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# An electrochemical approach to total organic carbon control in printed circuit board copper sulfate plating baths
## Part II: Overall system

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## Abstract

An electrochemical system for oxidative removal of high levels of total organic carbon (TOC) in printed circuit board (PCB) copper sulfate plating baths has been developed. These organic contaminants build-up over the course of pattern plating of PCBs, and at high concentrations they interfere with the quality of the plated copper. The chemistry of the electrochemical oxidation of the plating bath contaminants was qualitatively followed using high performance liquid chromatography (HPLC) and chemical oxygen demand (COD) measurements. A complete treatment system is described and rough calculations are given showing, for a given set of conditions, how the proper choice of electrode material and current density can minimize the system cost.

## 1. Introduction

In Part I it was shown that electrochemical oxidation could be used to remove problem organic contaminants from printed circuit board (PCB) plating baths [1]. The plating baths initially contain copper sulfate and sulfuric acid, as well as organic additives (typically levellers, brighteners and wetting agents) designed to improve the quality and speed of the electroplating. During the course of plating, fresh additives are added to make-up for those consumed by incorporation into the copper plate and by decomposition reactions (with air, and at the anode). Over time, the decomposed additives will build-up in the plating bath. Other causes of contamination include: organic compounds leached from the printed circuit boards and in particular their photoresist, contaminants carried in on the surfaces of the boards from previous process steps ('drag in'), and airborne contaminants. This slow build-up of organic contamination can be followed by monitoring the plating bath total organic carbon (TOC). When problem TOC values are reached, the normal procedure is to treat the plating solution by contacting it with activated carbon, which acts to adsorb the contaminants. After such a treatment, the additive concentrations are readjusted and plating can continue (at some operations the solution may also be filtered to remove carbon particle fines). Because of the carbon high surface area and high porosity, the used carbon retains significant amounts of copper sulfate and sulfuric acid and for this reason is classed as a hazardous waste for handling and disposal. There are concerns that the cost of waste disposal may increase in the future, and there is also a desire for a rapid and convenient method that can be frequently used and thus maintain the plating bath quality within narrower limits.

In Part I the possible use of electrochemical oxidation for removing the organic contaminants was proposed [1]. The key aspects of an electrochemical approach are shown in Figure 1. At the anode various organic compounds in the plating bath are oxidized (as indicated in Figure 1 by the oxidation of polyethylene oxide, a common carrier), and oxygen gas is evolved through the oxidation of water. It is hoped that this oxidation of the organic contaminants will progress to $CO_2$, thus providing a clean starting solution for further plating. One requirement for such an electrochemical process is an anode material that is stable in strong sulfuric acid, and also provides reasonable selectivity for the destruction of the target compounds versus oxygen evolution, as discussed in Part I [1]. The desired counter electrode reaction is the evolution of hydrogen. It is the aim to carry out these reactions without changing other properties of the plating bath chemistry (e.g., copper and acid concentrations) thus allowing the plating bath solutions to be recycled to the plating operations with minimal processing steps. To accomplish this a divided

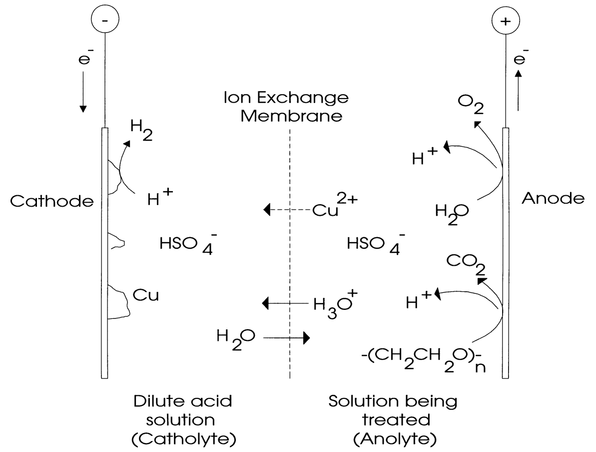

*Fig. 1.* Key chemical processes involved in electrochemical treatment.

cell is needed where an ion exchange type membrane separates the anode and cathode. Ideally this would allow the plating solution to have contact with the anode (where oxidation of the organic contaminants will occur) without contacting the cathode (where copper plating would otherwise occur).

## 2. Experimental details

Testing was carried out using a divided flow-by electrochemical cell (an AB Microcell from AB Electrocell) described in more detail in Part I [1]. Both anode and cathode solutions were continuously recirculated through the cell at 100 ml min$^{-1}$ and the cathode material was 316 stainless steel. Some tests were also carried out using a small glass electrochemical 'H'-type cell. This consisted of separate anode and cathode compartments connected via a horizontal pipe in which a membrane could be fitted. (A model C-600 Membrane Cell from the Electrosynthesis Co.) Tysar-EP electrode material (titanium felt coated with electrolessly deposited platinum [2]) was made by the Olin Corp. and obtained through the Electrosynthesis Co. Doped tin dioxide coated titanium anodes were obtained from the Eltech Co. The ion exchange membranes tested were obtained from the Electrosynthesis Co., except for the Asahi HSF membrane, which was obtained from Asahi Glass.

