



An electrochemical approach to total organic carbon control in printed circuit board copper sulfate plating baths

Part I: Anode performances

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Abstract

An electrochemical approach to decreasing high levels of total organic carbon (TOC) in printed circuit board (PCB) copper sulfate plating baths has been investigated. The 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 electrochemical approach involves destroying the organic contaminants using electrochemical oxidation. Various anode materials (glassy carbon, lead, lead dioxide, platinum, iridium dioxide and doped tin dioxide) were screened for this application. Some corrosion data is presented for these anodes and their performance for TOC removal at various current densities has been roughly quantified using an apparent first order rate constant. The three best performing anode materials gave increasing oxidation rates going from platinum to doped tin dioxide to lead dioxide, unfortunately anode stability decreased in the same order.

1. Introduction

In the course of printed circuit board (PCB) manufacturing, a common process involves building-up of copper lines to their required thickness by electroplating from copper sulfate baths (pattern plating) [1, 2]. As well as copper sulfate and sulfuric acid these plating baths contain organic additives (typically levellers, brighteners, and wetting agents) designed to improve the quality and speed of the electroplating. Over time, contaminants will build-up in the plating bath including: organic compounds leached from the printed circuit boards and in particular their photo resist, additive decomposition products, contaminants carried in on the surfaces of the boards from previous process steps ('drag in'), and airborne contaminants.

This slow contamination of the plating bath can be followed by monitoring the bath total organic carbon (TOC). At higher TOC levels the quality of the copper plating deteriorates (around 1800 ppm TOC for the baths tested in this work). This is characterized by a change in the crystal structure (from equiaxial to columnar) and loss in copper ductility. Copper lines plated under these conditions may fail when subjected to the thermal stress of soldering or after repeated thermal cycles (especially important for aerospace, automotive,

and military applications). Thus for quantitative quality control purposes, for a given process environment (i.e., given additives, resists etc.), the TOC values are often correlated to the thermal shock or elongation test data for the resulting plated copper.

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. Because of the 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.

Other methods that have been considered for treating contaminated plating baths include using ozone or hydrogen peroxide to oxidize the organic contaminants to CO₂. Hydrogen peroxide usually requires heating the bath mixture to get reasonable reaction rates and complete treatment, and in some cases still requires an activated carbon polishing step [1]. Ozone can be expensive for small-scale use (because of the costs for air or oxygen purification equipment [3]) and concerns

have been raised about metal dust contamination from the plasma arc electrodes [4]. The use of electrochemical oxidation does not appear to have been investigated. A key requirement for electrochemical oxidation of organic contaminants in these solutions is a material that is stable as an anode in strong sulfuric acid and also provides reasonable selectivity for the destruction of the target compounds versus oxygen evolution (i.e., high current efficiency).

2. Experimental details

Testing was carried out using a divided flow-by electrochemical cell (an AB Microcell from AB Electrocell) with the set-up shown schematically in Figure 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. The system used glass reservoirs, Teflon diaphragm type pumps, and Viton connecting tubing because of the corrosive nature of the solutions. For most runs a Tokuyama CMS-1 monovalent cation exchange membrane was used, though some tests were also carried out using a Tokuyama BP-1 bipolar membrane. 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.).

The iridium dioxide on titanium, platinum on titanium, lead, glassy carbon, and 316 stainless steel electrodes used in this work were obtained from AB Electrocell. TySAR-EP (made by the Olin Corp.) and Permelec (made by the Permelec company) electrode materials were obtained through the Electrosynthesis Co. Doped tin dioxide coated titanium anodes were obtained from the Eltech Co. Lead dioxide electrodes

(other than Permelec) were prepared by depositing PbO_2 from a solution of 1.6 M HNO_3 and $0.26 \text{ M Pb(NO}_3)_2$ at 10 mA cm^{-2} onto either an iridium dioxide anode or an Eltech doped tin dioxide anode. Also lead 6% antimony alloy electrode material (1/16 inch thick, rolled) was used.

