

Review Article

Anodic Materials for Electrocatalytic Ozone Generation

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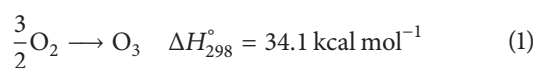
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Ozone has wide applications in various fields. Electrocatalytic ozone generation technology as an alternative method to produce ozone is attractive. Anodic materials have significant effect on the ozone generation efficiency. The research progress on anodic materials for electrocatalytic ozone generation including the cell configuration and mechanism is addressed in this review. The lead dioxide and nickel-antimony-doped tin dioxide anode materials are introduced in detail, including their structure, property, and preparation. Advantages and disadvantages of different anode materials are also discussed.

1. Introduction

Ozone is one of the most powerful oxidants currently available [1, 2] and it has an oxidation potential of 2.07 V. Due to its potent oxidative property, ozone has been recognized as a useful chemical in disinfection and sterilization processes. It kills microorganisms, decomposes organic molecules, and removes cyanide, phenols, manganese, detergents, and coloration from aqueous systems. It is used to disinfect portable water, food, and surgical equipment and to treat sewage water, swimming pool, and so forth. It may also be employed as a raw material in the manufacture of certain organic compounds such as oleic acid and peroxyacetic acid [3]. The use of ozone for the purification of water is particularly advantageous as it does not leave any harmful residuals in water [3]. But ozone is unstable and its half lifetime is only about 30 min in water. Thus, it is commonly used by on-site production technology.

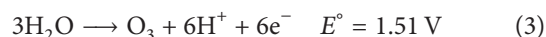
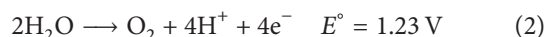
Traditional ozone production method is corona discharge to air or pure oxygen with the following reaction occurred [3]:



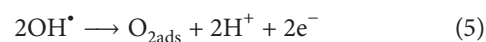
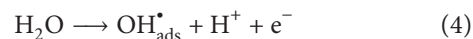
In this method, due to the high-frequency AC electric field applied, certain amount of harmful nitrogen oxides will be produced if air is used as the gas source. What is more, the ozone concentration cannot be higher than 3% (by weight). Even by using pure oxygen as the gas source,

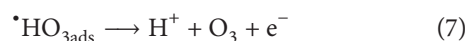
the ozone gas concentration cannot reach as high as 10% (by weight). The low ozone concentration may have various disadvantages. In particular, because of its low concentration, the dissolved ozone is insufficient to treat the water and results in low operational efficiency. Additionally, dry ozone from the discharge method takes a longer time to dissolve in water than wet ozone from the electrolytic process. To avoid these disadvantages of discharge method, more and more attention shifted to the electrocatalytic method.

The electrocatalytic ozone generation method is to oxidize water to ozone on the anode. It is well known that water is more favorable to be oxidized to oxygen than ozone, because the oxygen evolution occurs under a much lower anodic potential than that for ozone evolution as shown in the following reactions:



For electro-catalytic ozone production, the formation of adsorbed hydroxyl free radicals and adsorbed oxygen is very important and the reaction steps are usually considered as reactions (4)–(7).





The current efficiency for ozone production can be influenced by many parameters. Thus, various electro-catalytic parameters were investigated to enhance the ozone evolution while to retard the oxygen evolution reaction in past years. These included the anodic materials, electrode morphology, cell configurations, current density, electrolyte, anodic potential, and temperature [4]. Stucki et al. studied the effect of temperature, current density, and water flow rate on the current efficiency by using a polymer membrane as electrolyte [5]. Except to the membrane electrolyte technology, the ozone evolution was usually studied in acidic solution by using HClO_4 , H_2SO_4 , H_3PO_4 , HBF_6 , and HBF_4 as electrolyte. People may add some additives to these solutions to enhance the ozone generation. Foller et al. studied the ozone generation on different anode materials in different acidic electrolyte, under different current densities [6, 7]. After the year of 2000, the research group of Da Silva published several papers on studying the effect of these parameters [8].

Among these parameters, the anodic material is one of the most important factors. Different anodic materials showed much different performance toward electrolytic ozone generation. To achieve appreciable ozone evolution with considerable efficiency, the anodic materials must be carefully chosen. Thus, the materials for electrolytic ozone generation must have a high over potential for oxygen evolution to prohibit the oxygen evolution and be stable to strong anodic polarization in the electrolyte [6]. Several anode materials have been explored, including Pt, DSA, Au, Pd, PbO_2 , SnO_2 , diamond, and glassy carbon. Till now, only Pt, lead dioxide and antimony-doped tin dioxide electrode was relatively widely investigated for their considerable current efficiency for ozone generation, though several other types of anode materials were also investigated in recent years.