The high TOC test solutions were provided from one of the plating lines of a local printed circuit manufacturer. The solutions were typically around 200 g l$^{-1}$ $H_2SO_4$, 20 g l$^{-1}$ copper, and c.a. 40 ppm chloride, with TOC values from 1600 to 2300 ppm. The plating solution treatment was monitored by measuring the TOC with a Shimadzu 5050 TOC analyser.

High performance liquid chromatography (HPLC) was carried out using a size exclusion chromatographic column for separating water soluble polymers with sizes less than that of 3000 g mol$^{-1}$ polyethylene glycol (a Tosoh G3000PW$_{XL}$ TSK–GEL column). Compounds were eluted from the column with a mobile phase of 10% acetonitrile and 90% pH 2.1 $H_2SO_4$ at a flowrate of 1 ml min$^{-1}$. The compounds were detected using ultraviolet adsorption monitored at 195 nm for water soluble polymers, and 210 nm for the brighteners (a modification of the method of Reid [3]).

Chemical oxygen demand (COD) measurements were carried out using the dichromate method. A Hach Co. COD system was used; including premeasured 0 to 1500 ppm COD reagent vials, a Hach digestor reactor (2 h at 150 C), and a DR/2010 spectrophotometer (at 620 nm). Blank samples containing 200 g l$^{-1}$ $H_2SO_4$ and 20 g l$^{-1}$ copper were also measured and the resulting values subtracted from other COD measurements to correct for the interference of copper sulfate at 620 nm.

## 3. Results and discussion

### 3.1. *Electrooxidation*

Initially a number of commonly available anodes were screened for activity and stability. Among these the antimony doped tin dioxide coated anode gave a good balance of performance (as measured by the apparent rate constant for TOC removal) and stability [1]. A TOC against charge plot using the doped tin dioxide anode is shown in Figure 2. It can be seen that electrooxidation can be used to decrease the TOC levels from 1530 ppm to about 200 ppm. It was also noted during these electrochemical treatments that the colour of the high TOC solutions changed from green–blue at the start, to typical copper sulfate blue. This recovery of the normal blue colour of the plating solutions occurred early in the treatment (often in the first 50 000 to 100 000 C l$^{-1}$), while there was still significant TOC.

Many of the plating additives and photoresists are proprietary, and the additive decomposition and photo-

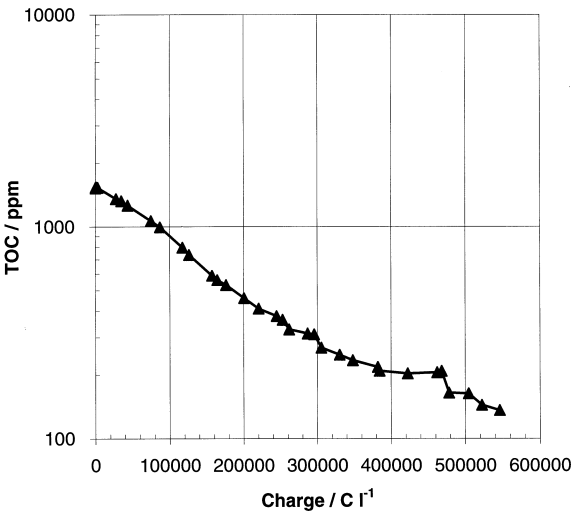

*Fig. 2.* TOC removal for plating solution recycle: performance of a doped tin dioxide coated anode. (AB Electrocell flowcell, 10 cm$^2$ flat plate, 25 mA cm$^{-2}$, 500 ml solution.)

resist leaching and decomposition chemistries are complex. The electrooxidation pathways of these compounds will also be complicated, producing more unknown compounds. To obtain more information about the electrooxidation chemistry, solution analysis was carried out using high performance liquid chromatography (HPLC). While, without standards, this technique does not identify compounds, it does separate various compounds in a mixture and thus allows the amounts of the various components to be qualitatively followed with time. Typical results are shown in Figures 3 and 4. The first set of chromatograms (Figure 3) shows the results for samples of a fresh plating bath (after carbon treatment and additive adjustment; about 400 ppm TOC) and an old plating bath (about 2000 ppm TOC). The chromatographic column is packed with a porous polymeric resin and separates the samples by two mechanisms. High molecular weight water soluble polymers (often used as carriers and/or levellers) are excluded from the resin pores (about 200 nm), thus are quickly washed out of the column, and are the first peak to appear on the chromatogram. The copper sulfate and sulfuric acid have relatively little interaction with the column packing, but pass through the pores, taking slightly longer to exit the column giving the very large peak at about 10 min. Finally, brighteners, brightener breakdown products and leachate from the circuit board photoresist can enter the packing pores and also tend to adsorb to some extent on the polymeric resin of the packing. This causes these compounds to come out of the column following the copper sulfate and sulfuric acid, with the compounds exact retention time depending on its degree of adsorption on the column polymeric resin and hence its hydrophobicity. It can be seen in the chromatograms in Figure 3 that the number of such compounds and the concentration of these increases dramatically as the plating bath ages. Occasionally some material was seen to exit the column at very long times (in some cases during following runs of other samples).

