Synthesis of Ozone in a Proton Exchange Membrane Electrochemical Reactor

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ABSTRACT

Deionized water was oxidized to ozone and oxygen at the anode in a proton exchange membrane electrochemical flow reactor. The optimum conditions for ozone generation were determined as a function of the applied voltage, electrode materials (lead dioxide powders obtained from two different commercial vendors), catalyst loadings, and reactant flow rates. Measured and calculated quantities included cell current, liquid- and gas-phase ozone concentrations, and current efficiency.

The synthesis of ozone in a proton exchange membrane (PEM) electrochemical flow reactor was explored. This study was undertaken as a part of an overall scheme to study the paired synthesis of ozone and hydrogen peroxide in the same PEM reactor. The research methodology for the paired synthesis has been divided into four reaction systems: 1, water electrolysis which involves oxygen evolution at the anode and hydrogen evolution at the cathode; 2, ozone + oxygen evolution at the anode and hydrogen evolution at the cathode; 3, oxygen reduction at the cathode (leading to hydrogen peroxide synthesis) and oxygen evolution at the anode: and 4, simultaneous synthesis of ozone and hydrogen peroxide.

Preliminary studies on the first two reaction systems[1] and studies on reaction system 3 have been conducted and reported.[2] This paper summarizes the investigation of the oxidation of water leading to the synthesis of ozone while generating hydrogen at the cathode (reaction system 2). Although there have been investigations on the electrochemical synthesis of ozone in aqueous acidic electrolytes[3] and on a solid polymer electrolyte,[4,5] this work is the first to discuss the synthesis of ozone using catalysts that are bonded directly to the solid polymer electrolyte.

The optimum conditions for electrochemical ozone generation were determined as a function of the applied voltage, electrode materials, catalyst loadings and reactant flow rates. Measured and calculated quantities included cell current, liquid- and gas-phase ozone concentrations, current efficiency, and ozone production rate.

Experimental

An electrochemical flow reactor was fabricated in house for the paired synthesis of the two oxidants. The reactor consisted of two blocks, each comprising one-half of the reactor. The cathode block was constructed from stainless steel, and titanium was used for the anode block. A cation exchange membrane (Nafion^R 117, Du Pont, Wilmington, Delaware) served as the electrolyte (by allowing cations to be transferred from the anode to the cathode) as well as a separator between the cathode and anode sides. Further details on the reactor and the flow circuit can be found in Ref. 1.

The anode material included powders of lead dioxide purchased from two different manufacturers (J. T. Baker Chemical Company, Phillipsburgh, New Jersey, and Aldrich Chemical Company, Milwaukee, Wisconsin) and were used as supplied by the manufacturer. X-ray diffraction analysis of both powders revealed that they were of the beta form. Studies done by previous investigators at low temperatures (0°C) and in aqueous electrolytes had revealed that the beta form yielded higher current efficiencies for ozone synthesis than the alpha form.[3]

The electrode assemblies used in this work were made by depositing a mixture of the catalyst powder and Teflon^R (TFE, Du Pont, Wilmington, DE) onto the surface of the membrane at an appreciably high temperature and pressure. The fuel cell division of Treadwell Corporation (Thomaston, Connecticut) which is now incorporated into U. S. Fuel Cells Manufacturing, Incorporated, located in West Palm Beach, Florida, fabricated these membrane electrode assemblies (M&Es). The cathode for all the experimental runs consisted of a platinum black (fuel cell grade)/TFE mixture which was deposited onto the membrane in a similar fashion. The platinum loading for each assembly was maintained at 4 mg/cm^2 with a 30 weight percent (w/o) TFE binder. The projected electrode area for both the anode and the cathode was 13 cm^2. This M&E assembly was sandwiched between a platinum mesh (52 mesh, Fisher Scientific, Pittsburgh, Pennsylvania) on the cathode side and a sintered titanium disk (20 μm pore diameter, Mott Metalurgicals, Farmington, Connecticut) on the anode side. The mesh and disk were used as current collectors.