The high TOC test solutions were provided from one of the plating lines of a local printed circuit manufacturer. The solutions were typically around $200 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$, 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. For some experiments, solutions were analysed by ICP-MS to check for anode corrosion products (the samples were sent to an external laboratory).

3. Results and discussion

3.1. Initial anode screening

A number of commonly available anodes were screened for activity and stability. This was done using the flowcell system with an anolyte volume of 100 ml of high TOC plating solution, a catholyte of 100 ml of $2 \text{ M H}_2\text{SO}_4$, and an applied current of 250 to 500 mA with an exposed anode area of 10 cm^2 and test runs lasting about 24 h. Glassy carbon and lead anodes were found to be severely corroded. Both iridium dioxide and platinum showed no visible corrosion, while the lead dioxide anode showed some dissolution. This being observable by etching of the surface, and lead sulfate crystals depositing on the electrode surface and in the system reservoir. The performances for the latter three anodes for TOC removal are shown in Figure 2. It can be seen that the current efficiency for TOC removal is significantly higher for the lead dioxide anode. This

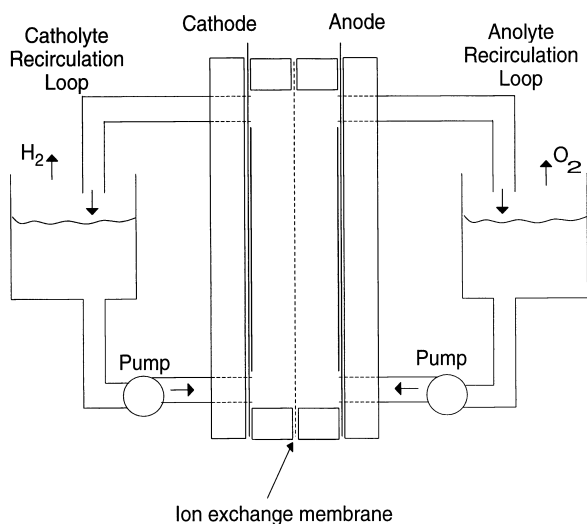


Fig. 1. A schematic of the flowcell test system.

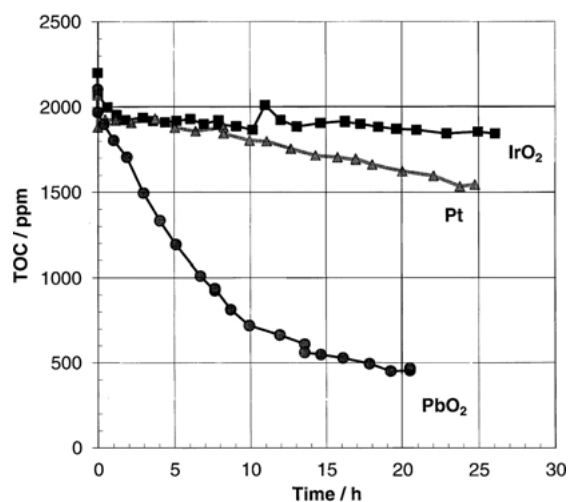


Fig. 2. Performance of various anode coatings for TOC removal for plating solution recycle (10 cm^2 anodes, 50 mA cm^{-2} , 100 ml solution).

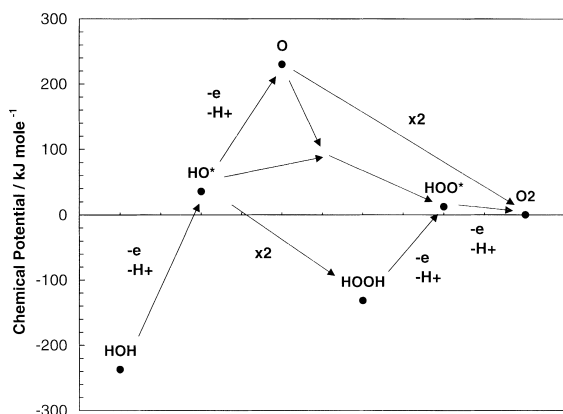


Fig. 3. Various possible oxygen evolution intermediates and their chemical potentials in their unassociated/unadsorbed forms.

result is consistent with ideas related to electrochemical oxidation of organic compounds developed in previous literature.

