ELECTROLYTIC REGENERATION OF ACID CUPRIC CHLORIDE
PRINTED CIRCUIT BOARD ETCHANT

by

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Final Report
August 1 1995 - October 31, 1996

Grant No. DE-FG01-95EE15650
Department of Energy

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April 18, 1997

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I. SUMMARY

The overall objective of this ERIP program was to make substantial progress in further developing a process for electrolytic regeneration of acid cupric chloride etchant - a process which was initially demonstrated in in-house studies and EPA Phase I and Phase II SBIRs. Specific objectives of the work were: (1) to define optimum system operating conditions by conducting a systematic study of process parameters, (2) to develop or find a superior electrolytic cell separator material, (3) to determine an optimum activation procedure for the flow-through carbon/graphite felt electrodes which are so critical to process performance, (4) to demonstrate - on the pre-prototype scale - electrolytic compensation for oxygen ingress - which causes etchant solution growth, and (5) to begin engineering design work on a prototype-scale regeneration unit.

Parametric studies looked at the effect that key plating parameters have on copper deposit quality. Parameters tested included (a) velocity past the plating cathodes, (b) copper concentration in the catholyte solution from which the copper is being plated, (c) plating current density, and (d) catholyte cupric ion concentration. The most significant effects were obtained for velocity changes. The work showed that catholyte velocities above 0.5 ft/sec were needed to get adequate plating at 77.5 mA/cm² and higher currents, and that even higher flow was better.

The search for a superior cell separator material began with plasma-treated and radiation-grafted porous polyolefin plates and development of a hydrophilicity test. Plasma-treated polyethylene lost its hydrophilicity after soaking in etchant and was unsatisfactory, while radiation grafting never succeeded for polypropylene. A reasonably-priced alumina-rich porous ceramic from Refractron Technologies was identified and found to be chemically compatible with the etchant.

We compared the performance of graphite felts that were furnace and steam activated and found that steam activation gave longer operating life and higher current carrying capability. Carbon felt activated in the same way as graphite felt had similar performance in initial limiting current testing. Extended steam activation time produced better early operating performance. Moderate temperature steam activation also showed promise as a way of reactivating felt/graphite plate electrodes whose behavior had deteriorated.

Bench scale tests, using 1" x 2" active area electrolytic cells showed that new, low resistance T&G proton permeable membranes, permitted too much "leakage" of Cu²⁺ and SO₄²⁻ ions to be used for oxygen ingress compensation. That testing also indicated that even the baseline membrane (formulation # 14118) was a variable product and needs more development. We were able to use that membrane in tests of a newly constructed 3" x 3" active area, oxygen ingress compensation cell setup to run with the pre-prototype scale regenerator. Though the new cell successfully reduced Cu²⁺ produced by the regenerator to Cu⁺ in over 3 hours of continuous operation, the unit showed high resistance (power to 20 volts) when operated at more than 1.5 Amps, probably because of O₂ buildup between the ceramic separator plate and the membrane.

The requirement to use plating cell cathode velocities approaching 1 foot/sec in the prototype design to enable reasonably high plating currents, has a major effect on system design - the need to use pressurized cell chambers. That raises the concern of electrolyte leakage. To learn whether a gasketed stack assembly with individual cell covers would allow leak free operation, we rebuilt the pre-prototype scale regenerator plating cell to test pressurized solution flow. Actual pre-prototype scale regeneration runs with copper deposition showed that the design techniques used to hold pressure in the pre-prototype unit worked and could be employed in the prototype design.

II. INTRODUCTION

Acid cupric chloride etchant is used widely in printed circuit board fabrication, in particular to produce the innerlayers of multilayer boards. The overall reaction during etching of copper by this etchant is:

The CuCl_2 concentration in commercial spray etching machines is typically around 300 g/l, while the concentration of Cu^+ is maintained in the range 1 - 2 g/l. Printed circuit board etching rates achieved with acid cupric chloride are 25 to 35 microns/min. This rate is dependent on concentration of Cu^+ ions, and is strongly retarded where Cu^+ concentration is above about 2 g/l.

In an "ideal" electrolytic regeneration process, reaction (1) should be exactly reversed. Copper metal etched into the system is continuously removed, while the cuprous chloride produced is turned back into cupric chloride thereby maintaining concentrations of cupric and cuprous ions at their initial, high etch-rate values. At the cathode of the "ideal" regenerator, Cu^+ is reduced to the metal (and Cu^{2+} is reduced to Cu^+), while at the anode, Cu^+ is oxidized to Cu^{2+} .

Our program to develop an electrolytic regeneration process for acid cupric chloride was initiated at Oxley Research in the fall of 1990 with in-house funding. From July through December 1991 the effort was supported by an SBIR Phase I contract from the Environmental Protection Agency. A follow-on Phase II contract was initiated in September 1992 and was completed at the end of September 1994. The Company was awarded a 2-year SBIR Phase III contract by EPA in September 1995. The present ERIP contract has been in support of the continuing development of the process.

Our original study of problems involved in electrolytic regeneration focused on the difficulty that other investigators had in anodically converting low concentration cuprous ion in the etch solution back to cupric at reasonable rates without exceeding that reaction's limiting current and thus generating Cl_2 . We ran early bench-scale tests with cells - first with 2" x 1" electrodes and later with 4" x 3" electrodes - based on flow-through graphite felt anodes, and flow-by graphite cathodes using etch solution as electrolyte in both cell chambers. Flow-through electrodes offer considerably improved efficiency in terms of solution-phase mass transfer, compared to flow-by electrodes, because of high active surface areas internal to the felt material.

The principal difficulty encountered in early work on this system was the strong tendency for dendritic copper deposition from the etchant. This causes formation of a rough, higher surface area cathode substrate which progressively lowers the real current density at the cathode. An increasing fraction of the applied current is thus consumed by the reduction of cupric to cuprous while correspondingly less goes to copper deposition, resulting in a progressive decrease in current efficiency. As a result, the maximum run duration in this mode was limited to six hours. Increasing the cell current had the effects, firstly of exacerbating dendrite growth, and secondly of overstressing the capabilities of the flow-through anode, necessitating very high anolyte flow rates to avoid that electrode polarizing into the chlorine evolution region.