In Figure 4, the effect of electrochemical treatment can be seen. The number and size of peaks eluting in the 11–20 min range are drastically reduced, though the removal is not straightforward, rather some peaks grow and appear while others disappear. This disappearance is also related to a corresponding decrease in the

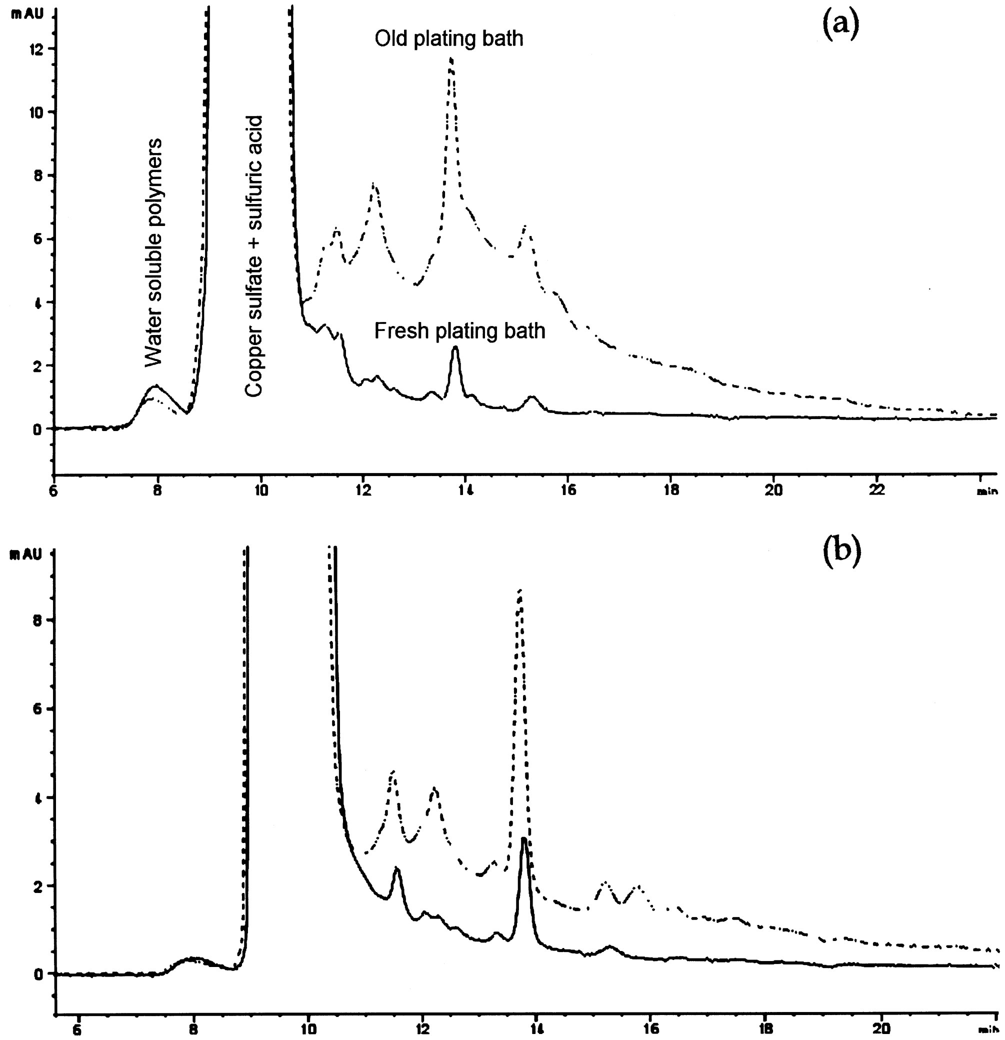

*Fig. 3.* HPLC chromatograms of fresh and old plating baths. (a) Ultraviolet detector at 195 nm; (b) ultraviolet detector at 210 nm.