The electrochemically driven oxidation of organic compounds can occur through direct electron transfer, redox reactions with anode surface oxides, and/or reactions with oxygen evolution intermediates. These three mechanisms are also interrelated. Figure 3 shows various possible oxygen evolution intermediates and their chemical potentials in their unassociated/unadsorbed forms (with the values taken from Pourbaix's 'Atlas' [5]). It can be seen that unless an adsorbed or associated form of the oxygen evolution intermediates occurs, a large amount of energy would be required to form the hydroxyl radical from water, and a further large amount of energy to form atomic oxygen from the hydroxyl radical. Thus it is generally felt that anode coatings of metal oxides with available higher valent states (like $\text{IrO}_2/\text{IrO}_3$), which can stabilize atomic oxygen thus lowering the required energy for its formation, will catalyse oxygen evolution [6]. Other metal oxides, without higher valent states, (like PbO_2) will have a higher overpotential for oxygen evolution. Also when oxygen evolution does occur, because the formation of atomic oxygen would be more difficult, the product of the previous mechanistic step (hydroxyl radical) will build up to a higher coverage. This greater availability of hydroxyl radicals is felt to be important for the electrochemical oxidation of organic compounds [7, 8]. Other factors that may also play a role are the higher anode potential, and the reactivity of the oxygen evolution intermediates at various electrode materials (related to their adsorption state). Other factors, unrelated to oxygen evolution, may also play a role in the oxidation of the organic compounds such as their adsorption at the electrode surface, and mediation by dissolved metal ions (if the anode corrodes). Oxygen evolution at platinum has been reported to change from uncatalysed to catalysed when the potential becomes sufficient to form a higher valent platinum oxide [9]. Thus on the basis of these ideas the performance differences observed in Figure 3 seem reasonable.

3.2. Quantification of electrooxidation performance

Following this preliminary screening, it was decided to investigate platinum more closely, it being the more efficient of the two more stable anodes. Because the solutions were to be recycled, they could not be altered chemically, so the main variable available for control was current density. To study a range of current densities and yet retain a reasonable treatment time, the lower real current densities were obtained, as much as possible, by using larger electrode areas (thus retaining reasonable total current values). This was done using high surface area electrodes made from Olin Corp. 'TySAR-EP'. This material is made by electrolessly depositing platinum onto a mat of sintered titanium fibres [10] and the material was spot-welded onto a titanium backing plate for testing. (Note: the spot-welding was done under argon, as recommended by the manufacturer, due to the high surface area of titanium involved and the potential fire hazard). The various resulting reaction conditions used are listed in Table 1.

This raised the issue of how to quantitatively compare results from experiments with different electrode areas, volumes, and ending TOC concentrations. Quantitative data is also needed in order to provide an initial estimate of equipment size and operating conditions for a given target performance. A complicating factor in trying to quantify the results is the unknown nature of the organic contaminants. Many of the plating additives and photoresists are proprietary, and the additive decomposition and photoresist leaching and decomposition chemistries are complex. The electrooxidation pathways of these compounds will also be complicated, producing more unknown compounds (discussed more in Part II). This makes fundamental electrochemical parameters difficult to evaluate.

