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Performance of a pressurized electrochemical ozone generator

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The performance of a novel electrolytic ozone generator using a solid polymer electrolyte and a PbO_2 anode is described. The operating parameters studied were: current density, water flow, temperature and pressure. Optimum current yields in the order of 20% are reached with a $30\,cm^2$ cell at a current of 40 A, a temperature of 30° C and a volume feed rate of water $> 30\,l\,h^{-1}$. The system pressure does not influence the current efficiency or the cell voltage. The specific power consumption of a state-of-the-art cell is in the order of $65\,W\,h\,g^{-1}$. The technique has been applied commercially in the field of disinfection of purified water for more than 3 years.

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1. Introduction

Ozone is applied as an effective oxidant in water treatment for disinfection, decolouration and deodorization of drinking and industrial process water. An increasingly important aspect of ozone application in water treatment is its use as a disinfectant in purified water loops for the pharmaceutical and electronic industries [1–3]. In these applications ozone is added to the pure water stream in very low concentrations in the order of 0.01–$0.06\,g\,m^{-3}$, and guarantees full disinfection of the product water and the loop hardware. A new type of electrochemical ozone generator using a solid polymer electrolyte, instead of a liquid electrolyte, and lead dioxide anodes [4] has proved particularly useful in these applications: BBC-Membrel cells have accumulated more than 3 years of industrial application since their first introduction into pure water disinfection. First performance data of a cell of this type in a laboratory pure-water loop at atmospheric pressure were published previously [4]. The following article describes measurements which were obtained in a pressurized system which provided detailed information about the performance of the cell as a function of the operating parameters temperature, current density, pressure and water flow.

2. Experimental details

2.1. *The cell*

A cell design similar to that previously described [4] was used for the present study. To allow pressure operation the cell was incorporated into an autoclave housing. Fig. 1 shows a schematic cross-section of the pressurized cell. The central element was formed by the membrane electrode assembly described elsewhere [4]. The active area of the cell was $30\,cm^2$. The electrodes were held together by a solid cell housing made of titanium and stainless steel. Lead dioxide was used as the ozone-evolving anode material throughout all the experiments. The cell components (electrodes and membrane) were exchanged for different experimental runs.

2.2. *Control and instrumentation scheme*

The apparatus (see Fig. 2) was fed with demineralized water from a high pressure membrane metering pump. The water flowed through the anode compartment, taking up the anodically formed gases (ozone and oxygen). In a subsequent static mixer the gas was dissolved in the water and fed to the UV absorption cell for analysis of the ozone concentration. The system

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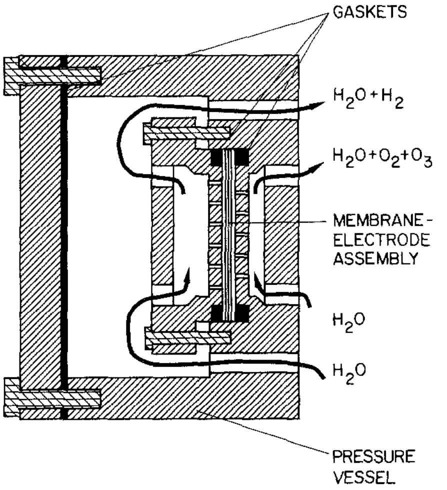

Fig. 1. Cross-section of the pressurized laboratory cell. Electrode area, 30 cm^2.

pressure was set by a control valve (PC). After a single pass through the system the water was rejected.

The cathode loop consisted of a gas–water separator and a tubing system, which ensured a small circulation of the water by gas lift pumping. The pressure in the cathode compartment was adjusted to the anode system pressure by measuring the differential pressure and regulating the H_2 release. A small water flux from the anode to the cathode was driven through the ion exchange membrane electrolyte by the electric current. This water was, in the present set-up, released with the hydrogen. The autoclave cell was immersed in a thermostated water bath and electric current was fed to the cell from a 100 A/10 V d.c. power supply.

