemical synthesis of ozone has been examined with a number of anode materials [5-11]. The electrolytic route to generate ozone has been reviewed recently [12,13]. Until now, only low efficiency has been demonstrated and the most efficient anode material, lead dioxide is environmentally prohibitive for a general usage. A high current efficiency and a high concentration of ozone have only been demonstrated recently by the authors using doped tin oxide electrode [14, 15]. Some previous reported investigations of water treatment used anodes with undoped tin oxide anodes [16] or tin oxide doped with different elements [17, 18]. The focus of these investigations were direct electro-oxidation and little ozone was detected. Our previous results of high ozone generation [14, 15] were obtained in a three-electrode test cell containing different acid electrolytes. For corrosion and safety consideration, it will be desirable to have an acid free process, particularly for domestic household applications. Furthermore, hydrogen generated at the cathode during electrolysis creates a safety concern. The water consumed during electrolysis will need to be replenished regularly to maintain the electrolyte for

sustained operation. We present here for the first time the use of the highly efficient nickel-antimony doped tin oxide as the anode in a water filled polymer electrolyte membrane (PEM) cell fitted with an air cathode. Oxygen from air is consumed in the porous cathode and ozone is produced in pure water and can subsequently evolve into the gas phase for gaseous ozone production. A 15% ozone concentration in the gas phase, 20 mg/L dissolved ozone, and a 15% percent current efficiency are observed here. These ozone concentrations reported are much higher than the CD process. In the following sections, we describe the experimental setup, the mechanism of the electrode processes, and the broader implications of the results for general environmental applications.

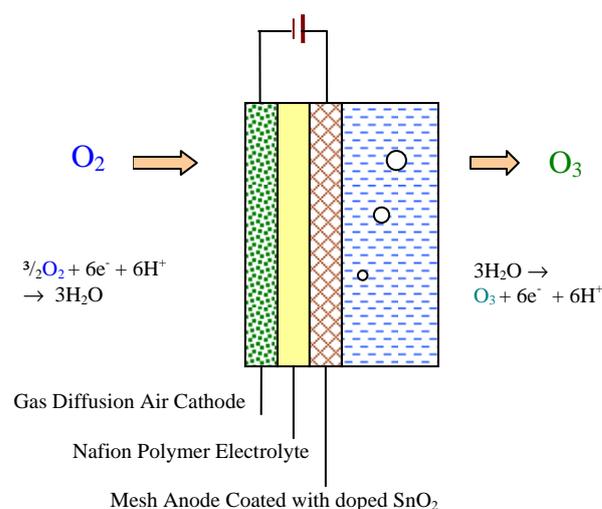


Fig. 1 Illustration of ozone generation in the electrochemical cell.

Experimental

The electrochemical cell

The operation of the electrochemical generator is shown schematically in Fig. 1. Oxygen from air diffuses into the gas diffusion cathode and combines with protons to form water when receiving electrons from the external circuit. Ozone is generated at the anode by oxidation of water with electrons released to the external circuit, whereas protons are simultaneously produced. The protons subsequently diffuse through the proton exchange membrane back to the cathode. The net reaction is converting oxygen to ozone without any consumption of water or protons. With the solid polymer electrolyte providing the protons, the ozone generation occurs

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in pure water without the need of an acid supporting electrolyte, and eliminate the corrosive hazard. The anode was prepared by repeated coating of a titanium mesh with an alcohol solution containing SbCl_3 (BDH, 99.5%), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98%, ABCR) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, 98%) precursors followed by pyrolysis at 500°C . The procedure was similar to that previously described [14,15]. A $4.0\text{ cm} \times 6.0\text{ cm}$ titanium mesh (99.5% Good Fellow) with a nominal aperture of 0.19 mm and wire diameter of 0.23 mm was spot-welded with a 1 mm diameter titanium wire (99.5% Good Fellow). The mesh and wire assembly was then treated in 10% boiling oxalic acid for 1 hour, washed with distilled water, and dried before dip-coated with the precursor solution and pyrolyzed in air. The dip coating and pyrolysis procedure was repeated 7 times and the loading on the Ti mesh was 61 mg as determined by the weight gained. The cathode was prepared by pasting 55% Pt/C catalyst (De Nora North America, ETEK Division) onto one side of a $4\text{ cm} \times 6\text{ cm}$ carbon cloth (ETEK, 30% wet proofed). The platinum loading on the cathode was $4.5\text{ mg}/\text{cm}^2$. The membrane-electrolyte-assembly (MEA) was prepared by hot pressing at 140°C the cathode, a solid electrolyte Nafion 117 membrane (Fuel Cell Scientific) and the anode.