2. Anodic Materials for Electrolytic Ozone Generation

2.1. Electrolytic Ozone Generation on Pt. Since Schonbein discovered that ozone could be liberated when electrolyzing aqueous acid and salt solutions in 1840, platinum had traditionally been used in ozone evolution studies. The oxygen evolution overvoltage on pure bright platinum is among the highest observed and is the highest of the noble metals and their alloys [9]. As reported by Seader and Tobias [10], many researchers had involved in electro-catalytic ozone generation on Pt in earlier years and they were Soret, McLeod, Targetti, Grafenberg, Wartenberg and Archibald, Malquori, Briner and coworkers, Putnam and coworkers, and Lash and coworkers.

However, the above mentioned research always employed concentrated sulfuric acid or perchloric acid as supporting electrolyte at very low temperature and under extremely high current density. The temperature usually ranged between -14°C and -64°C and the current density was usually several

tens of amperes per square centimeter. In these configurations, due to the high current density applied, the heat generated on the electrode was very large and thus the cooling system had great influence on ozone generation efficiency. They believed that the heat transfer rate and mode of electrolytic gas evolution were the critical factors to affect the efficiency of ozone generation because of ozone decomposition and enhanced oxygen evolution on the anode at a higher temperature. From Seader and Tobias' report [10], the lower the temperature used is, the higher efficiency would be achieved. Under the temperature of 0°C , the efficiency decreased sharply to not more than 1% on Pt anode.

Even Pt is used at current density of tens of amperes per square centimeter for ozone generation, the electrode is stable and experiences only minimal weight loss. Research involving the electrolytic ozone production on Pt was limited in later time due to the high cost including electrode materials and operating cost related to this technology. From the late 1950s to the early 1970s, few reports about electrolytic ozone generation on Pt anode were published before efficient anode materials were discovered. From the late 1970s, due to the increasing interest in the use of ozone as an alternative in water and waste treatment, several groups reopened the research on electrolytic ozone generation on lead dioxide anode and other anode materials.

2.2. Electrolytic Ozone Generation on PbO_2 . Use of PbO_2 as anodic material for the evolution of ozone was a significant progress for electrochemical ozone production technology. Due to its lower cost, supporting high current density without considerable wear and higher current efficiency compared with Pt as anode under the same electrolysis condition, it replaced Pt quickly and no more investigations on Pt were published since the discovery of its application for electrolytic ozone production.

Lead dioxide has two major polymorphs, alpha and beta, which occur naturally as rare minerals scrutinyite and plattnerite, respectively. The alpha form has orthorhombic symmetry with lattice constants $a = 0.497\text{ nm}$, $b = 0.596\text{ nm}$, $c = 0.544\text{ nm}$, and $Z = 4$ (four formula units per unit cell), while the symmetry of the beta form is tetragonal with lattice constants $a = 0.491\text{ nm}$, $c = 0.3385\text{ nm}$, and $Z = 2$. The beta form is usually believed to be favorable for ozone evolution. The beta form lead dioxide was usually prepared by anodic deposition method, which employed an anodic current through the electrodeposition cell with lead(II) salt as electrolyte.

From 1970s, PbO_2 as anode materials for ozone generation was systematically studied by several groups [6, 11, 12]. Firstly, in order to improve the ozone generation efficiency, they follow the experience for Pt anode by using a lower temperature and high concentrated acid as electrolyte. The temperature could be as low as -12°C and the acid concentration could reach up to 70%. This would inevitably increase the technique's total cost, though it was already much lower than that using Pt. Thus, people had to further investigate new cell configurations and modifications of lead dioxide to reduce the cost.

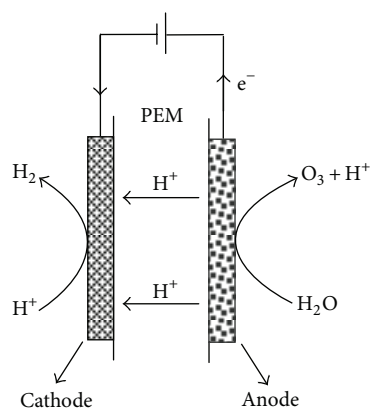


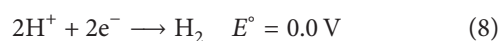
FIGURE 1: Schematic drawing of the new cell configuration without acid electrolyte.