2.3. *Chemical analysis*

The ozone concentration, C_{O_3}, which is needed for the calculation of the current efficiency of the cell, was measured by UV absorption in water (point Q_O in Fig. 2). The UV spectrometer (Shimadzu UV-120-02) was adjusted to a wavelength of 258 nm. To convert the extinction data into concentrations the extinction coefficient for ozone from [5] i.e. $\varepsilon = 2900\,\text{cm}^{-1}\text{mol}^{-1}$ was used. The UV absorption cell was a specially designed pressure compatible flow-through cell with an optical path length of 2 mm.

The residence time of the water between the electrochemical cell and the UV absorption measurment depended on the volume of the tubing and the mixer and on the water flow rate, and was typically in the order of 60 s. In order to be able to control and minimize the rate of the unavoidable decay reaction of the ozone during this residence time, the water was given a constant pH by bubbling CO_2 through the feedstream before the metering pump at ambient pressure. The rate constant was drastically

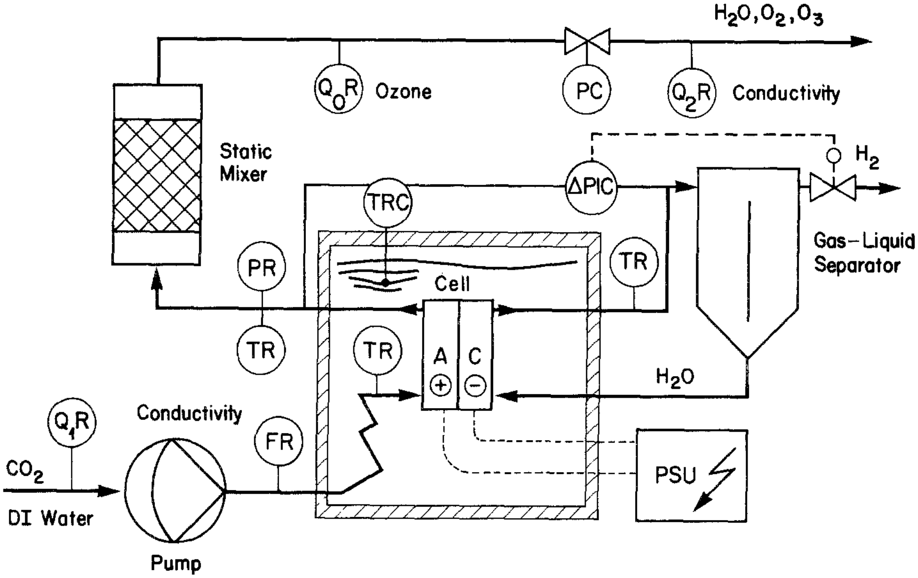

Fig. 2. P-l-scheme of the experimental set-up. Legend for symbols in circles: F, flow; P, pressure; T, temperature; Q, quality (see text); I, indicated parameter; R, registrated parameter; C, controlled parameter.

diminished by reducing the solution pH [6]. Furthermore, the HCO_3^- ion is known to act as a chain interrupter in radical initiated decomposition reactions [7]. The levels of CO_2 in the feed-water were controlled by the conductivity sensors Q_1 and Q_2 (see Fig. 2); the conductivity was maintained at $10\,\mu S\,cm^{-1}$.

2.4. *Calculation of current efficiency and energy demand*

The current efficiency for the ozone formation reaction, η, was calculated from the experimental data. Under steady state conditions,

$$\eta = \frac{\dot{V}_w C_{O_3} z F}{MI} \times 100\% \qquad (1)$$

where $\dot{V}_w$ is the volume feed rate of water, C_{O_3} is the (mass) concentration of ozone, z is the number of electrons transferred ($z = 6$); F is the Faraday constant, I is the cell current and M is the molecular weight.

Equation 1 holds for the condition that the operating parameters are such that the anodically formed gases are dissolved completely in the water (no gas phase present). Since O_2 and O_3 are the only significant reaction products at the anode, η is identical with the wt % of ozone in the total oxygen produced.

The specific power consumption of the cell is defined as

$$P = \frac{UI}{\dot{m}_O} = \frac{UI}{C_{O_3}\dot{V}_w} = \frac{UzF}{M\eta_i} \qquad (2)$$

where $\dot{m}_O$ is the total produced oxygen (mass flow) and U is the cell voltage.