Quantification of ozone production

The amount of ozone generated was determined by a setup as shown in Fig. 2. The water side of the MEA was housed in an acrylic chamber with an gas outlet connected to a 10% potassium iodide bath for idometric measurement. The ozone oxidized iodide to iodine stoichiometrically and the amount of iodine can be determined by titration with sodium thiosulfate with a starch end point, as described in the literature [19]. The volume of the water chamber is 10 ml . After about 20 min . of electrolysis, the ozone concentration in gas and water phase would have reached equilibrium. The generated gas was then let out through the tube and absorbed by the KI solution. The unabsorbed residual gas was collected at the top of an inverted graduated cylinder to determine its volume, which was about 7 ml after 30 min . This unabsorbed gas is mainly oxygen generated from the reaction of ozone with KI, or from the electrolysis of water in the PEM. The ozone concentration in the water phase was determined by UV spectrometer (Perkin Elmer Lambda 20). Water samples were extracted with a syringe from an opening fitted with a rubber septum. The ozone concentration in the gas phase can be calculated by the amount of ozone absorbed by the KI solution and the residual gas volume at the top of the inverted cylinder.

The electrolysis was performed at constant cell voltage and controlled by a Radiometer Copenhagen/Dynamic-Eis Voltalab PGZ301 potentiostat/galvanostat. The number of coulombs passed during the electrolysis was accurately counted by a built-in integrator. All experiments were carried at room temperature of 20°C .

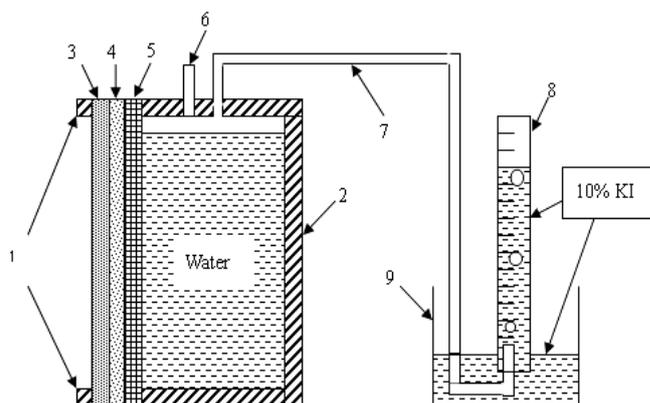


Fig. 2 The schematic drawing of the experimental apparatus. 1. Acrylic frame; 2. Acrylic chamber; 3. Cathode; 4. Nafion membrane; 5. Anode; 6. Hole for extracting water sample; 7. Tube for gas transfer; 8. 10ml cylinder with scale bar; 9. Beaker.

Results and Discussion

Ozone concentration

Using our experimental setup, we examine the issues of ozone synthesis in terms of ozone concentrations, current efficiency, and energy efficiency. Upon application of a constant voltage across the PEM cell, ozone will be generated in water and accumulate until part of the ozone leaves the water phase to the gas phase above. As shown in the aqueous ozone concentration time profiles in Fig. 3, a steady-state is reached after 25 minutes of applied voltage. At this point, ozone is generated steadily in water, enters into the gas phase, and is eventually absorbed by the KI solution in the absorption chamber. The steady-state dissolved ozone concentration depends on the applied voltage and varies in the range of $5\text{ mg}/\text{L}$ to $20\text{ mg}/\text{L}$. This level of dissolved ozone concentration is more than sufficient for most applications and is usually not attained in the conventional CD process [20]. Solubility of ozone in water depends on the gas phase ozone concentration, temperature, pH, and the presence of other dissolved species. For a $48.5\text{ mg}/\text{L}$ ozone concentration ($\sim 2\%$) generated in the gas phase, the dissolved ozone concentration is $6.7\text{ mg}/\text{L}$ in a pH 7.1 solution at 25°C [21].

