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Link to DOI: [http://dx.doi.org/10.1016/j.electacta.2014.05.013](http://dx.doi.org/10.1016/j.electacta.2014.05.013)

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Date deposited: 07th October 2014

Version of file: Author

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The Use of Ni/Sb – SnO$_2$-based Membrane Electrode Assembly for Electrochemical Generation of Ozone and the Decolourisation of Reactive Blue 50 Dye Solutions

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Abstract

Electrochemical ozone generation with ozone current efficiencies up to 33% and power consumption as low as 25 kWh kg$^{-1}$ O$_3$ at room temperature using Ni/Sb-SnO$_2$ anodes in a membrane electrode assembly (MEA) based cell with platinised titanium cathodes separated by Nafton membrane is reported. The complete decolourisation of 200 cm$^3$ of 1000 mg dm$^{-3}$ Reactive Blue 50 (RB50) dye within 8 minutes at 2.7 V with 100% current efficiency for the first 5 minutes and specific power consumption as low as ca. 8 kWh kg$^{-1}$ COD using the MEA – based cell is also described. The byproducts of the dye oxidation were investigated and the formation of various organic acids confirmed.

Keywords:

Ozone, MEA, Decolourisation, Electrolysis, Ozonation.

1 Introduction

To date, electrochemical technologies for wastewater treatment have developed such that
they are more efficient and more compact than other technologies, but cost is still an issue [1].

Highly efficient chemical oxidants such as ozone, hydroxyl radicals or hydrogen peroxide can be generated electrochemically [2]. Electrochemical oxidation is a popular electrochemical procedure for removing organic pollutants, such as dyes [3], from industrial wastewaters [4]. The electrochemical oxidation of pollutants can be either direct or indirect [3-7]. During indirect oxidation at the electrode/electrolyte interface, organic molecules are attacked by electrogenerated oxidants, while in direct electro-oxidation, organics are attacked at the anode surface by chemisorbed, active oxygen species [8, 9].

The electrochemical generation of ozone has many advantages over conventional ozone generators, such as Cold Corona Discharge or Dielectric Barrier Discharge units [10], including: low voltage operation, the possibility of generating high concentrations of ozone in the gas and liquid phases with very high ozone current efficiency, no need for gas feeds of any description and robust and simple system design [11].

Ni/Sb-SnO$_2$ (NATO) ozone anodes have been reported to show high ozone current efficiencies for the production of ozone at room temperature in acidic electrolytes [11-17] or de-ionised water [16, 18], with ozone current efficiencies up to 50% [11, 16].

There are a number of types of electrochemical cell employed in the electrochemical generation of ozone [16]. Such cells fall broadly into two categories: single compartment [12, 13] and two compartments [11, 19]; the compartments of the latter are separated by a membrane that is either porous or an ionic conductor such as Nafion (as an example of a Polymer Electrolyte Membrane or PEM) [18].

In contrast to, for example PbO$_2$ [20], NATO anode – based MEA cells have not been researched extensively with respect to ozone generation. The only such work reported in the literature was carried out by the Chan group in Hong Kong University [18, 19] using 24 cm$^2$
[19] or 104 cm$^2$ [18] NATO anodes on Ti mesh (ca. 50% open area). Thus, the chan group [19] reported a ozone current efficiency of 15% at 2 V and ca.13 mA cm$^{-2}$ using a single cell and static deionised (DI) water as anolyte. With 104 cm$^2$ NATO anodes and flowing DI water as anolyte, efficiencies up to 17% at ca. 3 V and 19.2 mA cm$^{-2}$ with a single cell, and 22% at ca. 3 V and ca. 30 mA cm$^{-2}$ for a 4 – cell stack were reported [18].

Ozone has been extensively investigated with respect to the oxidative treatment of water and wastewater [21], reacting with a large number of organic compounds either by direct oxidation as molecular ozone (in acidic solutions) or by indirect oxidation through the formation of secondary oxidants such as hydroxyl radicals (in alkaline solutions) [22].

Wastewater containing organic dyes is becoming an increasing problem worldwide due to the extensive use of these compounds, with production estimated at over $7 \times 10^5$ tons/annum [4, 23, 24].