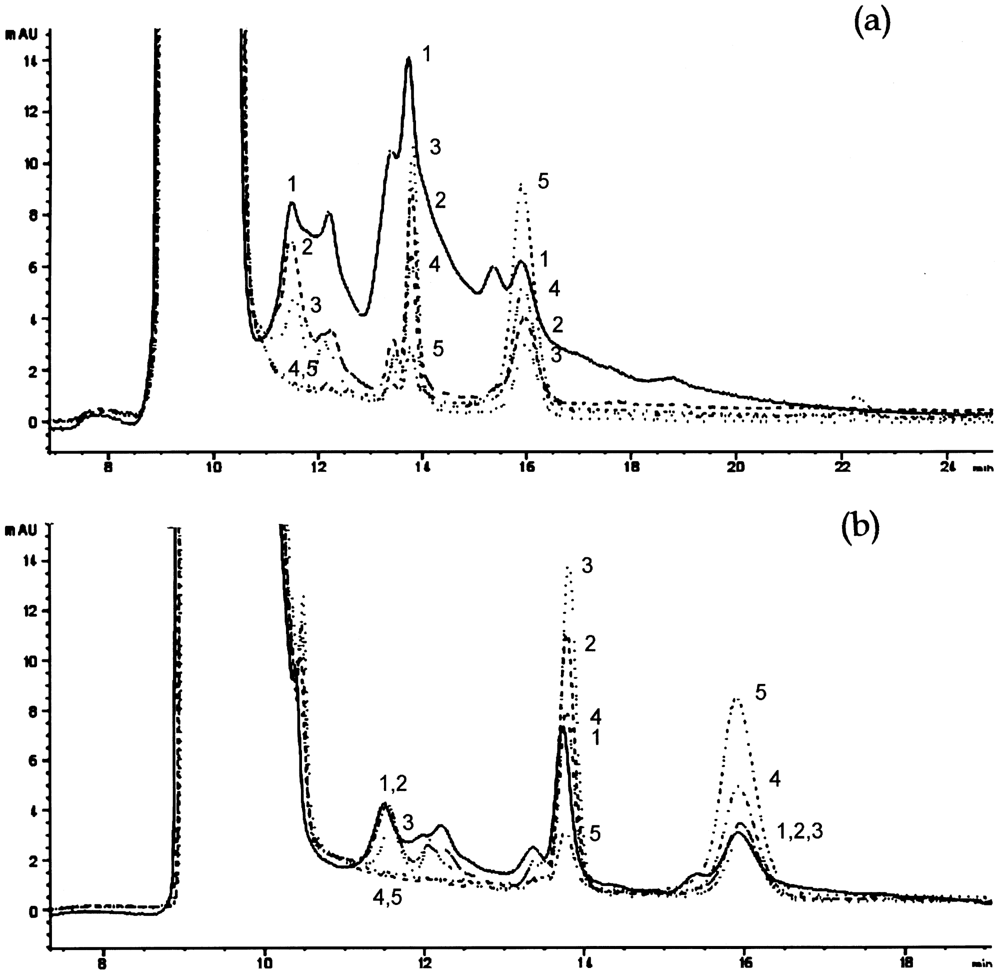

*Fig. 4.* HPLC chromatograms at various stages of electrochemical treatment of plating solution using an $SnO_2$ plate anode. (Samples from the run shown in Figure 2). (a) Ultraviolet detector at 195 nm; (b) ultraviolet detector at 210 nm. TOC: (1) 1520 ppm, 0 C $l^{-1}$; (2) 1260 ppm, 43 320 C $l^{-1}$; (3) 736 ppm, 126 150 C $l^{-1}$; (4) 310 ppm, 295 650 C $l^{-1}$; (5) 136 ppm, 546 150 C $l^{-1}$.

solution TOC. Comparing the final treated solution (curve 5 in Figure 4) with the carbon treated solution, the peak at 14 min is common to both solutions, while a peak at 16 min, which builds up during the electrochemical treatment, does not appear in the carbon treated solution. However, the electrochemically treated solution shows fewer peaks around 11.5 min. This appears to suggest that the chemistry of the electrochemically treated plating bath may vary slightly from the carbon treated bath. Though no significant difference was noted between the samples treated with doped tin dioxide and platinum coated anodes.

Thus the HPLC provides a qualitative conformation of the effectiveness of the electrochemical treatment in removing many of the organic compounds. It also provides a useful window on the complex chemistry involved in the plating bath ageing and treatment.

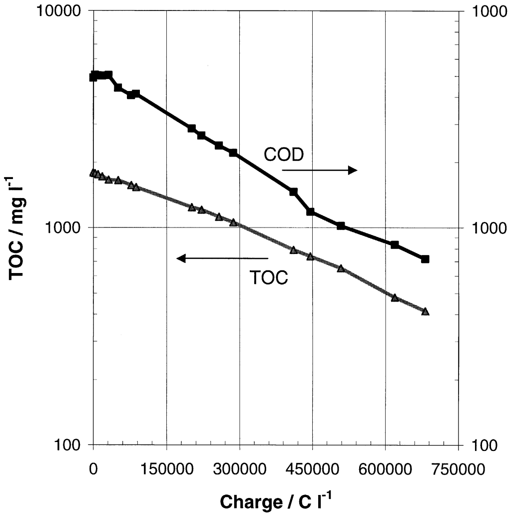

*Fig. 5.* TOC and COD changes during electrooxidation. (H-cell, doped tin dioxide coated mesh, 7.8 $cm^2$ projected area, c.a. 10.4 $cm^2$ real area, 360 mA, 150 ml anolyte).