3. Results

Prior to studying the influence of individual operating parameters on the cell efficiency a preliminary set of experiments was performed with simultaneous permutation of all relevant operating parameters (pressure, temperature, water flux and current density) at two levels. This method is known as factorial design [8]. The analysis of the experiments showed that the parameters do not show interference with respect to efficiency. This then enabled us to measure the effect of the individual operating parameters over their whole range, holding the other parameters constant at their respective optimum.

3.1. *Pressure*

In a previous communication concerning the BBC-Membrel ozone generator, a mechanism for the anodic ozone formation was suggested which involved dissolved O_2 reacting with free or loosely adsorbed atomic oxygen [4]. It was expected, therefore, that the pressure would affect, in one way or another, the current yield of the cell.

The experiments performed in a pressure range of $1 \leqq p \leqq 100$ bar did not show any significant influence of the pressure on either the cell voltage or the current efficiency. Small deviations from constancy of cell voltage and current efficiency can be explained by minor temperature changes within the cell due to varying gas void fraction with varying pressure.

3.2. *Water flow rate*

Fig. 3 shows the dependence of the current efficiency on the water flow rate through the $30\,cm^2$ cell. For high flow rates the yield is independent of flow. Below a critical flow rate of $\sim 30\,l\,h^{-1}$ a rapid decrease of efficiency is observed, which is probably due to insufficient removal of product gases and insufficient water supply to the membrane surface.

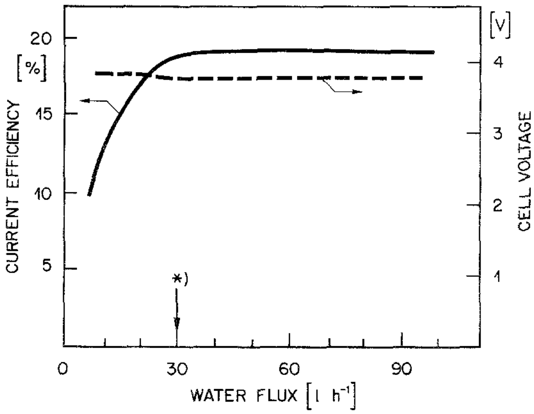

Fig. 3. Current efficiency and cell voltage of the laboratory ozone cell as a function of water flux, $\dot{V}_w$. Operating conditions: $T = 30°C$, $p = 25$ bar, $i = 1.3\,A\,cm^{-2}$.

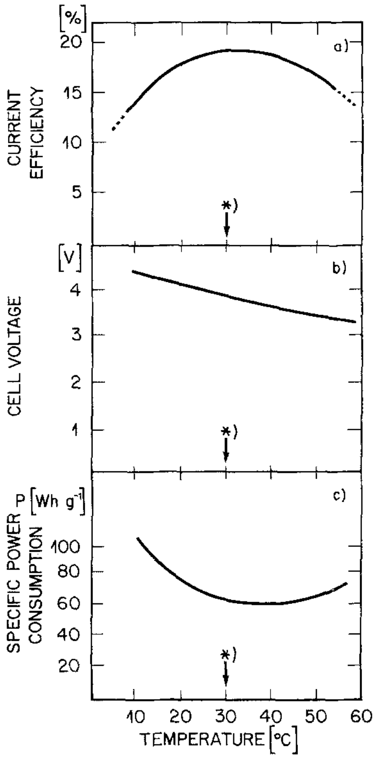

Fig. 4. Current efficiency (a), cell voltage (b) and specific power consumption (c) of the laboratory ozone cell as a function of temperature, T. Operating conditions: $\dot{V}_w = 30 \, \mathrm{l\,h^{-1}}$, $i = 1.3 \, \mathrm{A\,cm^{-2}}$, $p = 25 \, \mathrm{bar}$.

3.3. *Temperature*

A maximum current yield at ~ 30° C under standard operating conditions is typical for the ozone evolution reaction in sulphate and sulphonate electrolytes [9]. In the present investigation the maximum is rather flat (Fig. 4a). Since the cell voltage is a decreasing function of temperature, the minimum for the energy consumption is found at higher temperatures (in the order of 35–40° C; see Fig. 4c). For practical purposes the temperature is usually maintained at room temperature.