The main characteristic of dyes is the chromophore group which includes: azo ($\sim N = N \sim$), antraquinone, indigoide, etc derivatives [25]. A polyaromatic structure, high molecular weight and atoms of nitrogen, sulphur and metals are characteristics of most dye molecules [22]. Dyes can be reactive, direct, etc according to the method by which they are fixed on fibres [26]. For example, reactive dyes are designed to improve colour fastness as they have functional groups in their structure which form covalent bonds with fibres [27]. Over 20-25 % of reactive dyes are lost from the dyeing process and leave with the wastewater [1]. As an example of a reactive dye, Reactive Blue 50 dye was studied in the work presented in this paper.

In general, conventional wastewater treatment plants are not capable of remediating dye-containing wastewaters due to the high photochemical and thermal stability of such dyes, and their resistance to microbial attack [4, 22-24]. As a result, there has been increasing interest...
in other methods to decolourise and degrade dye wastewaters such as: physico-chemical
techniques [4, 7, 28]; Advanced Oxidation Processes (AOPs) [4, 7, 25, 29]; membranes [4]
and electrochemical technologies [4-7, 29, 30].

It has been found that the nature of the anode material influences strongly both the selectivity
and efficiency of the electrochemical oxidation process. Comninellis [8] divided the
behaviour of the anodes in electrochemical oxidation into two types: active and inactive.

Typical examples of the former are: Pt, IrO$_2$ and RuO$_2$ [4, 30, 31] and of the latter: PbO$_2$,
SnO$_2$ and BDD [4, 30, 31]. Inactive electrodes do not participate in the oxidation of organics
and do not provide any catalytically active site for their adsorption from aqueous media [4,
30, 31], acting only as an inert source and sink for electrons; in contrast, active anodes
participate directly in organic oxidation, with the oxidation byproducts adsorbing on the
anode surface [4, 30, 31].

For some industrial wastewaters, electrochemical technologies may be the indispensable step
in the treatment of refractory pollutants [6]. The main advantage of electrochemical methods
is that added chemicals are not required and sludge is not produced [23].

The aim of the work reported in this paper was to investigate the electrochemical generation
of ozone at NATO anodes in a Membrane Electrode Assembly (MEA) – based cell, and to
explore the decolourisation of Reactive Blue 50 (RB50) dye solutions in the MEA cell.

2 Experimental

2.1 Chemicals

HClO$_4$ (Puriss, Fluka) and Reactive Blue 50 (RB50) dye (Langholm Dying Company,
Scotland) were used as received without further purification. Millipore Milli-Q water (18 MΩ
cm) was used to prepare all solutions. Table 1 shows the molecular formula and structure of the RB50.

### 2.2 Electrode Preparation

The catalysts were prepared according to the methodology reported previously by Christensen et al. [14] by dipcoating onto 7.0 cm × 5.0 cm Ti mesh (ca. 50% open area) substrates (Dexmet, USA) from ethanolic solutions of the Sn, Sb and Ni metal salts. The concentrations of Sn: Sb: Ni in the coating solutions were 93.0 at.%:6.0 at.%: 1.0 at.%. The coating cycle was repeated 20 times [11, 32]).

A 7.0 cm × 5.0 cm platinised Ti mesh (Pt/Ti) (50% open area) was employed as the counter electrode (NRK Electrochem).

The 7.0 cm × 5.0 cm anodes and cathodes were spot welded into a titanium frame, giving an active area of 6 cm × 4 cm, see figs 1(a) and (b).

### 2.3 Membrane Electrode Assembly

The Membrane Electrode Assembly was fabricated by hot-pressing (Elcometer, heated press / $250 \, ^{\circ}\text{C} / 30000 \, \text{N}$) the framed NATO mesh anode and framed Pt/Ti mesh cathode either side of 5 cm × 7 cm Nafion 117 membrane (DuPont Corp., USA) at 150 °C and 800 N for 3 minutes, after which the MEA was turned through 180° and the process repeated.

The MEA was mounted between the cathodic and anodic compartments (each ca. 10 cm$^3$ volume) of the polycarbonate cell, with sealing maintained using silicon “O” rings. A schematic representation of the polycarbonate cell and the MEA are shown in fig. 1(a) and anode and cathode with the Ti frames are in fig. 1(b).
2.4 The Ozone Generation System

The flow (single pass) system is shown elsewhere (see Christensen et al [14]), which employed the polycarbonate cell housing the MEA.