The approach taken involved assuming that the rate of removal of TOC at a given current density was primarily dependent on the TOC level. (This assumes that the experiment is not current limited). In other words the approach involves using an approximate first

Table 1. Experimental conditions for platinum current density measurements

Electrode	Projected area /cm ² cm ⁻²	Projected current density /mA cm ⁻²	Real current density /mA cm ⁻²
Platinized titanium plate	1	250	250
Platinized titanium plate	1	50	50
TySAR-EP 10% dense	19	200	10.5
TySAR-EP 15% dense	28.6	50	1.75
TySAR-EP 15% dense	28.6	10	0.35

Where, for the TySAR, the density represents the volume fraction of the electrode that is titanium fibre and the surface area to volumes used are manufacturer's data for the titanium fibre surface (the manufacturer suggests that the nodular surface of the platinum deposit is possibly 2 to 3 times higher).

order rate constant for the TOC removal, which can be written for a batch system as

$$V \frac{dC}{dt} = -AkC \quad (1)$$

and

$$k = -\frac{V}{At} \ln\left(\frac{C_t}{C_0}\right) \quad (2)$$

where k is the apparent rate constant, A and V are electrode area and solution volume respectively and C_0 and C_t are the concentrations of organic carbon initially and at time ' t ', respectively.

Because the work was for an industrial application, galvanostatic operation was used. In such a case one can rearrange Equation 2 and substitute charge (Q) for iAt yielding:

$$\ln\left(\frac{C_t}{C_0}\right) = -k\left(\frac{At}{V}\right) = -\frac{k}{i}\left(\frac{Q}{V}\right) \quad (3)$$

Thus a plot of logarithm of TOC against the charge per volume should yield a slope dependent on the rate constant for removal of organic carbon and on the current density. If one is not operating in a mass transfer controlled region, k will be based on chemical and/or electrochemical rate constants, and so the value k/i with units of volume per charge will be sensitive to the type of anode material. This can be related to electrochemical efficiency for the galvanostatic case by

$$\begin{aligned} Eff = EOI &= \frac{nFV(C_0 - C_\tau)}{iA\tau} \\ &= nF\left(\frac{k}{i}\right)\left(\frac{C_0 - C_\tau}{\ln C_0 - \ln C_\tau}\right) \\ &= nF\left(\frac{k}{i}\right)C_{\ln} \end{aligned} \quad (4)$$

where EOI is the 'electrochemical oxidation index' as defined by Comninellis [11], n is the average number of electrons to oxidize each carbon to CO_2 , τ is the runtime, and C_{\ln} is the logarithmic mean of the concentration. (Such logarithmic means commonly occur in macroscopic mass and heat balances over systems with large changes in the key parameter [12]).

This approach involves two key assumptions. One involves the use of A/V or Q/V to normalize results. This is only valid if the reaction per unit electrode area is unaffected by the solution volume. Two cases where this may not be true are when there is significant oxidation of the organic compounds by, for example, dissolved oxygen in the bulk, or when adsorption of some key component of the reactant mixture at the electrode surface occurs to a sufficient extent to alter the bulk solution concentration. The second key assumption is that of an unchanging rate constant. In fact the rate

constant is expected to vary with anode potential, anode surface changes (e.g., fouling, changes in an oxide film etc.), and reactant composition. For galvanostatic operation, the assumption improves when the organic oxidation reaction has a low efficiency and hence changing concentrations of the organic compounds have little effect on the anode potential. Similarly, if the organic compounds react mainly with oxygen evolution intermediates, the anode potential may be determined by the initial water discharge step common to both the oxygen evolution and the organic oxidation. Thus, the anode potential would be less influenced by changes in the concentrations and types of the organic compounds. Also if the products of the oxidation of the initial organic compounds react much more easily than the initial reactant, their influence on the rate of TOC removal will be lessened (in the most extreme case, no intermediates would be obtained).

This approach, while not completely satisfactory from a fundamental point of view, is useful when dealing with complex and often unknown industrial solutions. The relationships are particularly useful for wastewater treatment applications where efficiencies are commonly low and one often needs to evaluate and predict the performance of an electrochemical system over a large reactant concentration range. The equations also allow data from different cells and measured with different starting and ending concentrations to be, albeit approximately, compared. Finally the approach provides a good diagnostic tool because, when the plots do not yield reasonably straight lines, it indicates that one of the factors mentioned above is playing a significant role.