To see the degree of oxidation of the organic compounds, chemical oxygen demand (COD) measurements were also carried out with some test runs. The results for one run are shown in Figure 5. It can be seen that as the TOC is decreased from about 1800 ppm to 400 ppm, the COD decreases from about 5000 ppm to 700 ppm. Both curves appear fairly linear on this plot, although it can be seen that they are converging. This can be understood by using the TOC and COD data to calculate the number of electrons per carbon required to

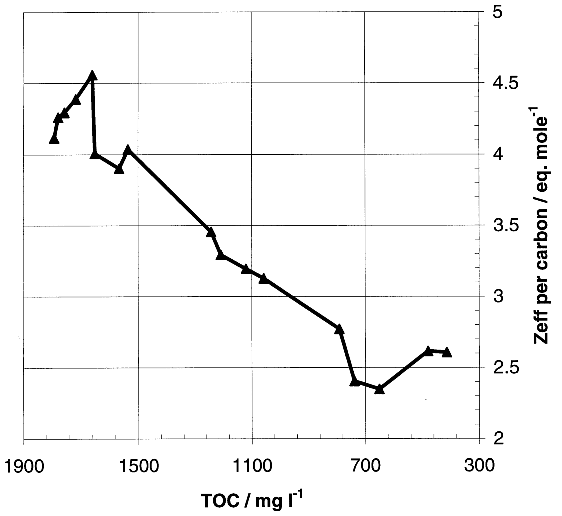

*Fig. 6.* Number of electrons per carbon, required for complete oxidation, calculated from the data in Figure 6.

convert it to $CO_2$. The results of such a calculation are shown in Figure 6. The number of equivalents of electrons required per mole of carbon to achieve complete oxidation starts around 4.5 eq. mol$^{-1}$ and decreases to about 2.5 eq. mol$^{-1}$ by the end of the experiment. This indicates that the average organic compound becomes more highly oxygenated as the electrooxidation proceeds.

## 3.2. *Membrane testing*

Another area of importance for such a system to be successful is the cell membrane. The membrane must minimise the undesirable loss of metal from the solutions to be treated (by deposition at the electrochemical cell's cathode) and also should not result in a significant change in the solution chemical composition (by water or electrolyte transport).

The best isolation of the anode and cathode compartments can be obtained using a bipolar membrane. Unfortunately problems occur due to precipitation of metal ions inside the membrane where a high pH region occurs (caused by the water splitting which occurs at the centre of the bipolar membrane [4]). This problem could be avoided at low membrane current densities (<25 mA cm$^{-2}$), probably due to the low solution pHs and the buffering capability of bisulfate ion (which can penetrate into the anion exchange side of the membrane). However, at more practical current densities the pH variation in the middle of the membrane was sufficient to cause copper precipitation. One surprising observation was that it was also possible to cause the deposition of metallic copper within the membrane. It is speculated that this is due to precipitated copper hydroxide converting to copper oxide, which being a semiconductor, can act as a bipolar electrode. (The copper metal within the membrane was observed to occur on the side of the black copper oxide deposit that faced the anode).

Anion membranes, although stopping copper, would allow bisulfate (or other anions) from the catholyte to cross, thus shifting the plating bath chemistry. Therefore work was focused on evaluating various types of cation exchange membranes for their ability to preferentially allow the passage of hydrogen ions versus metal ions. The small H-type cell was used with a doped tin dioxide anode, 2.5 cm dia. membrane, and a platinum gauze cathode. The anolyte was 85 ml of copper plating solution and the catholyte was 40 ml of around 0.61 M sulfuric acid. Tests were carried out until significant copper was visible on the cathode. The cathode was then removed and the copper deposit weighed. The results of this testing are given in Table 1. Good results were obtained using monovalent cation selective membranes (e.g., Tokoyama Soda Neosepta CMS [6] or Asahi Glass HSF [7]) and perfluorosulfonic acid cation membranes. Somewhat better selectivity had been hoped for from the monovalent cation selective membranes. However, due to the high concentration of ions in the plating solutions, a significant amount of the copper would be expected to exist in ion pairs rather than as a doubly charged ion [8].

As well as electrolyte transport, a second concern is water transport through the membranes. Water is

*Table 1.* Selectivity test results for various cation membranes for protons against copper ions (40 mA cm$^{-2}$ membrane current density anolyte, 2 M $H_2SO_4$, 0.31 M copper)

| Membrane | Total charge passed /C | Copper on cathode /g | Current efficiency of copper transport /% | Selectivity $\frac{i_{H^+}C_{Cu^{2+}}}{i_{Cu}C_{H^+}}$ |
|---|---|---|---|---|
| Perfluorinated cation (Nafion® 117) | 51 840 | 0.045 | 0.27 | 59 |
| Polystyrene cation (ESC 7000) | 36 540 | 0.176 | 1.47 | 11 |
| Polystyrene monovalent cation (Tokuyama CMS) | 69 300 | 0.064 | 0.28 | 56 |
| Polysulfone monovalent cation (Asahi HSF) | 342 360 | 0.267 | 0.24 | 66 |