An aqueous solution of 1 M HClO₄, or water from the Millipore Milli – Q system were employed as the anolyte and/or catholyte, which were kept separate by the MEA. The catholyte was stationary and supplied from a glass reservoir via polyethylene (PE) tubing (Portex 800/012/425/800 7.0 mm x 10.5 mm). The anolyte was pumped in the flow system through the anodic compartment of the polycarbonate cell using a Masterflex Digital Standard Cartridge Pump (Cole-Palmer) via PE tubing. The cell voltage or current density were controlled with a TTi TSX 1820P programmable DC power supply unit (PSU).

A Cole- Palmer WU series flowmeter was used to control the flowrate of nitrogen gas from a cryogenic boil-off which was employed to dilute the ozone gas generated by the MEA. The ozone then exhausted into a fume hood.

2.5 Ozone Measurement

Both gaseous and dissolved ozone were monitored using (b = 1 cm) pathlength UV-Vis cells (Astranet), and Astranet UV-Vis fibre optic spectrometer systems (Cambridge, UK). The value employed for the extinction coefficient $\epsilon$ of gas and solution phase ozone at ca. 255 nm and 258 nm was 3000 mol$^{-1}$ dm$^3$ cm$^{-1}$ [33].

\[
\text{Ozone concentration (mg dm}^{-3} \text{)} = \frac{A \cdot 48.1000}{\epsilon \cdot b} = 16.A
\]  

(1)

The ozone current efficiency can be calculated from [14]:

\[
\eta(\%) = 0.32A f/I
\]  

(2)

Where $A$ is the ozone absorbance in the solution or gas phases, $f$ is the anolyte flow rate or
the nitrogen + ozone flow rate (for gas phase) in cm$^3$ min$^{-1}$ and I is the current (A). The derivation of equation (2) is presented elsewhere [14]. All experiments were conducted at room temperature, 20–25 °C.

The ozone production rate (OPR) was calculated according to:

$$\text{OPR (mg h}^{-1}\text{ cm}^{-2}) = I.\eta.t.48.1000.3600/6F.a = 299.I.\eta/a$$

(3)

Where: $\eta$ is the ozone current efficiency (as a decimal), $t$ is the time (s), 48 is the molecular weight of ozone (g mol$^{-1}$), 6 is the number of electrons involved, $F$ is Faraday’s constant (96480 C mol$^{-1}$) and $a$ is the electrode geometric area (24 cm$^2$).

The power consumption was calculated from:

$$P (\text{kWh kgO}_3^{-1}) = 3.35 \frac{V}{\eta}$$

(4)

Where $V$ is the cell voltage (V).

2.6 Decolourisation

The system used for decolourisation is shown in fig. 2 and was operated in recycle mode; thus, 200 cm$^3$ of the stock RB50 solution, as anolyte, was recycled through the anodic compartment of the MEA – based cell using a peristaltic pump at recycle flow rate of 200 cm$^3$ min$^{-1}$. The solution then entered a gas separator to separate ozone bubbles from the anolyte, the gas phase ozone in the separator was diluted and carried by N$_2$ gas through a 1 cm path length UV – Vis flow cell (Astranet). The catholyte was 1 M HClO$_4$, static and supplied from a reservoir, and was kept separated from the dye solution by the MEA. The various system components were connected by polyethylene (PE) tubes. Nitrogen gas from a cryogenic boil-off was supplied at a carefully-controlled rate (typically 120 cm$^3$ min$^{-1}$) using a Cole-Palmer WU series flow meter system. 200 cm$^3$ of 100 or 1000 mg dm$^{-3}$ RB50 solution
was recycled at constant cell voltage of 2.7 V. Samples were withdrawn using a sampling port (see fig. 2) at regular intervals during 60 minutes runs and the absorbance measured using 1 cm path length quartz cuvette in a UV mini 1240 Shimadzu spectrophotometer.

When decolourising the 1000 mg dm$^{-3}$ of dye solution, the absorbance of the solution was too high to obtain meaningful data; hence 1 cm$^3$ samples of the dye solution were diluted by a factor of 10 with Millipore water prior to obtaining UV – Vis spectra.

The Closed Reflux Titrimetric Method was used to measure chemical oxygen demand (COD, procedure 5220 C, American Public Health Association [34]) and a Shimadzu TOC analyzer 5050 A ASI- 5000 was used for estimating the total organic carbon (TOC).

Intermediates were investigated using Ion Chromatography (IC) via a Dionex ICS-1000 with an AS40 auto sampler. The column was an IonPac AS14A, 4x250mm analytical column. The flow rate was 1ml/min, eluent was a 8.0mM Na$_2$CO$_3$/1.0mM NaHCO$_3$ solution. Injection loop was 25ul.