3.3. Detailed testing of promising anodes

The results of the various platinum current density tests are shown in Figure 4 plotted as logarithm of TOC versus charge per litre. It can be seen that there is a large increase in coulometric efficiency with decreasing cur-

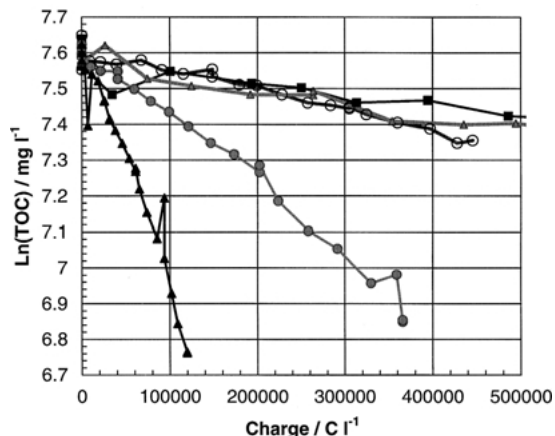


Fig. 4. TOC removal from plating bath solutions using platinum coated anodes at various current densities (100 ml solution; other conditions in Table 1.) c.d.: (■) 250, (○) 50, (▲ upper) 10.5, (●) 1.75 and (▲ lower) 0.35 mA cm⁻².

rent density. The only exception to this trend was the run at 10.5 mA cm^{-2} . However, inspection of the anode at the end of that run under an optical microscope revealed that most of the electrolessly deposited platinum nodules had been removed from the electrode surface. Thus the real current density at the remaining platinum would have increased as the run progressed. Thus for the 10.5 mA cm^{-2} run, only data before $190\,000 \text{ C l}^{-1}$ (the point at which the slope flattens noticeably) was used for characterizing platinum as an anode coating.

To see the longer term performance of this type of electrode, experiments were carried out using 10 cm^{-2} of 15% dense TySAR-EP with a total current of 250 mA giving a real current density of 0.875 mA cm^{-2} . The volume of solution to treat was increased to 500 ml. Two runs with the same anode but different batches of high TOC plating solution are shown in Figure 5. In both cases the TOC could be decreased to 400 ppm or less after around $850\,000 \text{ C l}^{-1}$. These combined runs represent 1050 h of operation for the anode. As was seen in the earlier PbO_2 results in Figure 2, there is some small amount of TOC that is more difficult to remove (~ 300 to 400 ppm, visible at the end of the batch 1 run).

As well as existing commercially available electrode materials, we were able to obtain (part way through this work) experimental antimony doped tin dioxide coated anodes from the Eltech Corporation. Work has also been reported with this Eltech material for use in oxidation of chlorophenols [13] and Eltech has a patent on their application to sewage treatment [14]. Similar materials have also been reported previously [15–17]. However, because our objective in this work was to investigate the possibility of a commercial electrochemical process, we had not pursued this material until we became aware of a possible commercial supplier. Anodes were obtained of both flat plate and flattened expanded mesh (1 mm thick, long way of design 13 mm, short way of design 7 mm, and an area of about

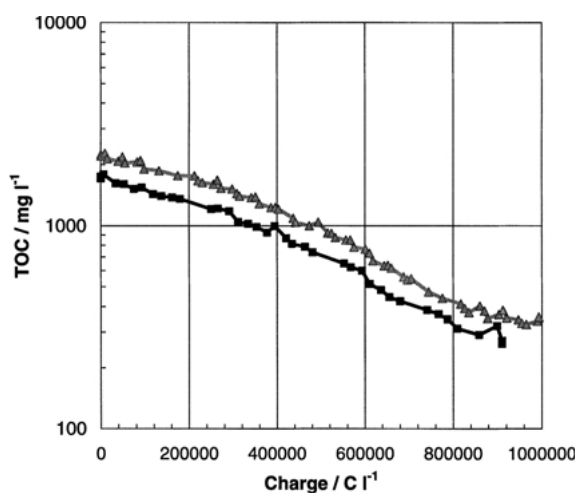


Fig. 5. TOC removal from plating bath solutions. Extended runs with a TySAR 15% EP anode, 500 ml anolyte, 25 mA cm^{-2} projected, c.a. 0.9 mA cm^{-2} real current density. Key: (▲) batch 1 and (■) batch 2.