Note: equivalent ionic conductivities ($\lambda$) for protons and copper(2+) are: $\lambda_{H^+} = 349.65$ cm$^2$ S mol$^{-1}$, $\lambda_{1/2Cu^{2+}} = 53.6$ cm$^2$ S mol$^{-1}$, [5] giving: $\lambda_{H^+}/\lambda_{1/2Cu^{2+}} = 6.5$.

transported across the membranes by electroosmotic drag from the ions moving in the applied electric field. For the cation membrane this would result in the slow movement of water from the anolyte to the catholyte. While the anolyte volume decrease could be corrected by the addition of water, the increase in catholyte volume would result in a dilute acid waste stream. This can be solved by using a catholyte with a lower ionic strength than the anolyte (the plating solution being treated) thus causing a reverse osmosis transport of water. By careful adjustment of the catholyte ionic strength for a given membrane current density, the reverse osmosis water transport and the electroosmotic water transport can be made to cancel. In the membrane tests in Table 1 (40 mA $\mathrm{cm}^{-2}$ membrane current density), the c.a. 2 M sulfuric acid of the plating solution was balanced with a 0.6 M sulfuric acid catholyte.

### 3.3. *Possible process layout and an example scale-up calculation*

Based on this work, an electrochemical treatment system could be conceived of as shown in Figure 7. In the layout shown, high TOC solution from a plating line is pumped into tank 1, and the plating line is refilled with previously treated and prepared solution from tank 2. The solution in tank 1 (the anolyte solution) is then recirculated through the anode compartments of the electrochemical cell. When the oxidation of the problem organic contaminants is sufficiently complete, the outflow of the cell is directed to tank 2. Once the treated solution is in tank 2, fresh additives can be added so it is ready for reuse in the plating line. By swapping solutions between two tanks, this design allows for minimal downtime for the plating line and gives more time for the electrochemical treatment allowing a smaller, less expensive, cell to be used.

Using this system layout and results from a previous paper in which different types of anodes were evaluated [1], a rough initial estimate can be made for the size and costs for such a system. In the previous paper, the rates of decrease of TOC under different conditions were reported using an apparent overall first order rate constant. This worked surprisingly well, especially in light of the complex and changing chemical composition of the plating solutions over the course of treatment that has been presented in this paper.

The approach taken involved assuming that the rate of removal of TOC at a given current density could be described by an approximate first order rate constant:

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = -AkC \tag{1}$$

thus,

$$C_t = C_0 \exp\left(\frac{-Ak}{V}t\right) \tag{2}$$

where $k$ is the apparent rate constant, $A$ and $V$ are real electrode area and solution volume respectively and $C_0$ and $C_t$ the concentrations of organic carbon initially and at time $t$, respectively.

The rate constants for TOC removal were evaluated for different electrodes, different batches of high TOC solutions, and different electrochemical cells. The results are complied in Figure 8 where the rate constants are plotted as a function of current density. These relationships between reaction rate and current density are likely related to the competition for oxygen evolution intermediates between organic oxidation and oxygen evolution [9, 10], as well as direct electron transfer reactions, and so may be quite complicated.

One can use this apparent first order rate constant data to easily develop initial size and cost estimates for such a system. As an example of the approach, an application might be to treat 3400 l from 8 plating lines, each twice per year. Swapping solutions between two tanks as discussed above, and staggering the treatments

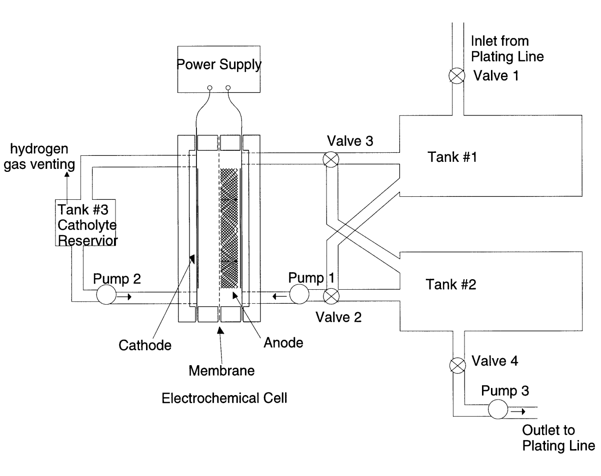

*Fig. 7.* A possible layout for an electrochemical plating bath treatment system.

