ELECTROLYTIC OXIDATION OF FORMATE AND OXALATE

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Abstract:

Results of bench and pilot tests are reported which indicate anodic oxidation of ammonium formate and ammonium oxalate can be achieved using an iridium oxide coated titanium anode. Oxidation appears to proceed to carbon dioxide with a preference for oxalate over formate. Anode life tests indicate a coating life (DSA® on Ti mesh) of one or more years can be expected. A separated electrolyzer is not required to prevent unwanted reduction of organics. Cathodic reduction of formate, oxalate, maleate, and formamide appears minimal or non-existent. Formate and oxalate oxidation efficiencies decline with decreasing organic concentration and at pH extremes but are increased by using a high surface area anode. Design of a full scale electrolyzer which will be installed in 1997 is discussed.

Introduction:

DuPont and ELTECH Research Corporation (ERC) have studied the use of electrolysis for oxidizing formate and oxalate. DuPont is interested in oxidizing formate and oxalate in four streams with different compositions . The objectives were to prevent corrosion, prevent accumulation of organics, and remove organics to enhance related unit operations. This paper discusses the feasibility tests and by-product analyses that have been conducted and describes a full scale system design.

Discussion:

Description of Streams:

The compositions of the four process streams of interest are shown in Table 1.

Table 1 Stream Compositions

Component	Stream 1 wt %	Stream 2 wt %	Stream 3 wt %	Stream 4 wt %
pH	5.6	5.6	12	5.6
H_2O	44.5	49.7	86.8	54
formate	7.8	0.8	0.5	2
oxalate	0.35	0.4	0.05	1
NH_3 equiv*	8	8.9	-	8
H_3PO_4 equiv.	35	39.1	-	35
Na3PO4	-	-	12.7	-

*Doesn't include ammonia ions on organics.

Chemistry:

It was speculated formate and oxalate would be oxidized at the anode of an electrochemical cell per the following reactions.

Direct Oxidation

Anode Reactions:

Formate

$$COOH^{-1} = CO_2 + H^+ + 2\ e^-$$

Oxalate

$$C_2O_4^{-2} = 2\ CO_2 + 2\ e^-$$

Oxidation by Hydroxyl Radicals

Formate

$$HCOOH + 2\ OH^* + 2\ e^- = CO_2 + 2\ H_2O$$

Oxalate

$$H_2C_2O_4 + 2\ OH^* + 2\ e^- = 2\ CO_2 + 2\ H_2O$$

The competing anode reaction is the production of oxygen per the following.

$$H_2O = 1/2\ O_2 + 2\ H^+ + 2\ e^-$$

The corresponding cathode reaction was expected to be hydrogen evolution via the following reaction.

$$2\ H^+ + 2\ e^- = H_2$$

A literature search was conducted[1] to evaluate some of the literature[2,3,4,5,6,7] available on the electrochemistry of formate. In general the oxidation of formate (or formic acid) appears to proceed completely to CO_2. The potential (V vs SCE) for this oxidation is in the range of -0.3 (pH 12) to +0.5 (pH 0). However one reference (8) indicates, a "...critical potential... (is) necessary to reach to achieve oxidation of the carboxylate ion...". For formate this potential is 1.7 to 1.9. The reason for the discrepancy was not clear.

The rate of the reaction does drop sharply at extreme pH's, with a plateau between 0 and 10 (4). An intermediate is apparently involved in the oxidation which can poison the electrode, reducing the rate of the reaction. However, there is an indication operation above about 0.6 V desorbs this intermediate. This may be related to the so-called "critical potential" mentioned above.

All of the experiments appear to have been done with Pt. No reports have been found, yet, dealing with oxide electrodes. With ELTECH anodes, if the operating potential were in the lower region, loss of lifetime from

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[1] Private communication, K. L. Hardee to R. J. Coin, "Proposed Feasibility Study for the Oxidation of Formate", March 10, 1993

[2] "Voltammetric and Chronopotentiometric Study of the Anodic Oxidation of Methanol, Formaldehyde, and Formic Acid", R.P. Buck and L. R. Griffth, J. Electrochem. Soc., 109 (1962) 1005-1013

[3] "The Electrochemical Oxidation of Formic Acid on Platinum", G. W. Fleishmann, G.K. Johnson and A.T. Kuhn, J. Electrochem. Soc., 111 (1964) 602-605

[4] "Catalytic Decomposition of Aqueous Formic Acid on Platinum Electrode", D.R. Rhodes and E.F. Steigelmann, J. Electrochem. Soc., 112 (1965) 16-21

[5] "Anodic Oxidation of Formic Acid at Platinum Electrodes", M.H. Gottlieb, J. Electrochem. Soc., 111 (1964) 465-472

[6] "The oxidation of Formic Acid at Noble Metal Electrodes. I Review of Previous Work", A.W. Capon and R. Parsons, J. Electroanalytical Chem. 44 (1973) 1-7

[7] Encyclopedia of Electrochemistry of the Elements, XII, Bard and Lund, eds., p. 267-269

substrate passivation and coating dissolution should be minimized, unless there is some complexation due to the formate. It thus appears that RuO_2-based coatings could be used. The higher potential region, however, would require IrO_2, coatings and ELTECH's new technology for longer lifetimes.