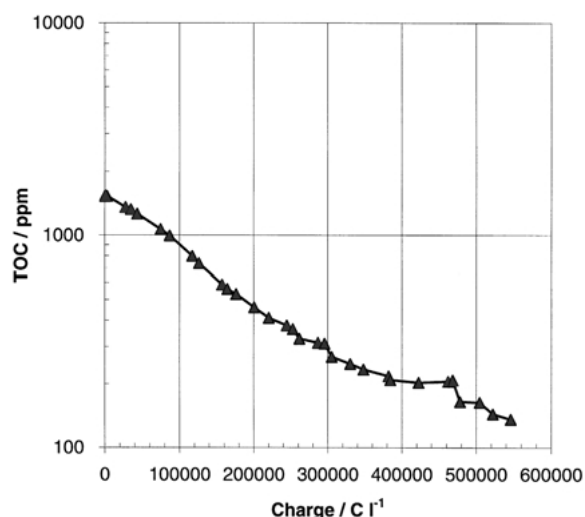


Fig. 6. TOC removal with a doped tin dioxide anode. (500 ml anolyte, 10 cm^2 flat plate, 25 mA cm^{-2}).

$1.3 \text{ cm}^2 \text{ cm}^{-2}$ counting both faces and ignoring the coating microroughness).

These electrodes gave very good TOC removal rates as can be seen in Figure 6, where the TOC is brought down to a few hundred ppm using roughly half the charge per litre of solution required for the platinum electrode (in Figure 5). A number of batches of doped tin dioxide anodes were tested with various batches of plating solutions. While the anode typically showed higher rates for removal of TOC, the performance showed a higher degree of variability than was found with platinum. The variability appeared not only in the rate of TOC removal, but also in the steady-state anode potential, and in the anode stability. (With a higher steady-state anode potential generally being associated with a higher TOC removal rate). Such variability was also observed with different samples cut from the same test piece (typically a 10 cm by 10 cm mesh). The Eltech coating process is proprietary and so analysis of anodes was not permitted, however based on the literature some speculations can be made. One possible source of variability is the difficulty of controlling the relative amounts and distributions of tin and antimony in the coating. It has been reported that the ratio of antimony to tin in electrode coatings will vary from that in the starting coating solutions [18] possibly due to their different volatilities [19]. This will be sensitive to parameters such as temperature and convection that will be more difficult to control when large quantities and large sizes of electrodes are made. Other factors in the coating process may also play a role. While this does not present an insurmountable problem, it does suggest that there would be some challenges to overcome if this type of anode was to be made in commercial sizes and quantities.

Because of the variability of the electrodes it is difficult to make general statements about their performance. However, it was noted that some electrodes

showed a decrease in the rate of removal of TOC after being left in solution at open circuit, after repeated treatment runs, or after polarization at lower potentials. The latter case was observed when carrying out a mass transport performance measurement on a stacked mesh anode by polarization in a ferri/ferrocyanide solution. TOC removal tests with that anode following the polarization in ferri/ferrocyanide showed a decrease in the rate constant of about 4 times.

Thus it seems that the efficiency of the doped tin dioxide anode coating (i.e., its selectivity for oxidation of the organic compounds versus oxygen evolution) is very sensitive to the state of the electrode surface. Some possible factors affecting current efficiency induce the dopant level, the surface hydration, the oxide structure (e.g., vacancies, grain size and defects) and macroscopic characteristics (e.g., surface porosity and the uniformity of surface properties). The dopant level is important because while it greatly improves the oxide conductivity when in solid solution, it has a negative impact when its solubility is exceeded (at 3–4 at % [20]). There has also been some speculation, related to doped lead dioxides, that the dopants can act as sites for catalytic production of hydroxyl radicals [21] or as sites for adsorption of organic reactants allowing them to interact with oxygen evolution intermediates [22]. In any case, better understanding and control of the key factors affecting the performance of these electrodes is important.