Experimental procedures.—Deionized (DI) water at room temperature and pressure was fed to the lower ports of the anodic and cathodic sections of the reactor at a flow rate of 28 liters/h. A fixed potential was applied to the reactor using a dc power supply (Nobatron, Norwalk, Connecticut). Studies were performed at a constant potential (as opposed to constant current) since this mode of operation allowed for an easier comparison of the results obtained from using different catalyst powders as well as different loadings of the same catalyst powder. A reference electrode could not be used in this system owing to the nature of the reactor design. Since the hydrogen evolution reaction occurring at the cathode is fairly constant and reproducible, the counterelectrode served as a "reference" electrode in this study.

The stream leaving the anode section was passed through a gas/liquid separator, and both the gaseous and the liquid streams were analyzed for O_3 after the reactor reached a steady-state current of ±0.1 A for at least 20 min. No attempts were made to detect the pH of the inlet or outlet streams. The sintered titanium disk, used as a current collector on the anode side, was dipped in boiling concentrated sulfuric acid for 2 to 5 s and rinsed several times in DI water prior to being used in an experiment. This was done to dissolve any titanium oxides present on the surface which could have led to an increased ohmic overpotential across the reactor.

Concentration measurements of ozone in the gas phase were performed using the indigo method.[6] The principle behind this method is that ozone rapidly and stoichiometrically (1:1) decolorizes indigo trisulfonate in acidic solution. The decrease in absorbance at 600 nm is linear with ozone residual ($\Delta\epsilon$ = 20,000 liter mol^{-1} cm^{-1}). The procedure[7] involves withdrawing a known volume of an oxygen-ozone sample into a gas-tight syringe and injecting it immediately into a bottle containing a known volume of potassium indigo trisulfonate. The mixture is then shaken for 30 s to 1 min and its absorbance is measured at 600 nm along with the absorbance of a blank solution. The difference in the absorbance of the two samples yields the ozone concentra-

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tion. The absorbance measurements were made using a Perkin Elmer Lambda 3B UV/Vis spectrophotometer (Perkin Elmer Corporation, Oak Brook, Illinois).

Concentration measurements of ozone in the aqueous phase were performed using a dissolved-ozone monitor which uses a direct sensing polarographic probe (Enterra Technologies Incorporated, Exton, Pennsylvania, Model No. 5160-1-1). No chemicals or sample preconditioning is required, response time is extremely fast, and there are very few potential interferences in normal water. Only strong oxidizers such as free bromine or free chlorine can interfere with ozone measurements. Reproducibility of data (*i.e.*, current and ozone concentrations) between two sets of M&Es were within 20%.

Results and Discussion

Initially, three different loadings, 1.8, 3.6, and 7.2 mg/cm^2, of PbO_2 powders obtained from the two commercial vendors were studied for the synthesis of ozone. These loadings were chosen in order to study the performance of M&Es with loadings similar to a 4 mg/cm^2 fuel cell anode. The TFE percentage for all the anode catalyst loadings was 30%.

The M&E assembly, consisting of PbO_2/TFE mixture (anode), the Nafion 117 membrane, and the Pt/TFE mixture (cathode) was sandwiched between a platinum mesh on the cathode side and a sintered titanium disk on the anode side. A sintered disk was used to enhance mass transport and saturate the aqueous stream with ozone. Polarization experiments were performed up to a maximum applied potential of 5.0 V since the electrochemical synthesis of ozone would become uneconomical beyond this potential due to an increase in the specific power consumption for ozone evolution.

Figure 1 is a bar chart which compares the maximum currents obtained using different catalyst loadings of the two lead dioxide powders and the potentials at which the maximums were obtained. The low current (≤4 A) obtained at high potentials (2 to 5 V) for the three lower loadings (1.8, 3.6, and 7.2 mg/cm^2) of the Aldrich powders and for the two lower loadings (1.8 and 3.6 mg/cm^2) of the J. T. Baker powders suggests that there was insufficient catalyst material (leading to a low surface area) available for ozone evolution to occur at the membrane electrode interface.