### 2.7 Calculations

#### 2.7.1 Removal Efficiency

The UV – Vis spectrum of RB50 solution shows bands in the visible region (associated with colour) and in the UV region (associated with aromatic rings); in particular, bands near 254 nm are associated with the benzene ring [23, 35, 36], and bands at 625 nm and 586 nm have been attributed to the anthraquinone moiety of the dye, see table 1.

The removal efficiency for colour and benzene rings were determined as follows:

\[
R(\%) = 100 \left( \frac{A_0 - A_t}{A_0} \right) \tag{5}
\]
Where: \( A_0 \) is the initial absorbance at 625 nm or 586 nm (colour), or 254 nm (benzene ring);
\( A_t \) is the absorbance at 625 nm, 586 nm or 254 nm at time \( t \) for colour and aromatic rings, respectively. 100% benzene ring removal was defined as when the peak at 254 nm disappeared.

### 2.7.2 Current efficiency

The dye removal current efficiency can be calculated as follows [7]:

\[
\text{CE} \% = \frac{F \cdot V_e \cdot (\text{COD}_0 - \text{COD}_t)}{8 \cdot I \cdot t} \quad (6)
\]

Where: \( V_e \) is the electrolyte volume (dm\(^3\)), \( \text{COD}_0 \) and \( \text{COD}_t \) are the chemical oxygen demands at times \( t=0 \) and \( t \), respectively.

### 2.7.3 Specific energy consumption

The specific energy consumption during the degradation of the dye can be estimated as follows [7]:

\[
E_{sp} = \frac{F \cdot V_c}{3600 \cdot 8 \cdot \text{CE}} \quad (7)
\]

Where: \( V_c \) is the cell voltage.

### 3 Results and Discussion

#### 3.1 Ozone Generation

Figure 3(a) shows the ozone concentration (in mg dm\(^{-3}\)) in the solution and gas phases, and the total concentration as a function of the cell voltage during ozone generation using the MEA in single pass (flow) experiments. The data points in fig. 3(a) represent steady state measurements after \( \geq 15 \) minutes at that particular cell voltage. It may be seen from the figure that \( O_3 \) concentration in both phase increased with increasing cell voltage up to 2.8 V after which it reached a plateau. The ozone in solution phase was higher than that in the gas phase when the cell voltages was <2.8 V which most likely reflecting a delay caused by the
arrangement of the system. However, the ozone concentration in both phases was almost equal at cell voltages $>$2.7 V. The total concentration reached ca. 20 mg dm$^{-3}$ at cell voltages $>$2.7 V. This concentration was comparable with that observed by Wang et al. [19], who reported 19 mg dm$^{-3}$ in solution phase only with the anolyte pumped through the cell, using an MEA with an air breathing cathode and NATO anode (4 cm $\times$ 6 cm Ti mesh 50% open area) at 2 V. In this study, the authors reported that the ozone concentration in both phases increased with cell voltage up to 2 V after which it decreased at higher voltages. In another paper, Wang et al. [12] reported 34 mg dm$^{-3}$ at 2.2 V vs. AgCl/Ag with static anolyte. They interpreted their data by stating that either more oxygen rather than ozone was produced or the ozone decomposed to oxygen at higher cell voltages.

Figure 3(b) shows the current density and ozone current efficiencies (solution, gas and total) vs. cell voltage for the experiments depicted in fig. 3(a). It may be seen from the figure that the current increased with increasing voltage up to 2.8 V, after which it increased more slowly. It is worth noting that other groups have not reported using such high current densities as the ones attained in the experiments depicted in fig. 3(b). Thus, the max current densities reported by Chan group are 58 mA cm$^{-2}$ using MEA based cells [18] and 15 mA cm$^{-2}$ using electrodes immersed directly in acid [12]. Ozone was produced at voltages $>$ 2.3 V. The current efficiency for dissolved ozone increased to a value of ca. 25% at 2.5 V and then decreased with increasing voltage, whereas the gas phase ozone current efficiency increased slowly to ca. 10 % at 2.6 V, then remained steady with increasing voltage. The total ozone current efficiency simply reflects the sum of these two contributions. As may be seen from the figure, irrespective of the cell voltage, more ozone was entrained in the solution phase than the gas; however, higher cell voltage result in an increasing fraction of ozone in the gas phase at the expense of that dissolved in solution, as well as a general decline in total efficiency.
Given that the distribution of ozone between solution and gas depends upon the system, further discussion will focus only on the total ozone production. The maximum current efficiency was about 33% compared to 21% reported by K. Y. Chan group [18] using a NATO anode in the MEA cell and an air breathing cathode; to our knowledge, 33% is the highest reported to date using an MEA with NATO anodes. The variation in ozone current efficiency with cell voltage suggests that the ozone active sites on the anode surface were switched on at voltages > 2.3 V, and the ratio of ozone/oxygen active sites increased with increasing voltage between 2.3 – 2.5 V. However, at voltages > 2.5 V, the ratio of ozone/oxygen sites decreased with increasing voltage, or the amount of ozone produced was less due to: (i) local heating effects that increase with increasing current density leading to a decrease in ozone efficiency [19, 37, 38], (ii) the switching over of ozone active sites to oxygen [12, 19, 39], (iii) the decomposition of ozone as a result of its reaction with OH radicals:

\[ \text{OH}^- + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2^- \quad (8) \]

with such radicals being produced at significant rates at higher current densities [19, 38, 40] and/or (iv) ozone decomposition:

\[ \text{O}_3 + \text{O}_3 \rightarrow 3\text{O}_2 \quad (9) \]

Equation (9) represents the sum of the equations given by Gardoni et al. [41] for ozone decomposition.

To the best of our knowledge, an MEA consisting of a NATO anode/Nafion117/Pt/Ti cathode has not been investigated for ozone generation previously. Therefore, it does not seem unreasonable to use the literature on MEA – based cells with anodes other than NATO as a
starting point for discussion.

The increase in current with voltage seen in fig. 3(b) was expected and has been reported by Wang et al. [19]. In a second paper, the same group [18] employed the MEA in a flow-through cell and applied constant current. They observed that the cell voltage increased with current density.

Ozone current efficiency passing through a maximum (see fig. 3(b)) with increasing current using MEA – based ozone cells has been reported many times for a range of different types of anode and cathode; see for example: Arihara et al. [42], Onda at al. [43] and Kraft et al. [38]. Kraft et al. [38] studied ozone generation from water (1 μS cm\(^{-1}\)) using boron doped diamond (BDD) anode and cathode, separated by Nafion N324 at 0.1 – 5 A in a flow – through reactor. The authors found that the current efficiency passed through a maximum at 1 – 1.5 A after which it decreased with increasing current. They interpreted the decrease in ozone current efficiency in terms of either: (i) the production of hydrogen peroxide accelerating ozone decomposition and/or (ii) local heating leading to lower ozone production or faster ozone decay.

Figure 3(c) shows the power consumption and ozone production rate for the experiments in fig 3(a). It may be seen from the figure that the power consumption decreased with increasing voltage to a value of ca. 25 kWh kg\(^{-1}\) O\(_3\) at 2.5 V after which it increased almost linearly. This is in general agreement with the work of Stucki et al. [44] and Onda et al. [43] who used an MEA consisted of PbO\(_2\) anode/Nafion 117/Pt cathode to generate ozone at constant current from water. The authors found that the power consumption decreased to a minimum (ca. 65 kWh kg\(^{-1}\) O\(_3\) at about 1 A cm\(^{-2}\) [44] or ca. 130 kWh kg\(^{-1}\) O\(_3\) at 1 A cm\(^{-2}\) [43]), after which it increased. In contrast, Arihara et al. [42] used an MEA consisting of a porous BDD plate anode and Pt mesh cathode from pure water at constant current of 1 – 10 A, and found
that the power consumption increased with increasing current. Da Silva et al. [20] using MEA found that power consumption decreased with increasing current. Arihara et al. and Da Silva et al. did not comment further on their data.

It may be seen from fig. 3(c) that the ozone production rate increased with increasing voltage up to 2.8 V then remained almost constant. This behaviour is in general agreement with the work of Kraft et al. [38] who reported that the ozone production rate increased with increasing current. Arihara et al. [40] and Da Silva et al. [20] also found that the ozone production rate increased with increasing current.