3.4. *Current density*

Current density was varied up to more than $3 \, \mathrm{A\,cm^{-2}}$ (Fig. 5) and, again, earlier measurements were confirmed qualitatively. The current efficiency reaches a plateau above $\sim 1.3 \, \mathrm{A\,cm^{-2}}$. The optimum for the overall efficiency (i.e. the minimum in specific energy consumption) lies at about $1 \, \mathrm{A\,cm^{-2}}$ (Fig. 5c). The applicable current density is not so much limited by mass transfer as by heat removal. Depending on cell design parameters, there is a danger of local overheating at very high current densities, i.e. above $3 \, \mathrm{A\,cm^{-2}}$.

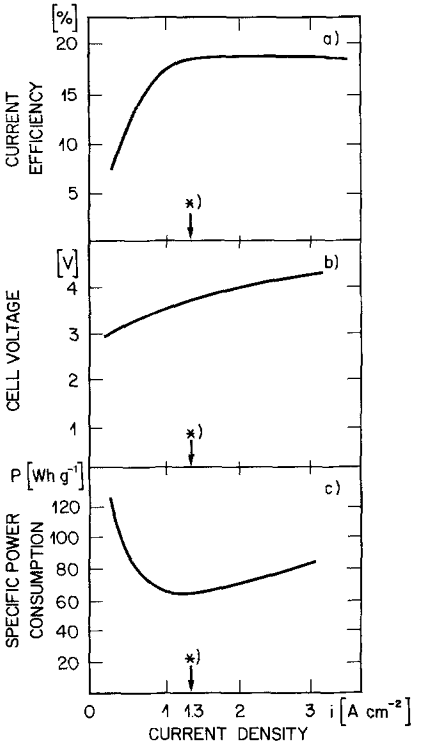

Fig. 5. Current efficiency (a), cell voltage (b) and specific power consumption (c) of the laboratory ozone cell as a function of current density, i. Operating conditions: $\dot{V}_w = 30 \, \mathrm{l\,h^{-1}}$, $T = 30° \mathrm{C}$, $p = 25 \, \mathrm{bar}$.

3.5. *Time effects*

Cells have been observed to show a considerable scatter with respect to the time they need to reach a steady state ozone yield. A current efficiency of ~ 10% is reached immediately after installation of the cell with a new electrode–membrane assembly (Fig. 6). The subsequent slow increase of the current efficiency with time (Fig. 6) is believed to be due to slow transformation processes at the membrane–anode interface leading eventually to a steady state. The duration of the transient behaviour can be influenced by appropriate modification of the interfacial layer prior to assembly of the cell.

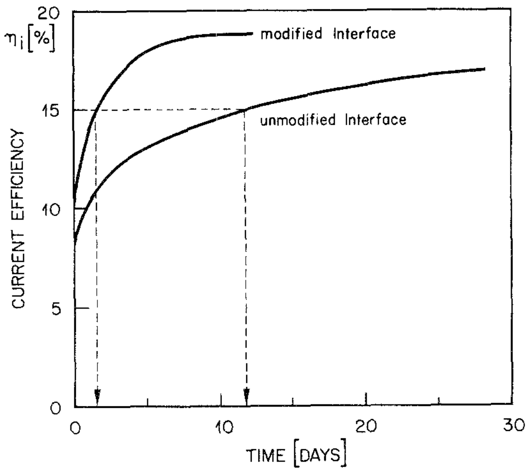

Fig. 6. Current efficiency of laboratory ozone cells as a function of operating time after start up of a new electrode–membrane assembly with modified and unmodified interface.

The upper curve in Fig. 6 shows the transient of a cell with a properly modified membrane surface. The value of $\eta_i = 15\%$ is reached after 2 instead of 12 days.

For technical applications, of course, the response time of the cell is important. It was found that a cell that has reached steady state performance shows a relatively slow transition to a new steady state if temperature changes are applied (in the order of 10 h), whereas changes in current density lead to an immediate response. The fast response of the cell productivity to current changes enables the application of the cell in controlled systems.

3.6. *Stability*

The excellent stability of the Membrel Ozone Generator has been confirmed by a 30 cm^2 cell that has been on continuous duty at $\sim 1\ \text{A cm}^{-2}$ for more than 3 years in a purified water plant in the pharmaceutical industry, disinfecting 10–20 m^3 h^{-1} of demineralized water [1]. No corrosion products of the cell (i.e. lead) have been detected in the treated water.