Dendrite propagation can often be averted by use of high electrolyte mass transfer rates. In the present system involving two consecutive electrochemical reductions, i.e cupric to cuprous followed by cuprous to the metal, this is only practical if deposition is caused to occur predominantly from the cuprous ion. The challenge therefore was to devise a system wherein copper could be plated out continuously from an electrolyte containing predominantly cuprous, while the etchant solution itself was predominantly cupric.

This was accomplished by means of a two-cell scheme, consisting of a "knockdown cell" where the cathode reaction is reduction of cupric to cuprous, and a "plating cell" where cuprous is reduced to the metal. A "catholyte control tank" feeds the cathode sides of both cells. The solution in this tank is predominantly cuprous, with cupric concentration being held at 0.5 - 1 g/l by the knockdown cell. Solution copper content remains constant since the copper is replenished with etch solution make-up. The anode side of both cells is fed from the etchant sump, and here the reaction is the oxidation of cuprous to cupric. The knockdown cell's anode and cathode are each flow-through graphite felt electrodes because of the low concentration of the ion whose reaction is being promoted at each electrode. The plating cell on the other hand has a flow-through graphite felt anode and a flow-by graphite plate cathode.

A pre-prototype scale unit based on this concept, with a copper removal rate of 14 gram/hr, was built and successfully demonstrated during our EPA SBIR Phase II contract. The copper deposits were uniform (same thickness over entire cathode area), and though grainy, were easily peeled off the 3" x 4" plating area in a single piece.

Another regeneration process issue concerns the effects of oxygen ingress at the spray etcher. Oxygen from the air will oxidize Cu^+ to Cu^{2+} via the reaction:

Although at first sight this might be viewed as a desirable reaction, since it restores cupric, the net effect is the same as chemical regeneration with e.g. hydrogen peroxide; it produces excess etchant solution which has to be disposed of. Depending on tightness of the spray etcher design, the magnitude of oxygen ingress may amount to 5% of the copper throughput.

For convenience, equation (2), albeit a homogeneous reaction, may be split into its component anodic and cathodic half-cell reactions as follows:

One way to reverse the oxidation reaction is to use an auxiliary electrolytic cell wherein the anodic reaction is oxygen evolution (reaction (3)), from e.g. H_2SO_4 , and the cathodic reaction is Cu^{2+} reduction to Cu^+ (reaction (4)).

Key to success of this approach is use of an "electropermeable" membrane developed by T & G Corporation in Lebanon, Connecticut. These membranes consist of a hydrogel dispersed in an inert non-porous plastic matrix and are selectively permeable to protons when these species are liberated at the anode during oxygen evolution. Other ionic species do not pass through the membrane at an appreciable rate. Non-ionic solvent species, e.g. water, are similarly prevented from being transported through the membrane.

The overall objective of the ERIP program was to provide further process and materials development and optimization, leading to the design and construction of an engineering prototype regenerator.

Contract effort has involved the following areas of work:

- o Parametric studies to define optimum system operating conditions. This has included studying ranges of current densities and flow rates in the plating cell, and copper concentration and cuprous/cupric ratio in the catholyte control tank.
- o Development of an improved separator assembly. In the pre-prototype unit cells, we employ a 15 mil microporous polyethylene separator (Daramic, Inc.) which in our initial design was laid on a rigid, 1/4" thick porous polyethylene plate to provide structural support for the flow-through graphite felt electrodes and avoid electrolyte channeling around their sides. We had to periodically treat the 1/4" polyethylene with a surfactant to make it hydrophilic. That treatment however wears off, and potentially permanent solutions have been explored during the ERIP contract.
- o Determination of optimum activation procedures for the graphite felt, flow-through electrodes. Achieving and maintaining sufficient electrocatalytic activity for reduction of cupric to cuprous and oxidation of cuprous to cupric are crucial for the ultimate success of this program.
- o In order to demonstrate electrolytic compensation for oxygen ingress, we constructed an appropriately sized flow cell in conjunction with the main etchant tank of our pre-prototype system. The separator in this cell was an "electropermeable membrane", sandwiched between two layers of Daramic for increased strength.
- o Finally we carried out design studies in support of construction of an engineering prototype having a copper recovery capacity of 2.5 kg/hr which is to be tested in conjunction with a commercial spray etcher.

III. RESULTS AND DISCUSSION

1. Plating Parameters Studies

One of the major goals of the project work was to study the effect that changes in some of the key process parameters have on deposit quality and other process measurements.

One parameter, whose importance was seen in a pair of runs just prior to the start of this grant effort, is catholyte velocity past the plating electrode. In those runs, we installed an "eggcrate" gap-filler in the plating cell cathode chamber and got dramatically improved deposits. The eggcrate assembly that we built - shown in Figure 1 - fills almost 2/3 of the gap cross-section with pockets of still electrolyte, thereby increasing velocity past the cathode by a nominal factor of 2.5. Using the "eggcrate" gap reducer is an inexpensive and easy way to get higher velocities in the pre-prototype test system's plating cell since it avoids the need to make new, thinner, chamber frames or fatter center separator plates, or to have to handle significantly higher flow quantities through the cathode chamber.

To study the velocity effect in a more systematic way we made a series of additional runs with and without the "eggcrate" assembly. A first set of 3 runs was done at 6.2 A plating current. There velocities varied from 0.37 to 0.52 to 1.35 ft/sec. The deposit quality was much better at the high velocity. Grains on the surface were significantly smaller at 1.35 ft/sec than at the lower flow rates, indicating that additional hours of plating would be less likely to grow dendrites there. All deposit coupons were fairly uniform in thickness, indicating uniform current densities.

Another group of runs was made at 7.5 A plating current and flows of 0.54, 0.96 and 1.48 ft/sec. Again the deposit is finer (smaller grains) at the highest velocity and poorest (coarsest grains) at the lowest velocity, although the gradation from best to worst was not as dramatic as at the lower current plating. Again, deposit plates were uniform in thickness and appearance. The velocity variation data clearly show the advantages of higher flow rate. With the higher flow rate it is possible to get better deposits at higher current densities than would otherwise be possible. This translates to smaller plating areas at a particular copper deposition rate requirement, i.e lbs/hr, and thus fewer (or smaller) cell modules. The reduced plating surface comes at the price of handling more gpm through each plating cell cathode module. Since the space available to install inlet and outlet lines on these modules is little different from pre-prototype to commercial scale unit - set to a great extent by the 3/8" gap needed to accumulate a day's copper deposit with space still left for flow past the cathode afterwards - this probably means pressurized cells and more difficult cell sealing.