3.2 Decolourisation of RB50 Solutions

In the first decolourisation experiment, 200 cm$^3$ of 100 mg dm$^{-3}$ RB50 solution was decolourised in the system depicted in fig. 2 at constant cell voltage of 2.7 V. Complete decolourisation took place within 3 minutes, (data not shown). Hence the decolourisation of a 1000 mg dm$^{-3}$ RB50 solution was investigated. Figure 4(a) shows the UV – Vis spectra of the latter solution during electrolysis in the MEA – based electrochemical cell in recycle mode. It may be seen from the figure that the spectrum of RB50 consists of three well – defined peaks, at 254 nm, 586 nm and 625 nm. All three bands decreased with time. The loss of the UV band near 254 nm suggest that the dye is being oxidised into fragments [45], while the decrease in the intensities of the 625 nm and 586 nm bands may be attributed to the destruction of the anthraquinone moiety [3].

Figure 4(b) shows plots of removal efficiencies of 254 nm, 586 nm and 625 nm bands as a function of time during the experiment in fig. 4(a). As can be seen from the figure, the decrease in intensity of the 586 nm and 625 nm features track each other as would be expected, as they are due to the same anthraquinone chromophore. Therefore, the removal of the 625 nm bands were taken as representative of colour removal. In addition, the decrease in
the intensity at and 254 nm was considered as representative of benzene ring removal. As can be seen from fig. 4(b), the complete removal of both colour and the benzene ring was achieved within 8 min. It is generally accepted that colour removal starts by the cleavage of the chromophore [22].

The first step in electrochemical generation of ozone is generally believed to be the formation of OH radicals [4, 8, 16, 17]:

\[
H_2O \rightarrow HO^- + H^+ + e^- \quad (8)
\]

which can either be released from the electrode surface and react with dye molecules in the near – electrode region, or oxidise adsorbed dye molecules. In general, reaction of OH radicals with organic molecules includes hydrogen abstraction from and/or addition to unsaturated (- C = C - ) carbon double bonds [46]. Hence it would be expected that OH radicals will attack the anthraquinone and benzene ring moieties, cleaving both. The cleavage of the anthraquinone and the benzene ring result in the initial formation of smaller molecules, mainly aliphatic acids [23]. It should be noted that the initial pH of the RB50 solution was 4.72 and decreased to 2 at the end of decolourisation process, confirming the formation of acidic byproducts (see below).

Figure 5(a) shows the COD and TOC removal as a function of time for the experiments in fig. 4(a). It may be seen from the figure that both the COD and the TOC decreased with time with more COD being removed. The decrease in COD and TOC reflect the degradation of the dye molecules. From fig. 5(a), it can be seen that ca. 35% of the dye is degraded (i.e. oxidised to smaller fragments) in 60 minutes but only 13% is mineralised to CO\(_2\) and H\(_2\)O. Further, a comparison with fig. 4(b) shows that both these processes are much slower that colour removal, suggesting that destruction of the chromophore is rapid and complete, after which
the oxidation of the remaining moieties takes place more slowly, with some mineralisation.

Figure 5(b) shows the current efficiency and specific power consumption as a function of time for the experiments in fig. 4(a). As can be seen, the current efficiency is ca 100% up to 5 min, and the power consumption correspondingly low at 8 kWh kg\textsuperscript{-1} COD\textsuperscript{-1}. However, at longer times, there is a marked and sudden drop in the current efficiency, and a concomitant rise in specific power consumption. Comparing with fig. 4(b) suggests this behaviour may be interpreted in terms of the initial attack on easily oxidised chromophores; once these have been removed (after 8 min), the remaining organic species are more recalcitrant.

In the beginning of the experiment when the dye concentration was high enough, the current efficiency was 100% meaning that all the current was used to degrade the dye molecule, then side reaction started to take place; including the generation of O\textsubscript{3} and O\textsubscript{2}. 100% current efficiency indicates that the applied current density was less than the limiting current density and the degradation process is under current control (kinetically controlled) \cite{5, 7}, 

\[ i_{\text{lim}} = 4.0F.K_m.COD, \]

where \( F \) is Faraday’s constant, \( K_m \) is the mass transfer coefficient \cite{5, 7} (in our cell, \( K_m = 1.3 \times 10^{-4} \text{ m s}^{-1} \)). It may be clear that the limiting current density changes with the COD value, so it is not fixed value. Applied current density higher than the limiting one resulted in current efficiency less than 100%, and the degradation process is under the mass transfer control\cite{5, 7}. When the dye concentration is high enough, at the beginning of the test, 100% of the current will be used to generate oxidants that will be used for dye decolourisation/degradation, sometime after that (about 5 min), the dye concentration become less and mass transfer of the dye towards the electrode become crucial and the current is enough now for side reactions (O\textsubscript{3}, O\textsubscript{2},..) and the current efficiency is decreasing exponentially. On the other hand, the specific power consumption increased as the dye concentration decreased, due to degradation, reflecting that the fact the power is being
consumed for side reactions (ozone). Due to the fact that NATO anodes has only been used a few times for organic degradation, see Wang et al (4-Chlorophenol) [47] and Chen et al. (Phenol) [48], there is no real power cost estimation. In addition, those researchers used different anode sizes and cell configuration that make the comparison to our results even more difficult.