3.7. *Reproducibility*

The current efficiency data have a scatter, due to measuring errors, which is smaller than 10%. The reproducibility of data between two sets of electrodes and membranes is within $\sim 20\%$. The curves of Figs 3–5 are averages from a series of experiments with different sets of cell components.

4. Discussion

From the data presented above, the performance of a BBC-Membrel cell as a function of the operating parameters can be evaluated and adapted to a given application. The optimum operating conditions regarding energy efficiency are $i = 1.0\ \text{A cm}^{-2}$, $T = 30°\text{C}$ and $\dot{V}_w > 25\ \text{l h}^{-1}$ for a cell with electrode area of 30 cm^2. The specific power consumption at these conditions for a state-of-the-art cell is in the order of 65 W h g^{-1}. This value exceeds the power consumption of modern corona discharge ozonizers 14 W h g^{-1} (air), 7 W h g^{-1} (oxygen) [10]. The applications of the technique are, therefore, limited to processes with small ozone demand. A typical, commercialized application is in the field of purified water disinfection, where the advantage of *in situ* production (simple and efficient transfer of ozone into the water) more than compensates the efficiency handicap [1].

The results have shown that pressure variation over two orders of magnitude does not influence the efficiency of the process. This result needs some more discussion, since it is rather unexpected.

The reversible potential of a water electrolyser depends on pressure and it is easily deduced from the Nernst equation that an increase of pressure by an order of magnitude leads to an increase of the reversible cell potential by ~ 45 mV. This also holds approximately for an ozone-evolving cell. Evidently the rise in reversible potential does not lead to a rise in the overall cell voltage. This has been observed for the cell voltage of water electrolysis cells [11, 12] and for the hydrogen evolution reaction on various metals [13]. According to Vetter [13] the pressure effect on the reversible potential is exactly compensated by the pressure dependence of the overvoltage, which stems – in the case of the hydrogen electrode – from the pressure dependence of the equilibrium coverage of adsorbed hydrogen. A similar compensation must be assumed for the oxygen–ozone evolution reaction.

The fact that the current efficiency of the ozone evolution reaction is unaffected by pressure can be explained qualitatively by a reaction scheme which is analogous to the generally accepted reaction scheme for ozone formation in the gas phase:

$$O^* + O_2 \xrightarrow{k_1} O_3 \tag{3}$$

$$O^* + O_3 \xrightarrow{k_2} 2O_2 \tag{4}$$

O^* represents an electrogenerated oxygen radical which is formed at the anode surface at $U > 2.5$ V from water [4] with a rate defined by the applied current. Reactions 3 and 4 are fast chemical reactions, far from equilibrium, the rates of which are given by the rate constants, k_1 and k_2, and the concentration of O^* on the surface and of the product gases O_2 and O_3 in the electrolyte. An increase in pressure causes a shift in the steady state concentrations of O^* (decrease) and O_3 and O_2 (increase) without affecting the ratio of the two reaction rates.

The same reasoning can be used to explain the constancy of the current efficiency as a function of current density which is typical for ozone evolution on anodes above a threshold cell voltage. Here, again, as long as the electrochemical formation of O^* is the rate limiting step, a dependence of η on i would not be expected using the above reaction scheme.

5. Conclusions

The current efficiency of BBC-Membrel cells for electrolytic ozone generation reaches values in the order of 20% at cell voltages of ~3.5 V. The set of parameters for optimum efficiency is given by: current density $i = 1\,\mathrm{A\,cm^{-1}}$, water flow $v_w > 30\,\mathrm{l\,h^{-1}}$ (depending on cell geometry) and temperature $T \simeq 30°\mathrm{C}$. Pressure has been found not to be of any influence on the efficiency of ozone production in the cell. After assembly a new cell shows a time dependence with a positive gradient with respect to current efficiency, which is believed to be due to self-optimizing slow processes at the interface between the anode and the membrane electrolyte. The membrane can be pretreated in order to accelerate the transient phase. After this transient phase the cell performance becomes stable and constant operation at $1\,\mathrm{A\,cm^{-2}}$ for more than 3 years has been demonstrated in an industrial application.

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