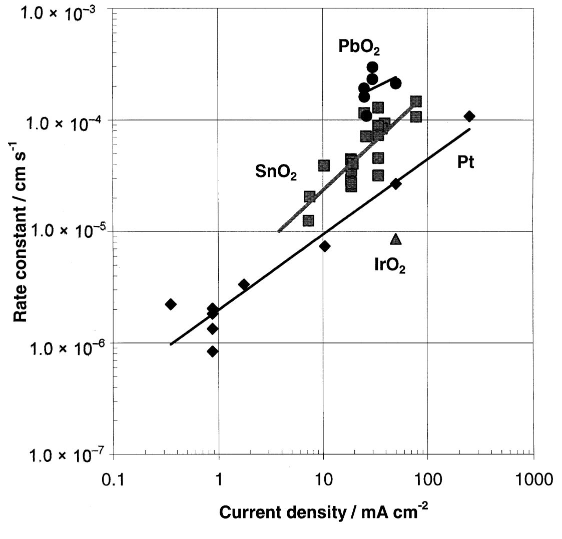

*Fig. 8.* TOC removal rate constants as a function of current density for various anode materials.

throughout the year would allow about 20 days for each treatment. If the target was to reduce the TOC in the 3400 l from 1600 ppm to 300 ppm, the real electrode area required ($A$) can be estimated using the approximate first order rate constant:

$$A = \frac{V}{k\tau} \ln\left(\frac{C_0}{C_\tau}\right) \tag{3}$$

where the rate constant can be estimated by a power curve fit of the data in Figure 8. (This is again a rough approximation and a better understanding of the relationships between the rate of TOC decrease, oxygen evolution, and current density would likely lead to a better function for fitting such data.) For this estimation method to be valid one must ensure that the reaction will not be mass transfer limited (i.e., ensure that the mass transfer coefficient is greater than the first order rate constant). Also sufficient current must be available to not be current limited at the initial reactant concentration (i.e., $i > nFkC_0$). Then for each current density one can estimate the real electrode area required and the total current required. These values can be combined with assumed costs to develop a relationship between costs and current density. The system would have a total cost made up of fixed costs, cell hardware costs, electrode and membrane costs, and electrical power costs.

The fixed costs relate to items such as tanks, plumbing, power supply, and control systems. For these examples the system fixed costs were chosen to be about C$40 000. The depreciation and maintenance of this equipment was then allocated per treatment using a cost of 20% per year with 16 treatments per year.

The electrochemical cell hardware, and the electrode and membrane costs will depend on the required electrode area. The cell hardware, probably a plate and frame type cell of a few square metres membrane area, was estimated at C$20 000 $\text{m}^{-2}$. Like the fixed costs, the depreciation and maintenance of this equipment was then allocated per treatment using a cost of 20% per year with 16 treatments per year. The anodes and membranes would have to be replaced periodically. Because long-term lifetime data are not available, for the purposes of this example a lifetime of three years was arbitrarily chosen. Both tin dioxide and platinum anode coatings will be considered using the costs listed in Table 2. The monovalent cation membrane was assumed to cost about C$2000 $\text{m}^{-2}$.

The power cost was estimated using C$0.06 per kWh. The cell voltage was calculated using 1.23 V plus a voltage drop based on an internal cell resistance of 20 $\Omega\ \text{cm}^2$ and the projected (or membrane) current density.

Using these values and the electrode areas calculated using the approximate first order rate data, the cost per treatment could be estimated for various current densities, resulting in the curves shown in Figures 9, 10 and 11. With the average current efficiencies being calculated for each current density, as described in Part I (and using a $z_{\text{eff}}$ 4.5 eq. $\text{mol}^{-1}$ of carbon). This type of plot predicts that the most economical range for operation is around 70 mA $\text{cm}^{-2}$ real current density (210 mA $\text{cm}^{-2}$ projected and about 1 $\text{m}^2$ of membrane area) for tin dioxide and 10 mA $\text{cm}^{-2}$ real current density (190 mA $\text{cm}^{-2}$ projected and about 2 $\text{m}^2$ of membrane area) for platinum. If the impact of current density on the electrode lifetime was also considered, these optimum current densities would probably be somewhat lower. Different geometries and arrangements of the anode materials (e.g., one versus two stacked meshes) would also affect the calculated cost curves. From Figure 11 it can be seen that the platinum electrode is more expensive to use than the doped tin dioxide. However, from Figure 10 it can be seen that this is not just due to its higher cost, but also its lower efficiency versus the doped tin dioxide especially at higher current densities. This can also be seen in Figure 8, where the increase in reaction rate with applied current was found to be lower for the platinum electrode versus the doped tin dioxide, hence its efficiency drops off faster with increasing current density.

It can be seen from these estimates that, while current efficiency is important, the best current density at which to operate is influenced by the costs of the various cell components, component lifetimes, system lifetime, cell internal resistance etc. These values must then be combined with knowledge of the relationship between reaction rate and current density to calculate the minimum system cost. Thus it is important not only to identify the most efficient anode materials, but also to find the relationship between reaction rate and current

*Table 2.* Assumed parameters for system cost calculations

| Anode | Rate constant power curve fit (from Figure 8) /cm $\text{s}^{-1}$ | Anode arrangement | Real area/ projected area | Assumed cost |
|---|---|---|---|---|
| Tin dioxide | $k = 3.10 \times 10^{-6}\ i^{0.876}$ | coated flat plate and one piece of mesh | 3 | 1/2 of flat plate plus mesh ≈ C$2000 $\text{m}^{-2}$ |
| Platinum | $k = 1.97 \times 10^{-6}\ i^{0.677}$ | titanium flat plate and one piece of TySAR (3.175 mm thick) | 38 | 1/2 of flat plate plus TySAR ≈ C$4000 $\text{m}^{-2}$ |

Note: real electrode areas were estimated without considering the microscopic coating roughness.