To confirm that side reactions were happening during the experiment shown in fig. 4(a), ozone was monitored at the outlet of the gas separator, and the results are shown in fig. 5(c) along with the variation in current during the experiment. As can be seen from fig. 5(c), ozone is generated after 3 min electrolysis, with increasing ozone current efficiency up to 8% at 16 minutes; whilst the current density falls steadily. Figures 5(b) and (c) suggests that, as the RB50 is consumed, OH radicals become available to form ozone [9, 24, 27, 30, 31].

From fig. 5(c), it may be seen that the current decreased with time from ca. 50 mA cm$^{-2}$ to ca. 25 mA cm$^{-2}$ during 16 minutes of the experiment; in order to ascertain the reason for this, the experiments discussed in the next section were carried out.

### 3.2.1 Reactivating the MEA

The current in fig. 4(c) not only decreased with time, but also it was much less than that observed during the ozone generation experiments at 2.7 V depicted in fig. 3(a). This may be due to: (i) poisoning of the anode, (ii) the membrane (Nafion) of the MEA becoming resistive and/or (iii) delamination of the MEA.

To investigate whether the anode had been poisoned and could be re-activated, ozone was generated using the MEA employed in the dye decolourisation experiments discussed above at 2.7 V under the same conditions using: (1) 1 M HClO$_4$ as anolyte with Millipore water as catholyte (see curves (ii) of figs. 5(a) and (b)), (2) 1 M HClO$_4$ as anolyte and catholyte (see
curves (iii) of figs. 5(a) and (b)), and (3) Millipore water again as anolyte and catholyte (see
curves (iv) of figs. 5(a) and (b)). Curves (i) of figs. 5(a) and (b) represent the use of Millipore
water as the anolyte and catholyte from fig 3(a). The currents and ozone current efficiencies
observed as a function of time from these experiments are shown in figs. 6(a) and (b),
respectively.

As may be seen from figs. 6(a) and (b), both the current and ozone current efficiency
observed using Millipore water as anolyte and catholyte are significantly lower than the
values observed prior to the dye decolourisation experiments, i.e. ca. 1.3 A compared to 3 A
and ca. 4 % compared to ca. 30 % gaseous ozone current efficiency (see fig 3(b)). However,
using 1 M HClO₄ as anolyte, with Millipore water or 1 M HClO₄ as catholyte, resulted in a
current of 3 A and ozone current efficiency up to 33%. Replacing the anolyte and catholyte
with Millipore water resulted in the current falling to ca. 1.5 A and ozone current efficiency
to ca. 8%. Whilst plots (i) and (iv) do suggest some poisoning of the NATO anode which is
ameliorated by electrolysis in acidic anolyte, it is clear that a major factor is the delamination
of the MEA and consequent loss of ionic contact between anode and Nafion. The
delamination of the MEA may have been enhanced by the fact that the anolyte was recycled
at 240 cm³ min⁻¹ whilst the catholyte was static (see fig. 2); given the pump operated on the
peristaltic principle, this could cause flexing of the Nafion. At the end of all the experiments
in this paper, the MEA was removed from the polycarbonate cell, and areas of delamination
could clearly be observed.

3.2.2 Intermediate formation

To confirm the formation of acids during the electrolysis of the dye solutions, IC was used to
investigate the dye oxidation byproducts. Figure 7 shows the peak area of different
byproducts obtained from the IC output as a function of electrolysis time. It may be seen
from the figure that organic and inorganic species were formed. The former were acetic acid and maleic acid; their concentration increased with electrolysis time, and the concentration of maleic acid increased up to a max after 30 min. The inorganic species were NO$_2^-$, NO$_3^-$, Br$^-$ and SO$_4^{2-}$. The concentration of Br$^-$ was constant concentration over the first 15 min of electrolysis, after which it decreased, suggesting the formation of OBr$^-$ and/or Br$_2$. A detailed study of the intermediates and the dye oxidation mechanism is to follow in a subsequent paper.