To avoid disturbance to the titration experiment and the determination of steady-state gas phase ozone concentration, liquid samples were not withdrawn for dissolved ozone measurements after the 30th minute. The steady-state concentration of ozone in the gas phase correlates to that in the water phase and varies with applied voltage in the same way, as shown in Fig. 4. The highest ozone concentration in gas phase was 15.6% (v/v) equivalent to $334.3\text{ mg}/\text{L}$ (STP), at the voltage of 2.0V . This concentration is much higher than that achieved by the CD process, which is about 10% (v/v) using a cool, dry, and pure oxygen supply [22].

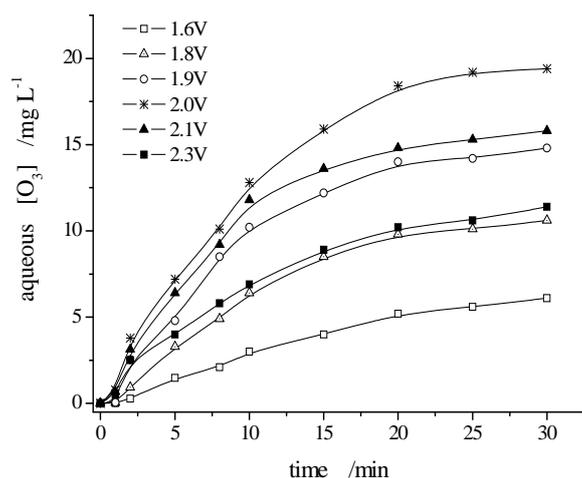


Fig. 3 Ozone concentration in water vs the electrolysis time at different voltage.

For applications requiring a source of high concentration gaseous ozone [22], the electrochemical process described here provides a convincing and convenient alternative to the CD process. Pure oxygen tank, cooling, and drying are not required in the electrochemical cell. The scalable and modularizable generation is particularly attractive for small and medium scale usage. Previously, a complex procedure was adopted to provide high concentration gaseous ozone to some processes of preparing semi-conductor surfaces [23].

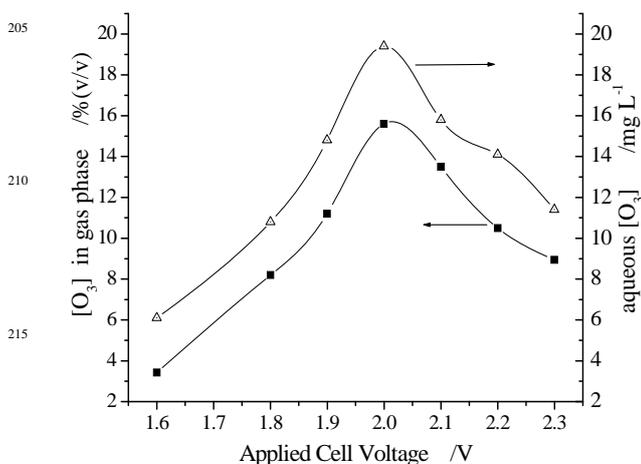
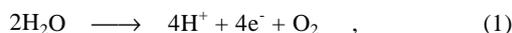


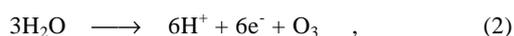
Figure 4. Applied voltage vs ozone concentration in gas and water phases.

Current efficiency

Figures 3 and 4 show an optimum cell voltage of 2.0 V for highest ozone concentration. The effect of the cell voltage can be partly analysed in light of the parallel electrochemical oxidation of water to form oxygen,



which has an equilibrium potential of 1.23 V (RHE). The oxygen evolution reaction is thermodynamically more favorable than the ozone reaction



which has an equilibrium potential of 1.52 V (RHE).