Testing was also done on different types of lead dioxide type anodes. As well as the in-house PbO₂ coated on either IrO₂ or doped SnO₂ coated titanium anodes, Permelec (a commercial PbO₂ coated anode) and lead 6% antimony rolled alloy anode were also tested. All the lead based electrodes provided similar rates of TOC removal, and the rates were better than either the platinum or doped tin dioxide anodes.

The Permelec anode coating was finer grained with a more powdery appearance than the in-house coatings. On polarization, some physical loss of fine coating particles was observed leaving a few black particles in the anolyte. The resistance of the Permelec coating to delamination was found to be superior to the in-house coatings. After testing, both types of coating were

observed with an optical microscope to have white crystals (believed to be lead sulfate) on the electrode surfaces indicating some loss of lead ions into the anolyte. This loss of lead from the PbO₂ coating is consistent with the slight solubility of lead(IV) in strong acid [5], and corrosion rates for similar anodes that increase with increasing acidity and current density [23].

The lead 6% antimony alloy anode quickly formed a PbO₂ coating upon polarization in the plating solution, but after about 24 h (about half way through the plating solution treatment) the anolyte began to become progressively darker as fine black particles fell from the anode and built-up at the bottom of the cell. While such anodes are routinely used for copper electrowinning, it has been reported that the anode shows a higher than normal amount of PbO₂ coating spalling when the sulfuric acid concentration is increased from 150 g l⁻¹ or less, to 200 g l⁻¹ [24]. The addition of 100 ppm cobalt to the plating solution, which has been reported to reduce the coating spalling [24] from such anodes was also tried. The cobalt resulted in a much more stable anode, but a significant amount of black powder still appeared in the anolyte over the course of a TOC treatment experiment.

Some testing was also done to obtain an idea about the possible stability of the platinum and doped tin dioxide anodes. Table 2 shows results from induced coupled plasma mass spectroscopic (ICP-MS) analysis of treated solutions from some test runs. For each case the measured concentration increase has been converted to a corrosion rate. Although this is only a single set of data from relatively short experiments, one can see approximately what range of coating thickness might be needed to obtain a reasonable anode lifetime.

It is also interesting that the starting high TOC solutions showed significant levels of tin and antimony. This is thought to be due to the presence of lead, antimony, and tin in the anodes used in electrowinning of the copper which, following electrorefining, is then used for the dissolving anodes used to replenish the plating bath copper levels [25, 26]. Finally it is interesting that the tin dioxide coating shows tin and antimony corrosion rates at open circuit that are not significantly

Table 2. ICP-MS solution analysis results

Test conditions	Metal	Start value /ppm	End value /ppm	Corrosion rate /mg cm ⁻² year ⁻¹
A. Doped tin dioxide at 25 mA cm ⁻²	Tin	20	22	3.0
	Antimony	0.41	0.83	0.64
B. Doped tin dioxide at open circuit	Tin	20	23	4.5
	Antimony	0.41	0.85	0.65
C. TySAR 15% EP at 25 mA cm ⁻² projected	Platinum	0	3	0.07

A. 25 mA cm⁻², 12 day run, 10 cm² flat plate, 500 ml solution.

B. Open circuit, 2 days, 1.23 cm² flat plate, 10 ml solution.

C. 25 mA cm⁻² projected (c.a. 0.9 mA cm⁻² real), 23 day run, 10 cm² × 0.3175 cm fibre mat (c.a. 286 cm²), 500 ml solution (Real area used for corrosion rate calculation).

different from those found when polarized. The data for the tin in solution should be used with caution, however, because of the very low solubility of tin(IV). During some experimental runs a small amount of a reddish paste was noticed in the foam that appeared at the top of the anolyte in the early stages of the treatment. Energy dispersive X-ray analysis indicated the paste contained sulfur, chloride and tin. Thus the true corrosion rate for the tin anodes may be significantly higher than that indicated by the ICP solution analysis.