A second plating parameter we looked at was the overall concentration of copper in the catholyte. It is known in plating that generally higher concentrations of the species being plated favors production of an improved deposit. We made runs at both 6.2 and 7.5 Amps where we employed concentrations of 21-23, 32-34, and 41-42 g/l of total copper in the catholyte at fixed flow rates. Each set showed the expected improved deposits with increased concentration, however differences in quality (smaller grains at higher [Cu]) were modest. Doubling of concentration (21-23 to 41-42 g/l) had much less effect on deposit quality than doubling flow rate in the tests described above. Increased copper concentration results in lower electrical efficiencies in our process - all other things being equal- since each gallon of etch fed to the catholyte to replenish copper plated has to also provide copper to replace the cuprous in the gallon of catholyte that is removed to make room for the incoming etch. That means more total electrolysis is needed at high catholyte copper/high replenishment than at low copper/low replenishment. It doesn't look like the highest copper concentrations pay the increased current cost - not to mention the increased precipitation possibilities - with enough deposit improvement to make them worthwhile.

Much of the work on this project has been done to evaluate the effect of plating current density, with the goal being to get good plating quality at increasingly higher currents. In this study, we looked at how plating varied over the range of 6.2 A (80 mA/cm²) to 8.7 A (112 mA/cm²). In the runs made to do this, all other important parameters were held essentially constant (flow of 0.96 ft/sec, and [Cu] at 21-22 g/l). As expected, deposit quality fell off with increasing current density, though not to a dramatic extent. It appears that the higher flow rate used for these runs was able to mitigate the effects of increased current density to a significant degree. The increase in roughness - larger deposit grain size - with current was significantly less than in earlier studies where increases in current density from 4.2 A (54 mA/cm²) to 6.2 A (80 mA/cm²) were tested at 0.35 to 0.51 ft/sec flow rates. An important parallel here is the increasing voltage drop at the plating cell with increasing plating current. From less than 2 volts at 6.2 A, it rose to about 2.35 volts at 8.7 A. This obviously reflects the higher iR drop and electrode potential, and indicates that 112 mA/cm² operation is near the highest current at which our goal of a 2 volt drop in the commercial unit is attainable.

The last parameter studied in the work was catholyte's cupric concentration and whether it too affects deposit quality. Our measure of cupric in the catholyte is that solution's ORP. At a fixed catholyte total copper concentration, solution ORP varies directly, but not linearly, with cupric content. We typically operate at a catholyte ORP of 230-250 mV, which corresponds to about 0.5 to 1 g/l Cu²⁺. The lower limit is the point where it becomes difficult to maintain knockdown cell current flow without plating on that cell's cathode, while the higher value corresponds to a solution for which the plating cell spends too much cathodic current converting cupric to cuprous ion.

To test the catholyte [Cu²⁺] effect, we made a set of 3 runs at 6.2 A using about 40 g/l total copper in the catholyte. Catholyte ORP levels were 219, 239 and 256 mV; these correspond to about 0.4, 0.85 and 1.5 g/l of cupric respectively. Deposits made in these runs all looked the same with uniform thickness and relatively small grain size. The biggest difference from run to run was deposit weight; as expected, the deposit weight fell as ORP increased. The deposit weight at the highest ORP was 88% of the copper recovered at the lowest ORP. Since there was no significant difference in plate quality, there isn't any major advantage in operating at the ORP extremes.

2. Separator Material Studies

In early work with the pre-prototype system, we learned about the importance of having a hydrophilic separator between the anode and cathode compartments of the cells - particularly for the plating cell. When we used off-the-shelf porous polyethylene, we got dendritic, non-uniform deposits, reflecting poor current distribution (typically high at the bottom of the cell and low near the top). Application of a topical surfactant significantly enhanced the separator's wettability and promoted uniform current density and good copper deposits with constant cross-sections. However, the treatment was continuously leached out and had to be re-applied periodically. To avoid this, we switched to a separator plate made with porous alumina which our tests showed to be both hydrophilic and unattacked by the electrolyte.

In the commercial scale unit, we will also need a porous hydrophilic material with good chemical resistance and moderate cost. Porous glass has desirable physical properties but is too expensive. Other porous ceramics are available, but etch solution reacts with them. Porous plastic is economical and won't be attacked by the process solutions, but as discussed above, it is not hydrophilic. Discussions with vendors, however, indicated that there might be processing which could solve this problem. Consequently, we sent out samples of porous polyethylene and propylene for plasma and radiation treatments. We also designed a test to measure hydrophilicity and used it on these and other porous specimens.

The test consists of dropping water from a buret onto framed specimens (PVC cement painted on the perimeter of pieces to define a square test area of 1 to 2.25 in²) that are sitting on a lightly dampened sponge. We use a 5 minute maximum period, or 25 ml maximum volume, and follow the volume of water over time that is passed through into the sponge. Water feed is halted when more than a few drops have accumulated on the specimen, and we use a glass rod to continually spread the water over the surface.

Table I shows results for several plasma treated samples received from Anatech Ltd., along with samples of untreated, standard-manufacturer-produced porous polyolefin, and a piece of the porous alumina now used in the pre-prototype cells. It is apparent that all 3 levels of plasma treatment made the porous polyethylene hydrophilic; the data show that untreated it allows no water penetration. The larger pores in the polyethylene account for the significantly higher water flow through the plastic vs the ceramic.

Next we tested the plasma-treated polyethylene materials further. Samples of each were stirred in CuCl₂/HCl etchant at 50-55°C for periods up to 240 hours to get an indication of how well they would survive process operating conditions. Results of our hydrophilicity test on these samples, summarized in Table II, show that none of the 3 treatment levels used was able to withstand the simulated process environment. Even a soaking period of only 75 hours destroyed hydrophilicity. Discussions with the engineers at Anatech indicated that there was little more that plasma treatment could offer; consequently we halted work on material made this way.

Radiation graft treatments were done on porous polyethylene and propylene by the University of Maryland's Dept. of Materials and Nuclear Engineering under the direction of their department head, Dr. W. Chappas. Initial samples received, however, were found to be hydrophobic as shown by the Table II data. A second set of samples was then prepared using a revised treatment, but these too were hydrophobic irregardless of which side was tested. After soaking the samples in CuCl₂/HCl etchant for about 70 hours at 30-35°C (and then rinsing and drying) however, the porous polyethylene -see Table II- had become hydrophilic. The porous polypropylene remained hydrophobic.