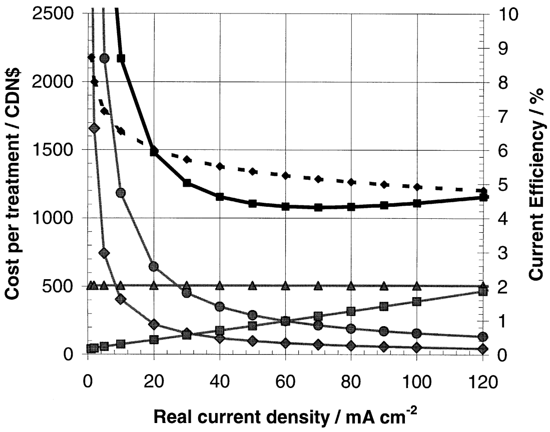

*Fig. 9.* Example of the impact of real current density on system costs using values for the doped tin dioxide coated anode. Key: (■ upper) total cost, (▲) fixed cost, (●) cell hardware, (♦) memb. + electrodes, (■ lower) power cost, and (- ← -) efficiency.

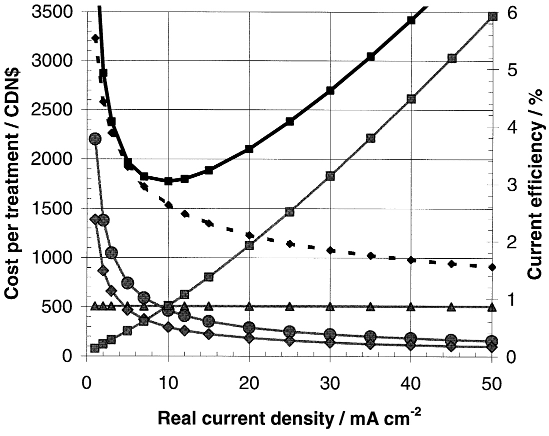

*Fig. 10.* Example of the impact of real current density on system costs using values for the platinum coated anode. Key: as for Figure 9.

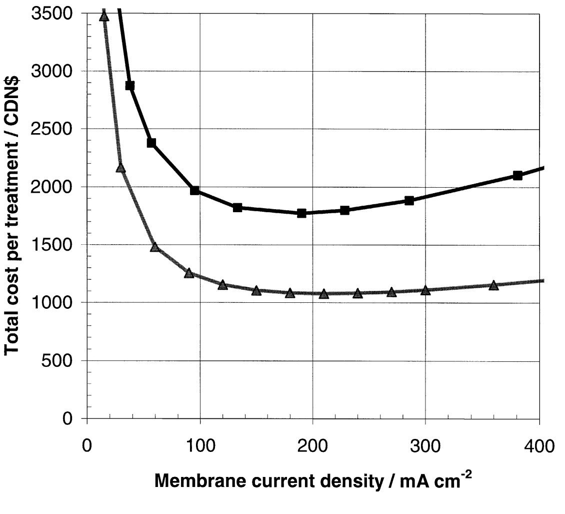

*Fig. 11.* Comparison of the total costs for the doped tin dioxide coated anode against the platinum coated anode as a function of the membrane current density. Key: (▲) tin dioxide and (■) platinum.

density (or potential) for each material (as has been suggested elsewhere [11]).

More work would, of course, be needed to refine these estimates and to decide if this electrochemical process could succeed. For example, data on the lifetimes of anodes and membranes at different current densities is needed. Different geometries and arrangements of the anode materials could be considered. The cell design will also have to be provided with some method for managing the slight leakage of copper through the membrane. One might as well want to also consider other costs, such as labour costs, to be able to compare such an electrochemical process to the existing plating solution treatment process. Finally work also needs to be done to investigate the quality of plating solutions after repeated treatment cycles, to ensure that problem compounds do not accumulate in such a closed loop system. (Some plating solution, lost through entrainment on the activated carbon, presently acts as a bleed on the plating line).

## 4. Conclusions

This work has successfully demonstrated that an electrochemical oxidation system can be used to decrease the TOC level in plating baths [12]. This oxidation of organic contaminants can be carried out with minimal disruption to the plating bath chemistry by careful choice of the anode, cell membrane, and catholyte composition. For the purposes of this initial study, a simple method based on an apparent first order rate was developed for normalizing data from different experimental set-ups and quantitatively comparing the performance of various anodes. This method was also extended to provide an initial rough estimate of the size, optimal current density and costs for a larger scale system. The results also highlight the need for a better understanding of the relationships between current density and the rate of organic oxidation, and the effect of current density on the corrosion rates of the anode coatings. The development of good quality mathematical estimations of these relationships would allow the electrochemical process be further optimized and more precisely evaluated.

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