Besides the anode lifetime, a second concern is the possible effects of the corrosion products on subsequent plating from the treated solutions. For example, it is recommended for PCB plating that tin be kept below 300 ppm and antimony below 25 ppm [1]. In the case of tin this is due to the possible formation of colloidal stannic acid that can adsorb on the cathode and lead to poor copper adhesion [2]. For lead, the upper concentration limit is due to its insolubility, which can result in lead sulfate crystals in the plating bath, causing roughness in the plated copper. However, other than these sorts of physical effects, copper plating is generally fairly tolerant of metal ion contaminants because few metals will deposit under similar conditions [2].

The rate constants for TOC removal obtained of the course of this study for different batches of electrodes and of high TOC solutions, both using the flowcell and the H-cell, are compiled in Figure 7. The rate constants have been plotted as a function of current density. The resulting relationships between reaction rate and current density are likely related to the competition for oxygen evolution intermediates between organic oxidation and oxygen evolution [27], as well as direct electron transfer reactions, and so may be quite complicated. For simpler systems, however, such a plot might provide insight into the interactions between the oxygen evolution and organic oxidation mechanisms. It can be seen in Figure 7 that the different anode coatings provided

different rates of TOC decrease for a given current density. Lead dioxide coated anodes were most effective at decreasing the plating solution TOC, then doped tin dioxide, then platinum, and finally iridium dioxide coated anodes. The current efficiency of the doped tin dioxide electrodes also appears to be less sensitive to current density than the platinum anodes (a curve showing a 10 times increase in rate for a 10 times increase in current density would indicate no change in current efficiency with current density). It should also be noted that a mass transfer controlled process would show a rate independent of current density, and so a horizontal line on this plot.

4. Conclusions

This work has successfully demonstrated that an electrochemical oxidation system can be used to decrease the TOC level in plating baths, with values as high as 1500 to 2000 ppm TOC being decreased to a few hundred ppm TOC. 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. Based on this the best anode was lead dioxide coated anodes, then doped tin dioxide, then platinum, and finally iridium dioxide coated anodes. The electrode stabilities appeared to follow roughly the opposite trend, with lead dioxide anodes showing visible corrosion, doped tin dioxide anodes showing somewhat better stability (with this being sensitive to the electrode coating method), and platinum and iridium dioxide showing good stability. To choose the best anode for this process would require additional work to better understand the factors related to the different electrode performances, and to better quantify electrode stabilities and lifetimes and the impact of their corrosion products on subsequent plating using the electrochemically treated plating solutions. Finally, as in any case where a process becomes more closed (i.e., with fewer discharges), longer term testing is required to determine if any contaminants build-up in the process over repeated treatment and plating cycles.

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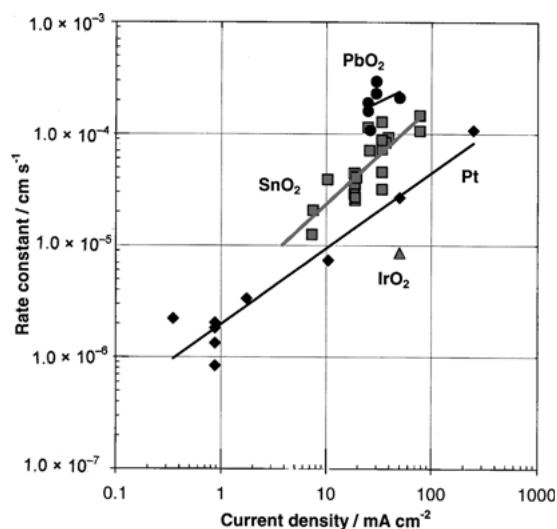


Fig. 7. TOC removal rate constants as a function of current density for various anode materials.

with Drs Thierry Guena, Eric Rudd, Laurie Wang, Christina Bock and Richard Menini.

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