We were fairly certain that the polyethylene change was not due to etchant soaking alone, since testing of an untreated polyethylene window in a pre-prototype regenerator cell separator plate used for almost a year, showed it to still be hydrophobic. Additional soaking of the second set of porous samples in hot, 50-60°C etchant didn't change the results; the polyethylene remained hydrophilic (somewhat more so), and the polypropylene remained hydrophobic. Additionally, a fresh untreated sample of porous polyethylene soaked in hot etchant over that time period also remained hydrophobic.

Dr. Chappas recommended that we could best pursue this investigation by working with Damalic, a small company involved in radiation grafting. The goal of the work would be to see if treatment similar to that which succeeded on porous polyethylene could be made to work on porous polypropylene, an inherently better material to use in the separator plates because of its increased rigidity and higher temperature capability. Discussions with Damalic, were not fruitful however, because that company could not justify these studies without some hope of significant commercial applicability. We may do a literature search in the future to show them what opportunities exist for porous, hydrophilic, polyolefins, since without that kind of data Damalic is unlikely to want to proceed.

As an alternative to radiation grafting, we also looked at samples of porous polyethylene which contained a surfactant that was incorporated in the matrix during the porous product's preparation. As the manufacturer Porex told us it would be, this product was quite hydrophilic; the buret water-dropping test data is shown in Table III. However, after this sample was soaked for 6⁺ days in hot (50°-60°C) etch, then washed and dried, it had - as the

Table III results show- lost its wettability. Thus its behavior was no better than the porous polyethylene separator used in our earliest cell tests which we kept hydrophilic by periodic applications of surfactant to the surface.

With these results making it unlikely that a cheap, hydrophilic, porous plastic separator could be ready for the initial commercialization efforts, we reconcentrated efforts on looking at porous ceramic materials. This effort intensified when we learned how expensive it would be to purchase the type of porous, acid-resistant alumina supplied by Coors and used as a separator in much of the pre-prototype cell testing. Coors price is \$330-\$380 (depending on total quantity) for each 12 1/2" x 19" x 3/8" plate - the size that we anticipate using in the scaled-up prototype unit being designed for higher capacity testing. In our lab tests, we have also made a few runs with a porous alumina from Ferro Corp.; though their price is significantly better - \$150 for a comparable sized plate, their material has 1 μ pores compared to Coor's 3 μ pores, and is significantly more resistive. Samples that they have sent also make us question their product quality.

Searching the directories showed that there is a fair number of other porous alumina/ceramic producers. By contacting a number of these suppliers, we learned that most of them produce reticulated, large-pore, foam-like product which is difficult to make in the 1/4"-3/8" thickness we seek. One manufacturer that was found though - Refractron Technologies, makes a dense alumina/silica/TiO₂ porous product which their data indicated would be compatible with CuCl₂ etchant, and which could be supplied in 12"x18"x3/8" sheets for \$108 each.

We tested a sample of their AF6 plate by immersing it in stirred etchant for 8 days at about 65° C. Its weight loss of less than 0.1% compares favorably to a Coors porous alumina sample's loss of about 0.5% in similiar testing, and since it has somewhat larger pores than the Coors product (3.5 μ vs 3.0 μ), its conductivity should be at least as good and probably better. Consequently, unless a superior material comes to light, it is anticipated that this is the product that will be used in the prototype and first commercial cells.

3. Graphite Felt Activation

While there are a number of important discoveries that have enabled development of this regeneration process, almost certainly, none is as important as the use of high surface area electrodes. Graphite or carbon felt is what we use (other high area materials could be employed) in the knockdown cell electrodes and as the plating cell anode. Previous work with earlier versions of these electrodes indicate that they might have been too short-lived. It is imperative for process acceptance in the real world that the felt maintains performance for "adequate" periods of time.

One measure of felt life is obtained by following its polarization behavior during process electrolysis. Electrode potentials were measured versus Ag/AgCl reference electrodes in our runs; that's one of the standard data items used to characterize performance. The change in potentials over time, with the comparisons made at otherwise constant conditions, is an indication of felt changes.

The usefulness of this method is shown in Table IV Section A. There are listed electrode potentials (at times when essentially equal current and flow existed) vs. charge passed (Ahrs) over the first six months of operation of the pre-prototype scale regenerator. This was done for both the plating cell and the knockdown cell anodes, though the table only shows data for the 4"x3"x3/8" knockdown cell anode. The increased potential as total charge passed increased, indicates that the felt's activity deteriorated over time. Similar analysis showed comparable deterioration in the plating cell anode and knockdown cell cathode. Because the knockdown cathode is typically operated at constant potential, the knockdown cell

cathode's loss of activity was shown by the need to hold a higher cuprous concentration in the catholyte (higher catholyte ORP) in order to support a particular knockdown cell current.

The first set of felt electrodes used in the pre-prototype system (the electrodes used in the first six months of operation) all appear to have ebbed to a condition of too little activity to handle current densities of 65-75 mA/cm² after about 450 - 650 Amphours of operation. All these were made by heating in air, in a furnace, to 450°C.

A second set of pre-prototype felt electrodes was made using steam to activate the felt. These were heated in an atmospheric pressure, steam-flushed chamber to 500°C. As shown for the 4"x3"x3/8" knockdown anode in Table IV Section B, those electrodes have exhibited significantly longer lives than the initial set. The 1327 Ahrs of knockdown cell operation with the Table IVB anode is more than double the 600-630 Ahrs when the first knockdown cell anode was seen to operate poorly, and that first set of steam activated electrodes operated at higher current densities - 80-95 mA/cm² - which is a more difficult environment too. Still, sensitivity of the first steam-activated knockdown anode's potential to modest etch ORP increases after accumulating about 1400 Ahrs, indicated that its activity was probably falling off there. Unexplained too, is the poor activity that this electrode showed over the first 250-300 Ahrs of operation; the other steam-activated felt electrodes in the second set, started up right away with very reasonable potentials.

It is apparant from the relatively long service life seen with those initial steam-activated felt electrodes that it will be difficult to determine relationships between activation method and felt activity life at the pre-prototype level. That is due to the limited speed at which experiments can be run in the system. Since accumulating 1000 Amp-hrs (per unit of pre-prototype electrode area) at the larger prototype level however will only take about a week, electrode life trends will be seen much faster there; consequently, that's obviously the place for in-depth evaluation of electrode life vs. activation method. However further tests of activation techniques or variations in method are required in this phase of the study. That work will need to use early-in-life electrode behavior as a preliminary measure of performance. The specific parameter to be examined is the limiting current value(s) for the felt; that parameter is a measure of how much electrolysis current can be handled by the electrode at a specific set of flow/concentration conditions before the next electrochemical process begins. It's a measure of electrode capacity; for system anodes its the current value where Cl₂ evolution begins and cuprous to cupric oxidation has reached a maximum.