Since the early 1980s, Foller and Tobias systematically studied ozone generation on PbO_2 and made considerable progress in this technology. They investigated the influence of different electrolytes and the addition of several different fluoroanions to the electrolyte (e.g., F^- , BF_4^- , BF_6^-). The highest ozone current efficiency could reach over 50% on beta- PbO_2 at 0°C with a current density of about $0.4\text{--}0.6\text{ A cm}^{-2}$ in 7.3 M HBF_6 [6]. The addition of fluoroanions to the electrolyte was believed to modify the adsorption of hydroxyl free radicals and oxygen molecules on the lead dioxide surface to enhance the ozone formation. The fundamental study also gave a correlation between anion surface absorption and the current efficiency for ozone generation [11]. But the fluoroanions are generally toxic to human beings and harmful to the environment.

With the increasing attention in the electrolytic ozone generation technology, more and more research groups involved in developing this technology under relatively mild experimental conditions by employing new electrolytic cell configurations and anode modifications. In order to overcome the shortage of acid electrolyte corrosion during electro-catalytic ozone generation, people developed new cell configuration as schematically shown in Figure 1.

In this configuration, the proton exchange membrane (PEM) was employed and the electrodes can be hot-pressed together with the PEM. During electrolysis, water was oxidized on anode to form ozone and release protons. The generated protons were then transferred to cathode through PEM and reduced to hydrogen on cathode. Thus, ozone production can be realized by water oxidation without acid electrolyte. Stucki et al. developed the ozone generation on PbO_2 anode in pure water by using the cell configuration illustrated in Figure 1 [5, 13]. As reported by Stucki et al., by using proton exchange membrane, the anode corrosion can be effectively prohibited. After a 2500 hour-operation, the anode did not show any degradation. The maximum efficiency of 20% was achieved at room temperature with a current density of about 1 A cm^{-2} . Onda et al. developed a multilayer electrode to improve the cell performance for ozone generation. By using a four-layer electrode, the efficiency could be improved by 40% compared to a single-layer electrode [14].

Katoh et al. further modified the cell design by using oxygen reduction replacing hydrogen evolution on cathode. This design could reduce the energy consumption efficiently [15] because the oxygen reduction potential (1.23 V, as shown in reaction (2)) is much higher than that for protons reduction (0.0 V, as shown in reaction (8)). Tatapudi and Fenton [16, 17] directly applied PbO_2 powder to the proton exchange membrane and achieved a current efficiency of 5.5% for ozone at room temperature with PbO_2 loading of 7.2 mg cm^{-2} while hydrogen peroxide was produced on cathode. This also had the potential to reduce the energy consumption because oxygen reduction to hydrogen peroxide (shown in reaction (9)) was easier than protons reduction to hydrogen, too. This cell configuration modification not only reduced the energy consumption, but also eliminated the explosion of hydrogen or harvested hydrogen peroxide:



In addition to the above-mentioned cell configuration investigations, many groups contributed to the anode preparation to improve the ozone production efficiency. Shepelin et al. lengthened the working life considerably by employing a new lead dioxide design [18]. Graves et al. deposited the PbO_2 onto a porous titanium ceramic and the anode is highly stable for electrolytic ozone generation [19]. Wen and Chang studied the PbO_2 structure changes during ozone evolution and proposed that the phosphate buffer electrolyte was more appropriate for ozone evolution [20]; people also studied the ozone generation on PbO_2 and developed new dopants such as F^- , Fe^{3+} , Co^{2+} , and Ni^{2+} to the PbO_2 to improve the efficiency and the stability for ozone generation [21–31]. Feng et al. also studied the effect of Fe doping for ozone generation and the efficiency increased from 6.1% to 14.6% by adding Fe dopant in the deposition solution [32]. Wang and Jing investigated the effect of lead dioxide particles size on ozone generation performance and found that the optimized particles size ranged 15–35 μm . They also tried to control the particle size by adding pore-forming agent [33]. Zhou et al. compared alpha- PbO_2 and beta- PbO_2 anode materials for ozone generation in water and achieved a current efficiency of 20% [34].