The current densities of the J. T. Baker M&E with the 7.2 mg/cm^2 loading, however, were five times higher than the corresponding Aldrich M&E for the potentials between 2 and 5 V. Furthermore, this M&E also showed a seven-fold increase over the highest current density obtained using an M&E with half the loading (3.6 mg/cm^2) of the same powder. The current densities for this 7.2 mg/cm^2 M&E increased linearly from 0.1 A/cm^2 at 2.5 V to 1.5 A/cm^2 at 4.0 V (as shown in Fig. 2). This linear behavior of the polarization data implies that the reaction system was under kinetic control coupled with ohmic (IR) losses occurring within the reactor (due to the presence of the titanium disk, the membrane, and catalyst powders, etc.).

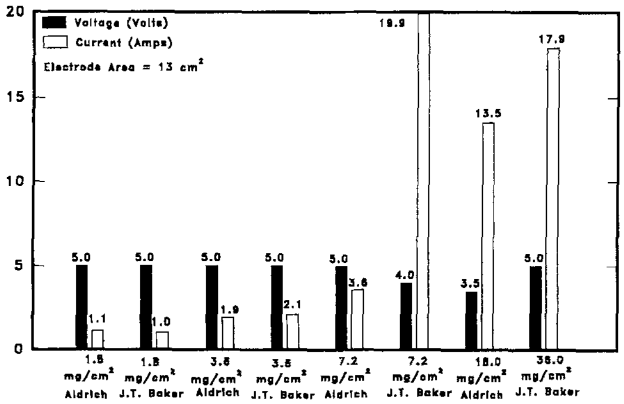

Fig. 1. Comparison of the maximum currents obtained using different catalyst loadings of the two lead dioxide powders and the potentials at which the maxima were obtained.

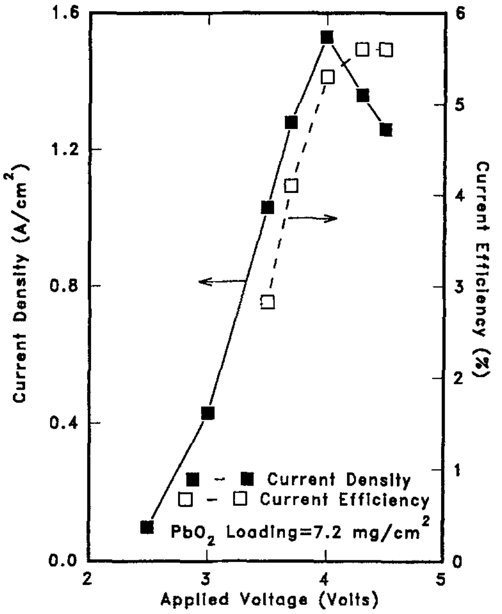

Fig. 2. Steady-state polarization plot and current efficiency for ozone evolution as a function of the applied voltage of a J. T. Baker PbO_2/Pt black M&E assembly. Experimental conditions: room temperature and atmospheric pressure; H_2O flow rate = 28 liters/h.

These relatively high current densities (>1 A/cm^2) suggest that a loading of 7.2 mg/cm^2 of the J. T. Baker powder provides an adequate surface area for the anodic decomposition of water. Moreover, the large difference in the current densities obtained using the same lead dioxide loading of the two powders suggests that the available surface area of the Aldrich particles is probably lower than the J. T. Baker particles.

To understand better the difference in performance of the two lead dioxide powders, they were inspected using scanning electron microscopy (SEM). At 7000 times magnification, the Aldrich powder revealed a more faceted structure and appeared to have more jagged edges than the J. T. Baker powder. Furthermore, the Aldrich powders appeared to have a larger particle size than the J. T. Baker particles. The larger particle sizes decrease the catalyst/membrane interfacial area, resulting in lower observed current densities.

When the applied voltage increased beyond 4.0 V, the current densities for the 7.2 mg/cm^2 J. T. Baker M&E started to drop (shown in Fig. 2). This drop in the current density at higher applied potentials (≥4.0 V) was observed for all the J. T. Baker M&Es that were examined. Moreover, when a similar experiment was repeated using the same M&E 8 to 10 h after the first experiment, a 35% decrease in the current density was observed for the same range of applied voltages. This decrease in current density during the repetition of the polarization experiments was also observed with all of the Aldrich and J. T. Baker M&Es. It appears that a definite change occurs in the morphology of both these lead dioxide powders when subjected to polarization at high applied potentials (≥4.0 V).