Because the first steam-activated pre-prototype scale knockdown cell anode was showing a fall-off in activity at the 1400 Ahr level, as evidenced by significant potential increases (200-300mV) in response to modest etch ORP increases, it was replaced with an electrode where the 500°C graphite felt, steam-activation holding period was extended from 15 minutes to 30 minutes. Operation with 500 mV etchant fed at 1.6 l/min, and knockdown currents of 9.5 and 9.8 amps in 3 runs made after installation showed good polarizations of 950-980 mV. Additionally, E/i curves produced for the first steam-activated anode just prior to it's removal from service -Figure 2- and the second one after 20 Ahrs of operation -Figure 3- show limiting currents and thus the activity differences graphically.

To get some indication of whether carbon felt is a better material than graphite felt for system flow-through electrodes, we removed the second steam-activated graphite knockdown cell anode and replaced it with a carbon felted one; the new electrode's activation was essentially identical to the graphite felt electrode it replaced. After using it in 2 runs with the relatively standard 1.6 l/min 500 mV etchant flow at 10 amps, we obtained the Figure 4 E/i curves for the electrode. Those curves showed $\text{Cu}^+ \Rightarrow \text{Cu}^{2+}$ "capacity" that was similar to that exhibited by the similarly activated graphite felt anode. Changes in limiting current with etchant ORP and flow were also about the same for both these electrodes, though carbon felt polarization values changed less with increasing current than did graphite felt before reaching the limiting current.

We also obtained E/i curves on both the extended service, 3/8" thick graphite pre-prototype plating cell anode (from the original set of steam-activated felt electrodes) -in use for 23 months with about 750 A hrs of electrolysis, and a new 0.8" thick graphite felted replacement plating cell anode installed to learn whether using a thicker, manufacturer's standard felt had any detrimental effects. As shown in Figures 5 and 6, both plating cell anodes showed significantly higher "capacity" than the earlier-tested knockdown cell anodes. The extended service anode was tested first. Its high capacity prompted a review of felt activation records, and we found that it alone, of all previous felts activated, had taken 2 hours to get to the 500°C hold temperature. The others took about 1 hour. Since this extra steam exposure had such a beneficial effect, we activated the new 0.8" thick anode felt the same way and got similar high "capacity" per unit volume. Thus it seems that extending the "in-steam" time, either by slowing the heat-up time, or increasing the "hold at 500°C" period -or both, offers promise of improved felt performance.

Final work in this area was a retest of a rejuvenation treatment of the knockdown cell flow-through cathode. It had been seen in late project pre-prototype testing, that higher catholyte ORPs ($\text{Cu}^+/\text{Cu}^{2+}$) had to be set for the system to avoid having the flow-through knockdown cell cathode polarization go more negative than -20 to -30 mv (vs. Ag/AgCl reference). Letting the cathode go too far negative would indicate the onset of Cu plating there, a very undesirable condition for the process. Setting catholyte ORP higher to avoid this though, reduces plating efficiency (amps to copper metal/total amps) at the plating cell. The knockdown cell electrode had been rejuvenated about 5 months before this grant effort began by heating it to 425°C and holding for 30 minutes, all with atmospheric pressure steam pushed through the activation kettle. The new rejuvenation, done under identical conditions after having run the cathode for about 1600 Ahrs of electrolysis, successfully restored the knockdown cell ability to operate with a catholyte ORP of 5-7 mv lower than the previous run and a cathode polarization of +30 to +50 mv (vs. Ag/AgCl reference). Being the second successful rejuvenation on this electrode, it indicates that all process felt electrodes may be capable of multiple "capacity" restorations after in-service deterioration.

4. Oxygen Ingress Compensation

In real-world etching with CuCl_2/HCl , consumption of untreated etchant over time is not quite as severe as stoichiometric calculations would show because of atmospheric oxidation -the chemical reaction of O_2 from the air with cuprous ion to produce cupric. That's fine, and actually advantageous when using chemical regeneration (it saves oxidant), but it is detrimental when the regeneration is electrochemical because the electrolytic reducing power of that solution is lost, and it thus winds up as excess etchant. Add to this the possibility of chemical oxidation in the high-cuprous catholyte, and it becomes obvious that even with electrochemical regeneration, there exists opportunity for generating excess etchant. Thus it might be important to incorporate within the regeneration process a way to counter chemical oxidation, a way to maintain solution cuprous content until it can be anodically converted to cupric in the system cells.

Previous work in EPA SBIR contracts demonstrated a method for doing this, an electrochemical process for reducing CuCl_2 produced by chemical oxidation back to CuCl . The major requirement for that "oxygen ingress compensation" process is availability of a separation membrane for cell chambers that only passes H^+ ions. The earlier work showed that a T&G Corporation "electropermeable" membrane works well here. That work had however only been done on a bench scale. It was a goal in this project to demonstrate that technology on the pre-prototype level, so that it could be more easily scaled up if larger-scale regenerator testing showed that it was needed for a commercial regeneration process.

Prior to building a larger than bench-top demonstration system for the oxygen ingress compensation process, we tested several "improved" T&G Corp membranes. It was expected

that results would provide a membrane of choice and a design value for the scaled-up compensator's allowable current density.

Testing began with a sample of T&G's 17118 membrane, a new formulation designed to have low resistivity. A sample of that membrane, 6 layers laid down on Celgard (a microporous polypropylene) film, was sandwiched between 2 pieces of Daramic (15 mil silica-embedded polyethylene battery separator product) and installed between the halves of one of our standard 1"x2" cells (2"x4" acrylic blocks with 1"x2" compartments machined into them for receiving anode and cathode plates). A graphite plate with activated graphite felt served as the cathode, while a platinum-clad niobium plate was the anode. Catholyte was a liter of standard lab etchant - 180 gm/l CuCl_2 plus 70 gm/l HCl , and anolyte was a liter of 2N H_2SO_4 . Periodically over 2 weeks, we heated solutions to 50°C, pumped them through the respective cell compartments at about 300 cc/min, and operated the cell at 200 mA. An E/i curve generated in the first hours of operation is shown in Figure 7, and indicates that the membrane might have significant current flow capability with only a modest iR drop.