The presumed role of the doped tin oxide material at the anode is to suppress the kinetics of oxygen evolution reaction and enhance the activation of the ozone generation reaction. Equations (1) and (2) represent only the overall reactions and the detailed mechanisms may involve individual steps of precursors and intermediates such as oxygen and hydroxyl free radicals, adsorbed oxygen, and other ions. The specific effect of voltage and materials to individual steps would require more refined experimental works. The electrochemical kinetics of the oxygen evolution reaction and the ozone generation reaction are different. The increase of voltage beyond a certain value may promote more oxygen generation than ozone generation. The decrease of ozone concentration beyond the optimum voltage of 2.0 V can be partly explained by this reasoning. It is also possible that the catalytic material or other electrode components are degraded by a high voltage.

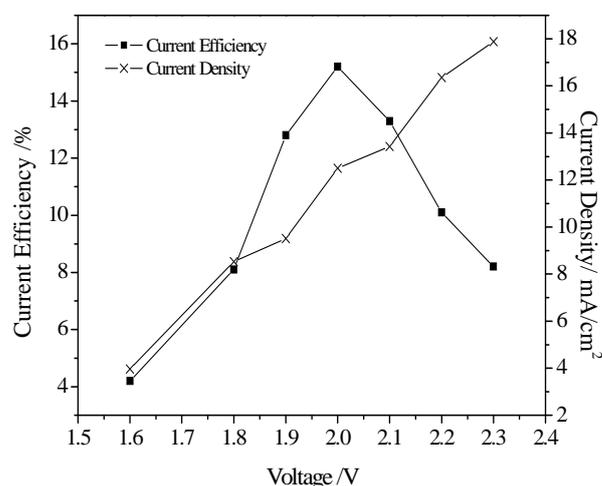
While the efficiency of ozone generation falls over beyond 2.0 V, the current increases steadily and linearly with applied voltage, as shown in Fig. 5. The effectiveness of using current to produce ozone can be quantified by the current efficiency which is defined according to Faraday's law as

$$\eta = [(\text{moles of ozone generated}) n * F / C] \times 100\% \quad (3)$$

where n is the number of electrons transferred ($n=6$ in equation 2), F is the Faraday's constant, and C is the amount of electric charge passed.

The 15.2% current efficiency observed at 2.0 V is the highest value reported for a MEA cell with a static water electrolyte, whereas a value of < 10% was reported for PbO₂ anode without water flow at room temperature [24-27].

The loss of current efficiency is mainly due to production of oxygen either directly as the parallel electrochemical step of equation (1) or the subsequent decomposition of ozone to oxygen in the water phase and in the gas phase. The half-life of ozone at room temperature is 30 minutes and some losses of ozone to oxygen are expected. It has been demonstrated that current efficiency will improve by as much as 50% with forced convection of water. We may therefore expect the current efficiency reaching over 20% in our MEA cell with flowing water.



A further increase in current efficiency can be envisaged by improving the interfacial contact of the anode and the solid polymer electrolyte. A 36.2% current efficiency was observed in our previous work using a wet acidic electrolyte where the immersed mesh electrode was in more complete contact with protons and water. In the MEA construction, the mesh anode and the solid electrolyte has a planer interfacial contact and the solid-solid interface has limited contact area. Onda et al. [26] has shown that by using a multi-layer mesh structure in contact with Nafion, interfacial contact can be improved and the ozone concentration can be increased by 40% compared to a single layer mesh electrode. We may expect a further improvement with a better interfacial construction between the anode and the solid polymer electrolyte.