X-ray diffraction analysis was also performed on a J. T. Baker powder sample after it was used in a polarization experiment (applied potentials of 2 to 5 V with current densities ≤1.3 A/cm^2) to synthesize ozone. The analysis of the powder after an experiment revealed that there was no change in the morphology of the powder and that it was still of the beta form.

Foller and Tobias[8] had proposed a mechanism for the surface modification of lead dioxide in acid electrolytes (low pH) and at high anodic potentials. Chemical dissolution of PbO_2 to Pb^{4+} occurs near the anode surface due to the potential and high proton concentration present during the anodic decomposition of water. As the Pb^{4+} ion diffuses away from the low pH and high potential region, it becomes unstable and PbO_2 is once again recrystallized.

J. T. Baker lead dioxide catalyst mixtures (*i.e.*, the powders plus the Teflon[R] particles) were inspected before and after an experiment using SEM. At 2000 times, the mixture before an experiment appears to be clustered forming closely packed units. After the polarization experiment, the mixture appears dispersed with a more faceted structure.

To investigate the possibility of the dissolution of the lead dioxide powder, water from the tank that was used for feedwater storage was analyzed for lead. The lead level found, 5.2 ppb (considerably lower than 2900 ppb; the value if all the lead dioxide was solubilized in the analyte stream), did not differ significantly from the initial value of 1.3 ppb.

Since no lead was detected in the feedwater, and since no transformation in the morphology of the lead dioxide took place, it is quite possible that the decrease in current density and ozone concentration occurs due to the anodic decomposition of the particles which recrystallize once again, in the beta form, but with a different structure.

Figure 3 shows that the aqueous ozone concentrations from the 7.2 mg/cm^2 J. T. Baker M&E ranged from 0.6 ppm at 3.0 V to 3.1 ppm at 4.0 V while the gaseous ozone concentrations ranged from 22 mg/liter at 3.5 V to 50 mg/liter at 4.0 V. As with the current densities, both, the aqueous and gaseous ozone concentrations decreased beyond an applied voltage of 4.0 V. The current densities obtained from the reactor appear to affect directly the synthesis of ozone.

Figure 2 shows a plot of the current efficiency for ozone evolution (percentage of current going toward the synthesis of ozone) *vs.* the applied potential for the 7.2 mg/cm^2 J. T. Baker M&E. The current efficiency, η, for ozone evolution, according to Faraday's law of electrolysis can be defined as

$$\eta = (q_w C^w + q_g C^g)\frac{nF}{Mi} 100\% \qquad [1]$$

where q_w and q_g are the flow rates of the feedwater and gaseous products in l/s; C^w and C^g are the concentrations of ozone in the aqueous and gas phases, respectively, (mg/liter); n is the number of electrons involved in the reaction (=6) F is Faraday's constant (96,500 coulombs/eq); M is the molecular weight of ozone, and i is the current (A). The current efficiencies for ozone evolution for this M&E varied from 2.5% at 3.0 V to 5.5% at 4.0 V, beyond which the current efficiency leveled off. It appears that the percentage of current that is involved in ozone evolution remains the same after 4.0 V.

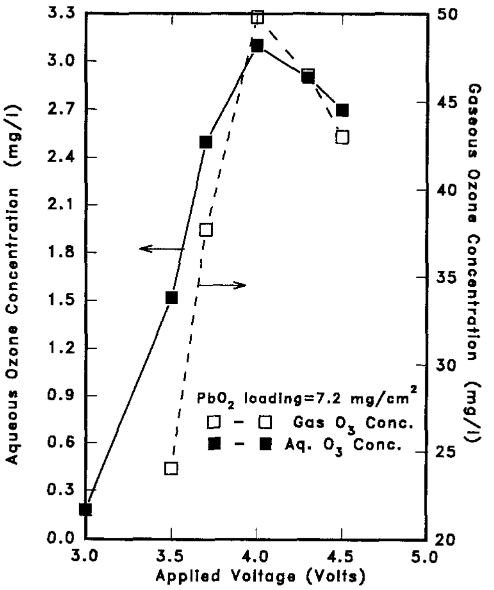

Fig. 3. Aqueous and gas-phase ozone concentrations as a function for the applied voltage. Experimental conditions: room temperature and atmospheric pressure; H_2O flow rate = 28 liters/h.