During the periodic operating time, 36 hours of 200 mA electrolysis and 42 hours of actual recirculation in the cell was accumulated. Anolyte and catholyte always remained in contact across the membrane during downtime. Early on in the test, the initially colorless H_2SO_4 electrolyte began turning faintly blue, indicating Cu ion transport across the membrane. Analyses verified transport of both Cu^{2+} and SO_4^{2-} between solutions over the run period as follows:

t(total contact time) <u>hrs</u>	Anolyte [Cu^{2+}] <u>g/l</u>	Catholyte [SO_4^{2-}] <u>ppm</u>
0	-	-
122	0.6	370
280	1.2	935

Cl^- concentration in the anolyte wasn't measured, but some free Cl_2 could be smelled in the anolyte reservoir.

Results show that this membrane is not satisfactory for use in compensating for oxygen ingress; operators could not tolerate that level of SO_4^{2-} contamination in the etchant.

The next membrane tested was a composite of T&G's 17118 material, 1 mil thick on Celgard with an added thin top layer of 10118 hydrogel-plastic polymer for improved conductivity. The membrane was installed in the 1"x2" cell as above, and in a first test, fresh 1 liter inventories of anolyte and catholyte were circulated at 50°C periodically over a 6 day period for a total of 26.6 hours. For 24.4 hours of that time, cell electrolysis ran at 200 mA. Even during shutdown, solutions stayed in contact across the membrane; that time and the recirculation periods totaled 127.7 hours.

This test showed substantial ionic leakage. Cu^{2+} migration to the anolyte was obvious from day 2 onward as the H_2SO_4 solution acquired a faint but visible blue tint. Cu^{2+} in the anolyte went from 0 to 1.86 g/l over the test period, while catholyte SO_4^{2-} went from 0 to about 450 ppm.

To insure that these results were not due to physical damage done to the membrane during the experimental setup, or to membrane variability, we repeated the test with a fresh piece of the 17118/10118/Celgard composite, a fresh liter of 2N H_2SO_4 anolyte, plus the previous test's catholyte diluted back to 1 liter (to make up for sample and evaporative losses). Particulars for this second test were:

- Total solutions contact time across the membrane = 201 hrs
- Actual solutions recirculation time (50°C) = 51.4 hrs
- Electrolysis time (at 200 mA) = 48.4 hrs

Again we saw ion transport in both directions across the membrane. Results are summarized below:

Hrs contact time	0	56	128	201
Anolyte Cu ²⁺ , g/l	0	0.23	0.28	0.36
Catholyte SO ₄ ²⁻ , ppm	421	-	704	690

As the data show, transport was not as severe as in the previous test, and seems to have slowed considerably from mid-test onward. Nevertheless, permeation over the 201 hr test period is too high.

While membrane testing was underway, we designed and built a larger-than-benchtop version of the oxygen ingress compensation process to enable testing it at the pre-prototype level when the membrane was selected. Basis of the scale-up was (a) the 1" x 2" bench-top cell testing, which set current density at the moderate 30 mA/cm² current density demonstrated in that work, and (b) a 9 in² active surface area (3"x3") based on a purposefully high 25% oxidation loss (about 4 grams Cu reduction load/hr) when operating the pre-prototype system at 7.5A - a bit in excess of the 6.75 A current determined for pre-commercial scale-up. A major feature of the cell design is use of a cell separator plate with a porous alumina window which acts as a fixed, rigid support for whatever proton-passing membrane is being tested. Figures 8 through 11 are the chief design drawings used to build the cell.

During cell design and construction, other compensator system equipment was purchased, installed and plumbed up. Major items in this area included anolyte and catholyte peristaltic pumps (with pump speed controllers and pump stands), titanium assembly screws, and the Pt-clad niobium anode plate, along with a 4 liter H₂SO₄ anolyte reservoir and its heater plus temperature controller.

During pre-prototype scale compensator system construction, membrane testing continued. Since neither of the 2 new "improved" T&G permeable membranes tested gave satisfactory performance, we obtained a sample of the T&G 14118 membrane that had worked in the EPA SBIR experiments and put it on test in the 1x2 bench-top system. Again we sandwiched a piece between 2 similar sized rectangles of 15 mil Daramic (1 3/4" x 3 3/4"), and again circulated 2N sulfuric anolyte and CuCl₂/HCl catholyte through the cell at 50 °C periodically over 7 days. When solutions weren't circulating, they remained in contact across the membrane. Total test time was 151 hours; circulation was established for 37.4 hours of this period, while 200 mA electrolysis was run for 34.5 hours.

Once again it was apparant from early in the test that the membrane was allowing undesirable ion transport since the anolyte began to turn blue. After 96 hours of total contact time, anolyte had 0.39 g/l Cu²⁺; at the end of the test, its copper content was 0.48 g/l. Discussions with T&G indicate that a plant fabrication problem was probably the reason for the 14118 membrane failure, and they sent us a freshly prepared 14118 sample.

The new 14118 membrane sample was tested in the standard manner with our bench-top 1"x2" cell. There we saw only a small amount of Cu ion crossover from the etchant (catholyte) chamber to the 2N H₂SO₄ anolyte over the first 7 days of solution contact across the membrane -during which time solutions were recirculated for 38.2 hours and electrolysis, at 200mA (.30 mA/cm²), ran for 34.7 hours. After this time though, anolyte Cu increased rapidly from the 7 day value of 0.08 g/l to 0.99 g/l at 9.25 days (an additional 24 hours of

recirculation and 23.4 hours of electrolysis). This data indicated that the membrane, while not good enough for a real operating regenerator system, would be adequate for at least several days of pre-prototype scale operation. Consequently, we fabricated a 4"x4 1/4" membrane assembly -15 mil Daramic sandwiching the 14118 membrane coating on Celgard with silicon caulk cementing the perimeter, and installed it in the new 3"x3" membrane area cell (excess membrane assembly area provided sealing surface for the hold-down frame).

