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ELECTROLYTIC REGENERATION OF ACID CUPRIC CHLORIDE
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by

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I. SUMMARY OF ACCCOMPLISHMENTS

We are abandoning study of porous polyolefins as regenerator cell separators for now since only radiation grafting seems a suitable technique to make them permanently hydrophilic, and the experts who could do this work need more financial incentive than our application generates. A vendor with a new, moderate cost porous ceramic which can be used for our separators was found though. We designed and built a demonstration scale oxygen ingress compensator cell and are adding it to our pre-prototype regeneration system; actual operation awaits completion of tests on the required proton-selective T&G Corp. membrane. Prototype flow demands require pressurized cell operation and modifications being made to the pre-prototype plating cell will allow testing of design concepts to handle that.

II. TASK ACTIVITIES AND RESULTS

Task 1. Parametric Studies

Work continued during the period to find materials that could be used for the regenerator system cells' porous separators.

Previously we had learned, from samples made by the niversity of Maryland's Department of Materials and Nuclear Engineering, that radiation grafting could modify normally hydrophobic porous polyethylene, and with subsequent etchant soaking, make it hydrophilic. These samples also showed that the polyethylene treatment did not work for porous polypropylene, a preferred material because of its stiffness and higher temperature capability. Discussions with Damilic, a small company that the University of Maryland's department head Dr. Chappas recommended to carry on the work were not fruitful, because that company could not justify these studies without some hope of significant commercial applicability. We plan to do a literature search in the future to show them what opportunities exist for porous, hydrophilic, polyolefins, since without that kind of data Damilic 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 I. However, after this sample was soaked for 6⁺ days in hot (50°-60°C) etch, then washed and dried, it had - as the Table I 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 a surfactant in isopropanol (to combat etch solution leaching).

With these results making it unlikely that a cheap, hydrophilic, porous plastic separator could be ready for the first commercialization efforts, we have reconcentrated efforts on looking at porous ceramic materials. This effort intensified during the quarter 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 cell testing over the last year. 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 now being designed for higher capacity testing

To ensure that we would have an oxygen ingress compensator unit operating and demonstrated with the pre-prototype regeneration system prior to contract's end, we designed and built a new cell for the process. 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 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. The other major feature of the 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 1 through 4 are the chief design drawings used to build the unit.

Much of the system's support equipment - pumps, titanium screws, Pt-clad niobium anode, pipe fittings, hose lines - have already been purchased. We expect to order short delivery items still required - H₂SO₄ reservoir and heater, temperature controller, and temperature sensor - in the next few weeks, and begin assembly then. Hopefully we will be able to demonstrate the new cell with one of T&G's improved membranes, otherwise we will be using their old #14118 membrane that showed such high selectivity in tests several years ago.

Task 4. Engineering Design

Our earlier 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 tests at Atotech's PA facility is 0.86 ft/sec and was set based on experimental work. Higher flow would work even better but would obviously require moving even more electrolyte. Gross flow is the product of the plating chamber cathode gap (distance between separator and electrode face), chamber width and the velocity value. 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 a 23 gpm flow to 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

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As a test of the design concept, we are revising the pre-prototype scale plating cell to have it operate in a pressurized condition. To do this we are installing a new, thicker separator plate with extra 5/32" wide blocks at the top to provide more surface area for seating individual anode and cathode chamber covers. In addition we will seal 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. If we are able to operate the rebuilt unit without leaks, we will have a lot more confidence in the prototype design.

Table I

Hydrophilicity of Surfactant Impregnated Polyethylene
(Before and after 50-60°C soak)

<u>Sample Description⁽¹⁾</u>	<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 hydrophilic.

Figure 1. Cell Elevational View

Figure 2.
MEMBRANE TEST CELL
ANODE/CATHODE CHAMBER FRAME

Figure 3. MEMBRANE TEST CELL
SHORT SIDE "STACK" VIEW