Stucki and coworkers,[4] using a Nafion 120 membrane had reported a 14% current efficiency for evolving ozone in electrolyte-free water at ambient temperature and atmospheric pressure. Their anode consisted of a lead dioxide layer (mixture of the alpha and the beta forms) that was deposited by a proprietary method directly onto the surface of a sintered titanium material (as opposed to this study in which the lead dioxide powder was deposited onto the membrane surface).

The maximum current efficiency obtained for ozone evolution with lead dioxide loadings up to 7.2 mg/cm^2 (≈5.5%) is 2.5 times lower than the maximum obtained by Stucki *et al.*[4] Based on the lower current efficiencies of this study, it was decided to try catalyst loadings of both powders that were greater than 7.2 mg/cm^2 (*i.e.*, 18 mg/cm^2). Furthermore, M&Es which had much larger loadings (36 and 54 mg/cm^2) were also studied to determine the influence of these high loadings on the polarization behavior of the lead dioxide powders as well as their impact on ozone evolution.

For the J. T. Baker M&E, maximum current densities obtained from these higher loadings were less than the maximum current density obtained with a 7.2 mg/cm^2 loading of J. T. Baker lead dioxide (shown in Fig. 1). This decrease in maximum current density suggests that the increased loading of lead dioxide is no longer providing additional surface area for the anodic reaction. On the contrary, the increased loading may be blocking the reactant feedwater from reaching the membrane electrode interface, causing a decrease in the observed current density (and also the ozone concentration). There is also a possibility that the additional lead dioxide powder could be adding to the ohmic resistance of the system.

Among the Aldrich powders, the M&E with a loading of 18 mg/cm^2 showed the highest current density (≈1 A/cm^2) at the lowest applied voltage (shown in Fig. 1). A loading of 18 mg/cm^2 of the Aldrich powder seems to provide an adequate surface area for the anodic decomposition of water to occur at reasonably high current densities (≈1 A/cm^2). Current densities of this magnitude, however, were obtained with loadings of only 7.2 mg/cm^2 using the J. T. Baker powder. This difference in current densities for different loadings of the two powders once again suggests that J. T. Baker lead dioxide particles have a higher surface area than the Aldrich particles.

The concentration of aqueous ozone as a function of the feedwater flow rate for a 36 mg/cm^2 J. T. Baker M&E was studied when the reactor was operated at 1.1 A/cm^2 and an applied potential of 4.0 V. As shown in Fig. 4, when the flow rate was varied from 20 to 58 liter/h, the aqueous ozone concentration varied correspondingly from 2.4 ppm to 1.4. The decrease in ozone concentration with increase in feedwater flow rate was also observed by Stucki *et al.*[4] Higher concentrations occur due to the longer residence time at low flow rates, which enhances the degree of saturation of the aqueous feedwater.

At constant (atmospheric) pressure, the ratio of the gas to liquid phase ozone concentrations for a 36 mg/cm^2 J. T. Baker M&E, shown in Fig. 4, increased with an increase in flow rate, which means that equilibrium between the phases is not achieved within the reactor. This ozone distribution ratio (ODR) can be defined as

$$ODR = \frac{C^g}{C^w} \qquad [2]$$

where C^g and C^w are the gas- and liquid-phase concentrations (measured in mg/liter), respectively. The *ODR* varied from 16 to 20 liters/h to 22 at 58 liters/h. These ratios are larger than those attained by Stucki *et al.*[4] (10 to 18 for the same change in flow rate). Apparently, the reactor designed by Stucki *et al.*[4] is more efficient in the mass transfer of ozone into the aqueous stream than the one used in this work. The overall production rate of ozone (not shown in