The new 3"x3" cell was run with electrolysis current for 3.5 hours, and successfully reduced etchant cupric ions to cuprous -as shown by its ability to hold a constant etchant ORP with concurrent etchant oxidation- at currents ranging from 1.0 to 2.0 Amps. Both knockdown cell operation, at currents from 1.0 - 2.5 Amps for 2.7 hours, and air oxidation from etchant recirculation, provided the etchant oxidation load. The major problem encountered with the larger scale oxygen ingress compensator was a very high voltage drop (up to 20 volts seen after running at 1.5 - 2.0 Amps), which kicked the power supply off and prevented testing at higher currents. It's believed that this high voltage is due to H_2SO_4 solution seeping between the cell's porous alumina separator window and the membrane assembly it supports with consequent anodic O_2 generation there. That would significantly hinder ion transport through the porous window and be manifested as a high resistance. In future versions of the cell, the membrane could be installed between porous plates to counter this problem; this would support the membrane on top and bottom, making solution by-passing less likely.

5. Engineering Design Studies

The study of plating parameters showed that the most effective way to improve the copper deposit and achieve higher plating currents was to increase plating cell cathode velocity. The flow basis for the 2.5 kg/hr prototype regenerator being designed for Beta site testing is 0.86 ft/sec, and was set as a compromise based on experimental work. Higher flow would work even better but would obviously require moving even more electrolyte. Prototype gap has been set at 3/8" - small enough to minimize gross flow and electrical resistance, but large enough to allow a copper deposit thickness corresponding to a 24 hour build and harvest cycle. This gap and the 11-1/2" wide plating surface set for each cathode, converts to an 11.5 gpm flow to each side of each double-sided cathode in the plating cell stack.

It is apparent that putting this much catholyte into and out of a 3/8" x 11-1/2" cross-section requires a pressurized cathode chamber; building a cell tall enough to allow gravity return and fitting lines large enough for that mode of operation - particularly considering the proximity of adjacent chambers in the stack - is just not practical. Hence an important aspect of the cell design is the question of what is the best way to deal with required cell pressure. The main concern here is electrolyte leakage.

Again different design requirements conflict. Just as gross flow could be reduced with a smaller gap but then the desired copper deposit time couldn't be accommodated, so leakage would be less likely if the cell was built as a single multi-chambered box, but then separators couldn't be accessed and anodes could be very hard to remove. Consequently the cell "stack" is really designed as a stack - of alternating anode and cathode chambers separated by gaskets. This method of separating cell chambers has been used successfully in our pre-prototype unit, but that unit runs with gravity overflow and thus has minimal internal pressure.

As a test of the prototype design concept, we revised the pre-prototype scale plating cell to have it operate in a pressurized condition. To do this we installed a new, thicker separator plate with extra 5/32" wide blocks at the top to provide more surface area for seating new individual anode and cathode chamber covers. In addition we sealed the titanium plate, anode and cathode current collectors in the slots of the chamber covers by (a) fastening them to each cover externally with PVC angle stock which is bolted to the plate and cemented to the cover, and (b) sealing the residual slot opening with a bead of acid-proof epoxy which covers and also

coats the in-chamber portion of the titanium, the PVC cover (inside), and the graphite plate where deposit is to be excluded.

Initial water pressure testing of the pre-prototype configured as detailed above showed only small leaks; these were seen at the inboard faces of both covers where sealing areas are only 6 1/2" long strips just 10/32" wide, which also have a line of four 1/8" holes down the center of the strip length. By both double gasketing (2 1/32" thick Viton sheets), and adding silicone caulk under the covers -which compensated for a slight misalignment of separator plate and chamber frames, we got a leak-free assembly at 8 psig pressure.

We made two 3-hour etchant regeneration, copper plating runs with the pre-prototype scale system using the plating cell configured for pressurized operation, and were able to feed it catholyte at 3.5 gpm without leaks, almost 50% higher than in previous testing. This is close to the flow value required for the prototype scale design (11.5 gpm across a 3x wider opening). That result and the fact that the prototype will have larger, hole-free sealing areas where there's better machining of mating frame and separator plate surfaces, indicates that handling the high flows required in the scaled-up cells should be straightforward.

6. Commercialization Issues

The next logical stage in development of this process prior to commercialization is construction and "beta-site" testing of an engineering prototype version of the regenerator system, in conjunction with a commercial-size spray etcher, fabricating printed circuit boards. For this to occur, the commitment of a PC board fabricator who would be willing to undertake the testing will obviously be required.

Our commercialization strategy since starting this development has been to license the technology to an equipment manufacturer who could then profitably market the regenerator as an "add-on" to its line of spray etch equipment. Retrofitting regenerators to existing spray etchers in the field might also be a viable opportunity. In support of this strategy, we obtained a U.S Patent in 1995, whose main claims cover the use of flow-through carbon/graphite felt electrodes. A second patent application covering our unique two cell regenerator design was filed in March 1996. Office action on the latter application is anticipated in the near future.

In support of our patent filing, licensing activities and planned "beta-site" testing, we obtained a \$50,000 Connecticut Technology Partnership Program award from Connecticut Innovations Inc. (CII) in November 1995. Repayment of the award monies (plus a royalty) is contingent upon achieving commercialization. There would be a significant financial incentive if commercialization is achieved in conjunction with a Connecticut-based company. The Commercialization Planning Workshop which we attended as part of the ERIP award prior to beginning ERIP program studies was valuable in helping to develop our commercialization plan.

The history and current status of our recent commercialization activities are summarized briefly as follows:

- o Licensing discussions were held with leading manufacturers of spray etch equipment in the U.S. One of these, namely Atotech USA agreed in principle in December 1995 to negotiate towards a formal License Agreement and plans were initiated for construction and testing of a 2.5 kg/hr engineering prototype. These negotiations were terminated by Atotech for marketing-related reasons in October 1996.
- o We are nearing completion of the engineering design for a 1/2 commercial scale (2.5 kgCu/hr) prototype regenerator, as part of our EPA SBIR Phase III contract.

o We were asked in December 1996 to submit a proposal for construction of our 2.5 kg/hr regenerator design by Teradyne Inc. in Nashua NH, a leading fabricator of multilayer printed circuit boards. Teradyne had expressed their wish to "beta-site" test our system in tandem with a new Develop, Etch and Strip (DES) line which they plan to install by the end of 1997. Our proposal to build the regenerator was submitted recently and we are now awaiting Teradyne's response. The proposal outlined two alternative scenarios for constructing the regenerator, (1) with Oxley Research acting as general contractor, or (2) subcontracting much of the construction to either MacDermid Equipment Company (Springfield, VT), or Advanced Chemill Systems (Temecula, CA), the two etchant equipment companies that Teradyne recommended to us. Both are also bidding on the main DES line.