Besides the cell configurations and anode preparation, several groups investigated the mechanisms and kinetics for ozone generation. Wabner et al. [35–37] studied the mechanisms for ozone generation on PbO_2 by monitoring the reactive intermediates and isotope marker. Da Silva et al. [4, 8, 38] also gave fundamental studies on ozone generation on PbO_2 since the year of 2000. By carefully studying the ozone generation in different electrolytes with different extensive and intensive parameters, they proposed the mechanism for ozone generation in detail. The proposed mechanism was similar to that mentioned in reactions (4)–(7). Chernik et al. studied ozone generation on PbO_2 in different electrolytes and the kinetics by cyclic voltammograms [39–41], while Ota et al. also investigated ozone generation in different acid electrolytes [42–45].

Though PbO_2 showed considerable efficiency for ozone generation, due to its possible leakage of toxic lead ion to the aqueous phase, nonlead contained new anode materials with higher efficiency for ozone generation should be further investigated.

2.3. Electrolytic Ozone Generation on Doped Tin Dioxide Electrode. Tin dioxide is a well-known n-type semiconductor with a wide band gap ($>3.7\text{ eV}$). It crystallizes with the rutile structure, also called cassiterite structure. It is usually prepared by thermal decomposition method, in which tin salt can be oxidized to tin oxide in air at high temperature. Tin dioxide as anode, due to its high oxygen evolution potential, may inhibit the thermal dynamic favorable reaction for oxygen evolution. Using tin dioxide as anode material for electrolytic ozone generation was firstly mentioned by Foller and Tobias and it was considered as unsuitable anode material at that time [6]. Since then, there were no more reports on tin dioxide as anode for electrolytic ozone generation until the promising results for ozone generation were published in 2004 by Cheng and Chan. They invented a novel Sb-doped tin dioxide coated on Ti electrode, which showed current efficiency as high as 15% in 0.1M HClO_4 solution at room temperature [46]. Later, it was found by Chan's group that the high efficiency for ozone generation on Sb-doped tin dioxide electrode was possibly due to trace amount of nickel contamination during the electrode preparation and by adding only 0.2% nickel (at% to Sn) to the coating solution to prepare nickel and antimony-doped tin oxide electrode (NATO), the current efficiency for ozone could reach 36% at room temperature [47]. This singular observation was later confirmed by several other groups [48–50]. This novel NATO anode also showed good performance for electro-catalytic oxidation of toxic organics [51, 52]. The mechanism for the enhancement of ozone generation via trace nickel doping seemed interesting and people made efforts to clarify the role of nickel via characterizing the NATO morphology, crystal structure, electrochemical properties, and so forth [53, 54]. It was well known that Sb(V) functioned as electron donors in tin dioxide lattice while Ni(III) functioned as electron acceptors. The charge compensation effect possibly arranged the nickel sites adjacent to antimony sites in tin dioxide lattice. Thus, the adsorbed oxygen molecules on nickel sites had more chances to react with adsorbed hydroxyl free radicals on antimony sites to form ozone. The mechanism for the enhancement of ozone generation via trace nickel doping was proposed in Figure 2.

The NATO anode was very promising for electro-catalytic ozone generation with high efficiency. People also seek to improve the system performance by using PEM electrolyte to avoid acid corrosion [55], by convective flow [56], electrode modification [57] to further improve the efficiency. However, the lifetime of the anode is a problem retarding its commercialization. It suffered a logarithmic decay in current efficiency with servicing time. After 270 hours electrolysis, the current efficiency decreased from 36% to lower than 7% [58]. Thus, efforts to enhance the lifetime were needed, and recently our group found that by adapting fluoride-doped tin dioxide as interlayer, the lifetime of the electrode

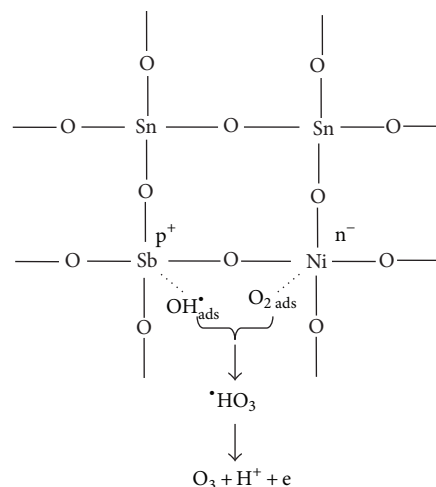


FIGURE 2: Mechanism for ozone formation on NATO.

could be lengthened to 6 times long without considerable depress of current efficiency [59]. In a recent report, the inhibition of ozone generation on NATO was observed with the presence of high concentration of dissolved ozone [60]. This observation indicated that the high performance for ozone generation on this anode was not sustainable presently, but it needed further evidence to guarantee the observation.