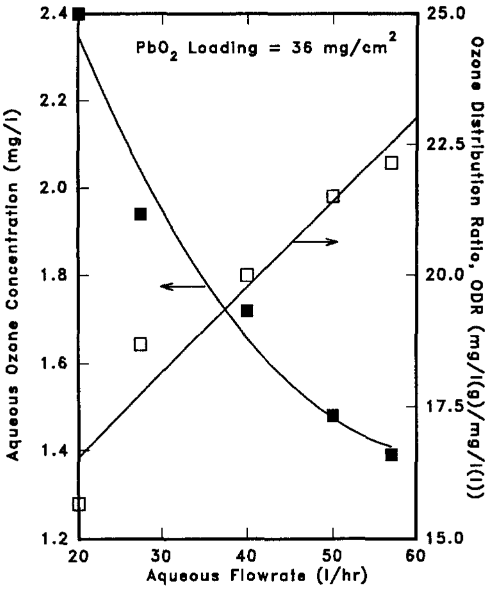

Fig. 4. Aqueous ozone concentration and ozone distribution ratio as a function of the aqueous flow rate. I = 1.1 A/cm^2, V = 4.0 V.

Fig. 4) remained unchanged (125 mg/h) with a change in the feedwater flow suggesting that the current efficiency is independent of the aqueous flow rate.

Conclusions

The type of anode assembly used in this study was made by depositing lead dioxide powders mixed with Teflon^R onto the surface of the membrane (referred to as a M&E assembly). It was anticipated that M&Es would provide an intimate contact of the electrocatalyst with the membrane leasing to an overall increase in the surface area of the electrode available for reaction as compared to a lead dioxide anode deposited on a sintered titanium disk (used by Stucki *et al.*)[4] Although the M&Es obtained high current densities (1.6 to 2.0 A/cm^2), the high currents occurred at high applied potentials resulting in lower current efficiencies (≈5.5%) when compared to those obtained by Stucki *et al.* (≈14%).[4]

The higher current efficiencies obtained by Stucki *et al.*[4] suggest that the ozone evolution reaction could also be occurring within the pores of the sintered titanium disk where additional lead dioxide sites were available for reaction. Another possibility for lower ozone current efficiencies in this study could be due to the inability of the gaseous products formed to move away from the membrane electrode interface (due to inefficient reactor design) resulting in a mass-transfer limitation of the reactant feedwater to the electrode.

Stucki *et al.*[4] had shown that the current efficiency for ozone evolution shows a maximum at a feedwater temperature of 25 to 30°C. While, the feedwater temperatures (measured at the inlet and the outlet of the anode stream) in this study did not increase beyond these numbers, the temperature at the membrane electrode interface (not measured in this study) could have been significantly higher since the applied voltages (≈5.0 V) were significantly higher than those used by the same workers (≈3.5 to 3.8 V),[4] thus leading to ozone degradation and lower current efficiencies.

J. T. Baker M&Es consistently yielded higher current densities than the Aldrich M&Es. They also generated higher amounts of ozone and as a result had higher current efficiencies. For example, the maximum current efficiency obtained by a J. T. Baker M&E (5.5% using a 7.2 mg/cm^2 loading) is considerably higher than the maximum current efficiency obtained by an Aldrich M&E (1.5% using an 18 mg/cm^2 loading). An explanation based on the different shape and size of the two powders (as seen through a SEM) accounts for the differences in performance of the two powders.

A drop in the current densities and ozone concentrations was observed for almost all lead dioxide loadings at higher potentials (≥4.0 V). When identical experiments were performed with a previously polarized M&E, reproducible results were unable to be obtained. It was concluded that the lead dioxide disintegrates at appreciably high potentials. An explanation for the disintegration of the lead dioxide powders was offered based on chemical dissolution of PbO_2 to Pb^{4+} at regions of high potentials and pH and subsequent recrystallization at regions of lower potential.[8] SEM photographs of lead dioxide catalyst mixtures taken before and after polarization experiments revealed a change in the shape, size, and distribution of the catalyst particles after an experiment.

This study synthesized ozone by oxidizing water in a proton exchange membrane reactor using catalysts directly bonded to the solid polymer electrolyte. Optimum conditions for ozone generation in this reactor were identified. However, low ozone current efficiencies (≈5.5%) resulting from a combination of ohmic losses and inefficient reactor design makes this process an uneconomical choice at this time.

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