Table I
Test Results: Porous Separator Materials

Sample # ⁽¹⁾	<u>Volume Water to sample Surface over Time, mls</u>					
	1	2	3*	4	5*	6*
1 min	2.7	0.35	2.8	0.6	1.1	3.7
2 min	2.8	0.35	4.1	0.75	5.8	10.0
3 min	2.95	0.35	8.6	0.75	20.8	23.0
4 min	3.1	0.35	22.6	0.75	25.0 ⁽³⁾	25.0 ⁽⁴⁾
5 min	3.15	0.35	25.0 ⁽²⁾	0.75	-	-
remainder ⁽⁵⁾	0	0.3	0	0.7	0	0

Notes

(1) Sample IDs

- #1 1/4" 100% alumina porous ceramic plate (Coors)
- #2 1/4" UHMW porous polyethylene (20 μ pores)
- #3 1/4" plasma treated porous polyethylene (90 μ pores)
150 Watt, 1 torr, 2 min
- #4 1/4" porous polypropylene (120 μ pores)
- #5 1/4" plasma treated porous polyethylene (90 μ pores)
50 Watt, 1 torr, 3 min
- #6 1/4" plasma treated porous polyethylene (90 μ pores)
75 Watt, 1 torr, 3 min

(2) 25 ml passed in 4' 15"

(3) 25 ml passed in 3' 22"

(4) 25 ml passed in 3' 11"

(5) Water removed from surface @ end of test. A value here indicates that sample was not hydrophilic

Note

* Sample surface was 2.25 in² (all others 1 in²)

Table II
Porous Polyolefin Hydrophilicity

<u>Sample No.</u>	<u>Volume H₂O to Sample Surface over Time, mls</u>					
<u>I Plasma Treated</u>	<u>1 min</u>	<u>2 min</u>	<u>3 min</u>	<u>4 min</u>	<u>5 min</u>	<u>Remainder⁽²⁾</u>
#I - 1(1)	1.65	1.65	1.65	1.65	1.65	1.3
#I - 2(1)	0.75	0.75	0.75	0.75	0.75	0.3
#I - 3(1)	0.8	0.8	0.8	0.8	0.8	0.4
<u>II Rad Graft 1st</u>						
#II - 1	0.25	0.25	0.25	0.25	0.25	0.1
#II - 2	0.6	0.6	0.6	0.6	0.6	0.5
<u>III Rad Graft 2nd</u> <u>& Etch Soak</u>						
#III - 1	1.15	2.0	2.75	3.4	4.0	0
#III - 2	0.5	0.5	0.5	0.5	0.5	0.4

Notes

Sample ID's:

- #I - 1 Plasma treated porous polyethylene (90 μ pores) @ 150 Watt, 1 torr, 2 min after 216 hrs in 50°C⁺ etch
- #I - 2 Plasma treated porous polyethylene (90 μ pores) @ 50 Watt, 1 torr, 3 min after 240 hrs in 45-55°C etch
- #I - 3 Plasma treated porous polyethylene (90 μ pores) @ 75 Watts, 1 torr, 3 min after 75 hrs in 50-55°C etch
- #II - 1 First radiation treatment on 1/4" UHMW porous polyethylene (20 μ pores)
- #II - 2 First radiation treatment on 3/8" porous polypropylene (125 μ pores)
- #III - 1 Second radiation treatment and 70 hours CuCl₂/HCl soak on II - 1 raw material
- #III - 2 Second radiation treatment and 70 hour CuCl₂/HCl soak on II - 2 raw material

Other:

- (1) Sample surface area = 2.25 in² (all others are 1 in²)
- (2) Water removed from surface at end of test. A positive value here indicates sample was not hydrophilic

Table III
Hydrophilicity of Surfactant Impregnated Polyethylene
 (before and after 50-60°C soak)

<u>Sample Description</u> ⁽¹⁾	<u>Vol H₂O delivered to Sample Surface over Time, ml</u>					
	1 min	2 min	3 min	4 min	5 min	Remainder ⁽²⁾
Poly E Before Soak	1.0	1.4	3.0	5.4	9.1	0
Poly E After Soak	0.35	0.35	0.35	0.35	0.35	0.17

Notes

- (1) 1/4" thick Porex porous polyethylene sample with 1 in² surface, 15-45 μ pores
- (2) Water removed from surface at end of test. A positive value here indicates sample was not hydrophobic

Table IV
Changes in Knockdown Cell Anode Behavior⁽¹⁾ Over Time

A. Hot Air, 450°C Furnace Activated Anode

<u>Charge Flows, Ahrs</u>									
31.5	153.3	300.1	344.1	405.2	501.2	540.7	612.5	632.9	
<u>Current, Amps</u>									
7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.5	7.0	
<u>Anode Potential, mV</u>									
950	710	750	840	870	950	990	1060	1450	

B. 500°C Steam Activated Anode

<u>Charge Flows, Ahrs</u>										
16	102	192	258	409	603	859	1040	1147	1225	1327
<u>Current, Amps</u>										
8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.6	8.6	8.6	7.7
<u>Anode Potential, mV</u>										
1330	1370	1400	990	710	780	730	800	760	780	780

Note

- (1) Following potential at the electrode (vs Ag/AgCl reference) in pre-prototype unit over time when etch ORP = 495-500 mV, temperature = 50°C, and flow through the anode compartment = 0.9-1.0 liter/min

Figure 1. "Eggcrate" Gap Reducer

Figure 2. Polarization Behavior of Knockdown Anode Used for Nearly 1400 Ahrs

Figure 3. Polarization Behavior of New Knockdown Cell Anode

Figure 4. E/i Characteristic of New Carbon Felt Knockdown Cell Anode

Figure 5. Polarization Behavior of Plating Cell Anode Used for 750 Ahrs

Figure 6. Polarization of New 0.8" Thick Plating Cell Anode.

Flows are ~% of 2.3 l/min

Figure 7. E/i Curve for Proton Compensator (1" x 2") Cell
(O₂ evolution Cu²⁺ reduction), T&G Membrane # 17118

Figure 8. Cell Elevational View

Figure 9.
Membrane Test Cell
Anode/Cathode Chamber Frame

Figure 10.
Membrane Test Cell
Short Side "Stack" View

Figure 11.
Membrane Test Cell Separator Plate
Assembly Details