### 4 Conclusions

Ozone current efficiencies as high as 33% and power consumption as low as 25 kWh kg$^{-1}$ O$_3$ have been reported for the first time for the generation of ozone from Millipore water using an MEA – based cell with a NATO anode and Pt/Ti cathode separated by Nafion at room temperature in flow mode.

The same MEA was found to be efficient with respect to the decolourisation of RB50 solution, a dye that has not been studied before in the literature. 1000 mg dm$^{-3}$ RB50 solution was completely decolourised within 8 minutes at 2.7 V, with a current efficiency of 100% and specific power consumption of 8 kWh kg$^{-1}$COD$^{-1}$ in the first 5 minutes of electrolysis. The removal of COD and TOC required longer times. The formation of organic and inorganic by products was observed.

### Acknowledgment

KZ would like to thank Damascus University / Syria for a scholarship and Newcastle University for funding.
Reference

**Figure Captions**

1. (a) The membrane electrode assembly and the polycarbonate (PC) electrochemical cell: (1) PC cell body, (2) NATO mesh anode spot-welded onto a Ti frame, (3) the Nafion 117 membrane, (4) the Pt/Ti mesh cathode spot-welded onto a Ti frame. (b) The cathode and anode meshes on the Ti frames.

2. Schematic of the decolourisation systems used for the decolourisation experiments using the MEA – based electrochemical cell.

3. (a) Plots of O$_3$ concentration as a function of cell voltage in (i) solution phase, (ii) gas phase and (iii) total (solution + gas) during an experiment in which Millipore water (as anolyte and catholyte) was electrolysed. The anolyte flow rate was 200 cm$^3$ min$^{-1}$ in single pass, or flow, mode. The N$_2$ flow rate was 120 cm$^3$ min$^{-1}$. The catholyte was static. (b) Plots of: (i) current density, (ii) solution ozone current efficiency, (iii) gas phase ozone current efficiency and (iv) total ozone current efficiency vs. cell voltage during the experiments in fig. 3(a). (c) Plots of: (i) power consumption and (ii) ozone production rate vs. cell voltage observed during the experiments in fig. 3(a).

4. (a) UV – Vis spectra collected during the decolourisation of 200 cm$^3$ of 1000 mg dm$^{-3}$ of RB50 in the MEA – based cell, the spectra were collected: (i) at the start of the electrolysis (t = 0), (ii) after 2 min and then every 2 min up to (ix) 16 min. (b) Plots of the removal efficiency vs. time of: (i) colour ($\lambda_{\text{max}} = 625$ nm), (ii) colour ($\lambda_{\text{max}} = 586$ nm) and (iii) benzene ring ($\lambda_{\text{max}} = 254$ nm). The cell voltage was 2.7 V, the N$_2$ flowrate 120 cm$^3$ min$^{-1}$, the anolyte flowrate was 200 cm$^3$ min$^{-1}$, at room temperature.

5. (a) Plots of: (i) COD removal and (ii) TOC removal vs. electrolysis time. (b) Plots of: (i) the current efficiency and (ii) the specific power consumption vs. electrolysis time.
(c) Plots of: (i) current density and (ii) ozone current efficiency as function of time observed during the experiments depicted in fig. 4(a).

6. (a) Plots of current as a function of time during the experiments conducted after those depicted in figs. 4(a). In each case, the anolyte flow rate was 200 cm$^3$ min$^{-1}$ and the catholyte was static. (i) Millipore water as catholyte and anolyte represent data from fig 3(b), (ii) 1 M HClO$_4$ as anolyte and Millipore water as catholyte, (iii) 1 M HClO$_4$ as catholyte and anolyte and (iv) Millipore water as anolyte and catholyte. The cell voltage was 2.7 V, at room temperature. (b) Plots of the ozone current efficiency vs. time for the experiments described in fig. 6(a). (i) - (iv) are as above in fig. 6(a).

7. Plots of the areas under the chromatographic peaks (determined using IC) as a function of electrolysis time for the byproducts observed during the experiment in fig 5(a). See text for details.
Figure 1.

(a) 

(b)
Figure 2.
Figure 3.
(a)
Figure 4.

(a) COD/COD<sub>r</sub> or TOC/TOC<sub>r</sub> vs. Time / min

(b) Removal Efficiency (%) vs. Time / min
Figure 5.
Figure 6.

(a) 

(b)
Figure 7.