2.4. Electrolytic Ozone Generation on Other Anodic Materials. Actually, since the discovery of PbO_2 anode for ozone generation, seeking other anode materials with high performance for ozone generation was simultaneously carried on. Foller and Tobias also studied some other new anode materials for ozone generation except PbO_2 [6]. They briefly compared Pt black, SnO_2 , Au, Pd, and DSAs, respectively, as anodes in 5 M H_2SO_4 . The DSAs, Pd, Au, and Pt black showed current efficiency as low as 0.1%. SnO_2 showed current efficiency lower than 4% and the SnO_2 coating film was corroded away quickly. They also mentioned the possibility of carbon materials (pressed carbon black, graphite, and glassy carbon) as anode for ozone generation. These carbon electrodes showed very poor ozone yields and exhibited rapid disintegration along with CO_2 evolution. Later, Foller et al. studied ozone generation on glassy carbon in fluoroboric acid and achieved much better results [61–63]. By using 48% HBF_4 as electrolyte, under 10°C , glassy carbon anode showed current efficiency for ozone as high as 35% and it was inert at current density of 0.4 A cm^{-2} [61]. However, HBF_4 and HBF_6 are highly toxic and corrosive.

With the increasing demand of green chemical process, investigations to find new suitable anodic materials for electrochemical ozone generation appeared emergent. Several research groups were involved in this research. Katsuki et al. used boron-doped diamond electrode under severe polarization where the current density was 10 A cm^{-2} in sulfuric acid and ozone was stably generated with a current efficiency of a few percentage at ambient temperature [64, 65]. Park et al. also improved the cell design by using the diamond electrode for electrochemical ozone generation [66, 67]. Kraft et al. employed PEM to perform ozone generation from water

on diamond anode and a current efficiency of 48% was achieved [68]. By using boron-doped diamond electrode for ozone generation, Park et al. achieved a considerable ozone concentration and proposed the electrode as a superior stable anode for ozone generation. However, the overvoltage for boron-doped diamond is much higher than that for PbO_2 and DSAs in the industrial current range [65], which means that, with the same current efficiency, the energy efficiency on boron-doped diamond will be much lower. Researchers developed several new DSA type electrodes by using Ta_2O_5 - IrO_2 , Nb_2O_5 - IrO_2 as active layer to study electrolytic ozone generation [69, 70]. Kaneda et al. [71, 72] also achieved considerable current efficiency for ozone generation by modifying the Ta_2O_5 with Pt and coating this active layer on Ti. However, this type of DSAs showed efficiency lower than 10%.

The mechanisms for ozone generation on different anode materials may be different. However, the reaction steps (4)–(7) are widely accepted and it is generally considered that the presence of adsorbed hydroxyl free radicals and adsorbed oxygen on adjacent sites on the electrode is important for ozone formation. In order to improve the efficiency for ozone generation, the anode material must have more adjacent sites for hydroxyl free radicals and oxygen adsorption. Generally, in metal oxide (SnO_2 , PbO_2 , Ta_2O_5 , and Nb_2O_5), there usually exist oxygen vacancies to provide negatively charged sites for oxygen adsorption and adjacent metal ions sites are positively charged for hydroxyl free radicals adsorption. Of course the sites concentration is only one factor to influence the ozone formation. The adsorption ability for hydroxyl free radicals and oxygen may also influence the efficiency for ozone generation. The mechanisms are relatively complex and presently most of them are proposed and lack solid evidence. Further deep insight in the mechanisms is needed, especially from the point of anode materials structure and properties.

3. Conclusions

Electro-catalytic method is a promising technology for ozone production, which has the advantages of high gaseous ozone concentration, high dissolving efficiency in water, and no harmful NO_x formation. In the electro-catalytic method, the anodic material is one of the key factors which influence the system performance greatly. Till now, only boron-doped diamond electrode and nickel-antimony-doped tin dioxide electrode show current efficiency of over 30% under mild experimental conditions. However, these two types of electrodes also suffer from high cost or short lifetime. It seems more effort shall be made to find new anode materials to improve the current efficiency and stability for ozone generation.

Acknowledgments

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