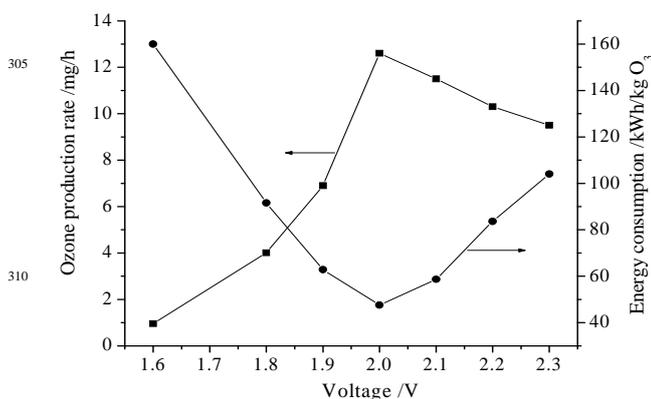


Figure 6. Applied voltage vs. ozone production rate and energy consumption

Energy efficiency

The ozone production rate was the amount of ozone generated in a unit time period, and changes with the applied voltage, as shown in Fig. 6. The ozone was generated on a 4.0 cm x 6.0 cm anode. In principle, the production rate scales with the electrode area, subject to limitations of uniform current distribution and mass transport. Experience of established electrochemical technologies, such as fuel cells and chloroalkaline production, are helpful to large scale electrochemical generation of ozone. From Fig. 6, the highest steady-state ozone production rate was 12.6 mg/h achieved at a cell voltage of 2.0 V over a period of hours. The corresponding energy consumption per unit ozone was also shown in Fig. 6. It varies with voltage in the trend opposite to that of production rate. The energy consumption E_p in kWh/kgO₃ is determined by:

$$E_p = (V \cdot I) / Q \quad (4)$$

where Q in kg/hr is the ozone production rate, I in A is the current, and V in volts is the applied cell voltage. From Fig. 6, the lowest energy consumption of 48 kWh/kg ozone was achieved at 2.0V. This energy consumption is lower than the lowest energy consumption reported (65 kWh/kg) on PbO₂ [27]. It was demonstrated on PbO₂ electrode that forced convection can improve energy consumption by 50%. We would expect a similar improvement when water is circulated through the anode compartment of the PEM cell. The best reported CD energy efficiency is 9.5 kWh/kg ozone, assuming the supplies of cooling water, dry and pure oxygen are

available [28]. Typical energy requirement is 2~3 times this value when drying, cooling, and oxygen purification are all considered. That should bring the energy efficiency of the electrochemical route compatible to the CD process.

The effect of current and voltage on efficiency as given in equation (4) gives some interesting insights to alternatives in the operation of electrolytic ozone generation. The electrochemical route requires a higher free energy barrier since the starting raw material is water, compared to oxygen in the CD process. The possibility of electrooxidation of oxygen to ozone exists with the reaction



which is a 2 electron process with an equilibrium potential of 2.03 V. If oxygen is produced electrochemically via equation (1), then the overall process is still a 6 e transfer and the energy consumption remains the same. If, however, oxygen can be supplied to the anode, eg. via aeration, and with efficient mass-transfer, then there should be a substantial gain in energy efficiency. The cell voltage may increase with reaction (5), but the 1/3 reduction in current per ozone produced can lead to an overall decrease in energy consumption, as shown in equation (4). The concept of areated anode therefore warrants further investigation.

On the other hand, there also exists an alternative of hydrogen evolution to replace the oxygen reduction reaction at the cathode, given as



which has an equilibrium potential of 0 V. The simultaneous production of hydrogen may be desirable in some applications. In renewable energy applications, hydrogen is produced by electrolysis of water as stored or transportable energy. Oxygen is a byproduct of electrolysis that may not be discarded. Co-generating of ozone instead of oxygen in electrolytic hydrogen production can be very desirable. The choice of hydrogen evolution in equation (6) over oxygen reduction in reverse of equation (1), however, will require a higher operating cell voltage due to the lower equilibrium potential. In addition, water will be consumed and needs to be replenished steadily to keep the function of the PEM cell. But the generation of two useful products: hydrogen and ozone are of interest in environmental applications.

Conclusions

The advantages of the electrochemical route for ozone generation are demonstrated with a polymer-electrolyte-membrane (PEM) cell housed with a novel doped tin oxide anode. Compared to the conventional corona discharge process, the ozone concentrations in gas and dissolved phases are higher, there is no risks of nitrogen oxides byproducts, and improved energy efficiencies are expected. The electrochemical route offers a modular, scalable production. Further improvements and optimization are expected by forced convection, more thoroughly contacted electrolyte-anode interface, and alternatives in anode and cathode operations. The green synthesis of ozone should widen applications of ozonation for a better environment.

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