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ELECTROLYTIC REGENERATION OF ACID CUPRIC CHLORIDE
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I. SUMMARY OF ACCOMPLISHMENTS

Tests on T&G Corp. proton selective membranes showed significant ion migration, so we don't yet have one that will allow a demonstration of oxygen ingress compensation (OIC) with our pre-prototype scale regenerator. T&G is remaking a 14118 membrane for us; that is the membrane type used in successful bench scale testing several years ago. Our modifications to enable pressurized operation of the pre-prototype scale plating cell were successful; the unit can withstand 8 psig pressure without leaking. This shows that our design for pressurized prototype cells should work.

II. TASK ACTIVITIES AND RESULTS

Task 2. Graphite Felt Activation

The pre-prototype regeneration system was down for modifications to the plating cell for most of the quarter (see Task 4 discussion), consequently we had no opportunity to get E/i curves on the new carbon felt anode that was installed in the pre-prototype system's knockdown cell in April. Now that the test system is back up and running, we expect to generate that data in the next few weeks. This information should give some indication of whether there's a benefit from employing carbon felt instead of graphite felt for system flow-through electrodes.

Task 3. Oxygen Ingress Compensation

During the quarter, we ran more bench tests using our standard 1"x 2" laboratory cell to evaluate proton selective membranes for oxygen ingress compensation. All the tests were made with T&G Corporation products.

The first membrane tested was a composite of T&G 17118 material, 1 mil thick on a Celgard (microporous polypropylene) film, which had an added thin top-layer of 10118 hydrogel-plastic polymer for improved conductivity. This was the membrane which we began testing at last quarter's end. It was sandwiched between 2 pieces of 15 mil Daramic for support. In a first test of this material, 1 liter inventories of anolyte (2N H₂SO₄ solution) and catholyte (163 g/l CuCl₂ + 70 g/l HCl) were circulated at 50 C through the 1" x 2" cell periodically over a 6-day period for a total of 26.6 hours. For 24.4 hours of this time, the cell operated electrically at 200 mA. Even during shut-downs the solutions stayed in contact across the cell membranes; that contact time totaled 127.7 hours.

This test showed substantial ionic leakage. Cu²⁺ migration to the anolyte was obvious from day 2 of the test onward as the H₂SO₄ solution acquired a faint but visible blue tint. Cu²⁺ in the anolyte went from 0 to 1.86 g/l over the test period, while SO₄²⁻ in the catholyte went from 0 to about 450 ppm. An odor of Cl₂ in the anolyte during the test showed that significant Cl⁻ had been transported too.

To insure that these results were not due to physical damage done to the membrane during the experimental set-up or to membrane variability, we repeated the test with a fresh piece of the 17118/10118/Celgard composite using a fresh liter of 2N H_2SO_4 anolyte plus the first test catholyte diluted with H_2O back to 1 liter (to make up for sample and evaporative losses). Particulars for this second membrane test were:

- Total solutions contact time across membrane = 201 hrs
- Actual solutions recirc 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 first test, and seems to have slowed considerably from mid-test onward. Whether better results were due to improved cell fabrication techniques - we used a wider, flatter silicone caulk bead around the perimeter of the Daramic/membrane sandwich - or to T&G membrane variation over their length of coated Celgard, is impossible to say. Nevertheless, even the reduced permeation seen over the 201 hr test is too high.

Since neither of the two new, improved T&G proton permeable membranes gave satisfactory performance (see Quarterly report No.2 for first membrane test), we obtained a sample of the T&G 14118 membrane that worked for us in our EPA SBIR Phase II experiments and put it to the test in our 1"x 2" bench top cell. Again we sandwiched a 1 3/4" x 3 3/4" piece between 2 same-sized rectangles of 15 mil Daramic in the cell, and again circulated 1 liter quantities of 2N H_2SO_4 (anolyte) plus CuCl_2/HCl solution (catholyte) - 75 g/l Cu + 75 g/l HCl - through the cell at 50 C periodically over a 7 day period. When solutions weren't circulating, they remained in contact across the membrane for a total contact time of 151.3 hrs; circulation was established for 37.4 hrs of this period while 200 mA electrolysis was employed for 34.5 hrs.

Again it was apparent from the second day of the test onward that the membrane was allowing undesirable ionic transport as the anolyte began to turn blue from Cu^{2+} migration. After 96 hours of total contact time the anolyte had 0.39 g/l Cu^{2+} ; at the end of the test its copper content was 0.48 g/l.

Discussions with T&G indicate that a plant fabrication problem is probably the reason for the 14118 membrane failure. They also believe that it is necessary in our application to orient the coated side of the Celgard support towards a particular electrode. At quarter's end T&G was sending us a freshly prepared 14118 membrane.

Construction of the demonstration 3"x 3" oxygen ingress compensation cell continued at a slow pace while awaiting an acceptable membrane. The alumina window was installed in the cell separator plate and some of PVC pipe and adapter fittings were attached to the cell anode and cathode chambers. All of the support equipment has now been received and will be installed when membrane testing shows that we have a good proton selective membrane formulation.

Task 4. Engineering Design

Over the last two quarters, we have made significant progress in the design of a pilot plant scale 2.5 kg/hr prototype regenerator system for proof-of-the-process tests at our commercial partner Atotech's PA facility. Over that time we have generated the P&ID's (process and instrument drawings) for the prototype system and a set of engineering drawings (about 25) showing details and dimensions of the system plating cell and its constituent parts and sections. Before all that of course we prepared the fundamental Process Flow Diagram (PFD) as one important component of the presentation package used to describe the regeneration process to Atotech; the PFD is a process schematic which diagrams the system material balance. Much of this design work has been undertaken as part of our EPA SBIR Phase III contract. As was discussed in an earlier report, that contract is targeted specifically at commercialization of our etchant regeneration process.

As discussed in the last report, the 2.5 kg/hr sized prototype scale regenerator we are designing will utilize pressurized cells to enable the relatively high flow rates required at the electrodes, particularly the ~ 23 gpm flow needed at each double-sided cathode to produce the target 0.86 ft/sec velocity past each cathode face.

During the quarter we completed revisions on our pre-prototype scale regenerator plating cell which converted it from a gravity-overflow to a pressurized flow unit. That work was done to be sure that the pressurized stack design we are providing to Atotech for the prototype cells will work.

To reiterate, the major pre-prototype cell changes were (a) provision of a new, thicker (3/8") separator plate with a pair of chamber-length, 5/32" wide blocks on the top to give extra seating surface area for (b) new, separate anode and cathode chamber covers which we made integral with the graphite electrodes by bolting them to the titanium collector plates which are fastened to the graphite plates, and then cementing and sealing the PVC cover/Ti/graphite assembly with acid-proof epoxy.

Initial pressure tests of the pre-prototype plating cell showed only small leaks; these were seen at both covers at their in-board faces where the sealing areas are 6 1/2" strips which are just 10/32" wide and which have a line of four 1/8" holes down the strip center. By both double gasketing and adding silicone caulk under the covers, which compensated for a slight misalignment of separator plate and chamber frames, we obtained a leak-free assembly at pressures of 8 psig. Because of this result we expect that the larger, hole-free sealing areas specified for the prototype, plus better machining of mating chamber frame and separator plate tops, will allow routine pressurized operation.

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