In addition, in an unseparated electrolyzer, the possibility of reducing some of the organics also existed. Figures 2 and 3 provide possible oxidation/reduction paths for formate and oxalate.

Figure 2 Formate Redox Sequence[8]

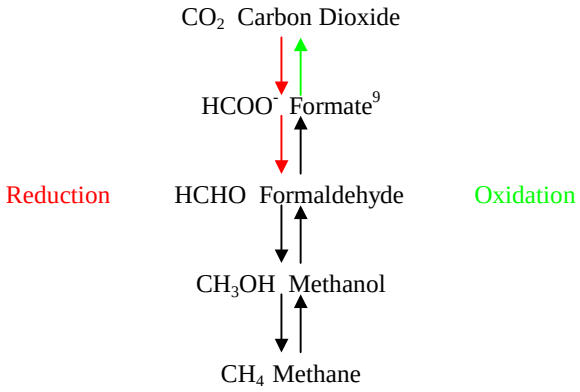
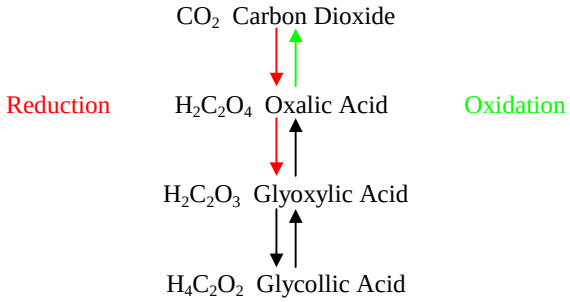


Figure 3 Oxalate Redox Sequence



While the literature reported the reduction of oxalic acid to glyoxylic acid, this reaction was typically carried out at reduced temperatures (20°C), high oxalate concentration, and low pH to maximize current efficiency. At the anticipated operating temperature of 60°C and pH 5.6 the rate of reduction was reported to be negligible.[10] Other factors minimizing the reduction of oxalate are the low concentration of oxalate, the relatively low H^+ concentration, and the high current density of a single layer cathode compared to the significantly lower current density on the multiple layer anode.

The overall conclusion of the literature review was that the oxidation of formate and oxalate without reduction appeared feasible but specific electrodes would have to be selected and characterization and life tests would have

[8] pg 1082, Electrochemistry and the Environment, K. Kajeshwar, J. G. Ibanez, and G. M. Swain, Journal of Applied Electrochemistry 24(1994) 1077-1091.
[9] Some Chemical Factors in the Kinetics of Processes at Electrodes, B. E. Conway, Progress in Reaction Kinetics, Vol. 4, Pergamon Press Oxford and New York 1967.
[10] The Role of Temperature in Oxalic Acid Electroreduction, K. Scott, Electrochimica Acta. Vol. 37, No. 8 pp 1381-1388, 1992.

to be conducted. Characterization tests would provide operating data required for scale-up to a commercial design and would help verify that undesired by-products would not complicate operation of the system.

Hardware:

The hardware used for feasibility and characterization tests varied. Bench tests were conducted in open 18 sq inch, unseparated, single cell electrolyzers (Figure 4) or in closed 25 sq inch single cell electrolyzers with or without a separator (Figure 5). Figures 6 and 7 are block flow diagrams of separated and unseparated systems respectively. Pilot cell tests were conducted in a separated single cell electrolyzer with 4.2 sq ft active area (Figure 8).

Figure 4
18 sq inch Open Unseparated Cell

Figure 5
Unseparated or Separated Closed 25 sq inch Cell

Figure 6
Unseparated Block Flow Diagram

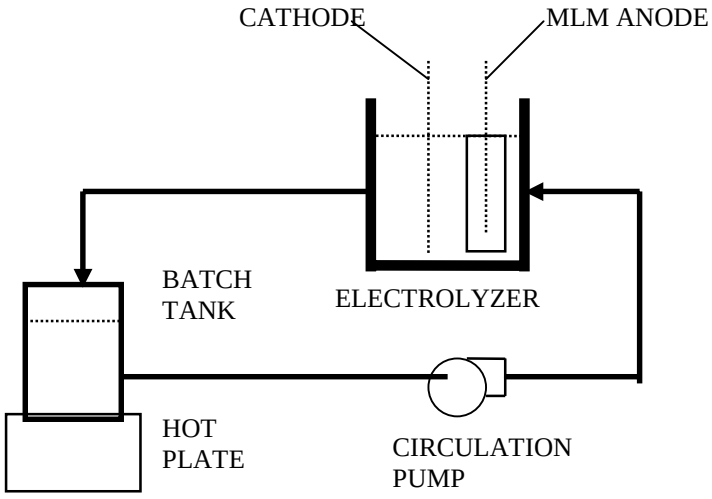


Figure 7
Separated Block Flow Diagrams

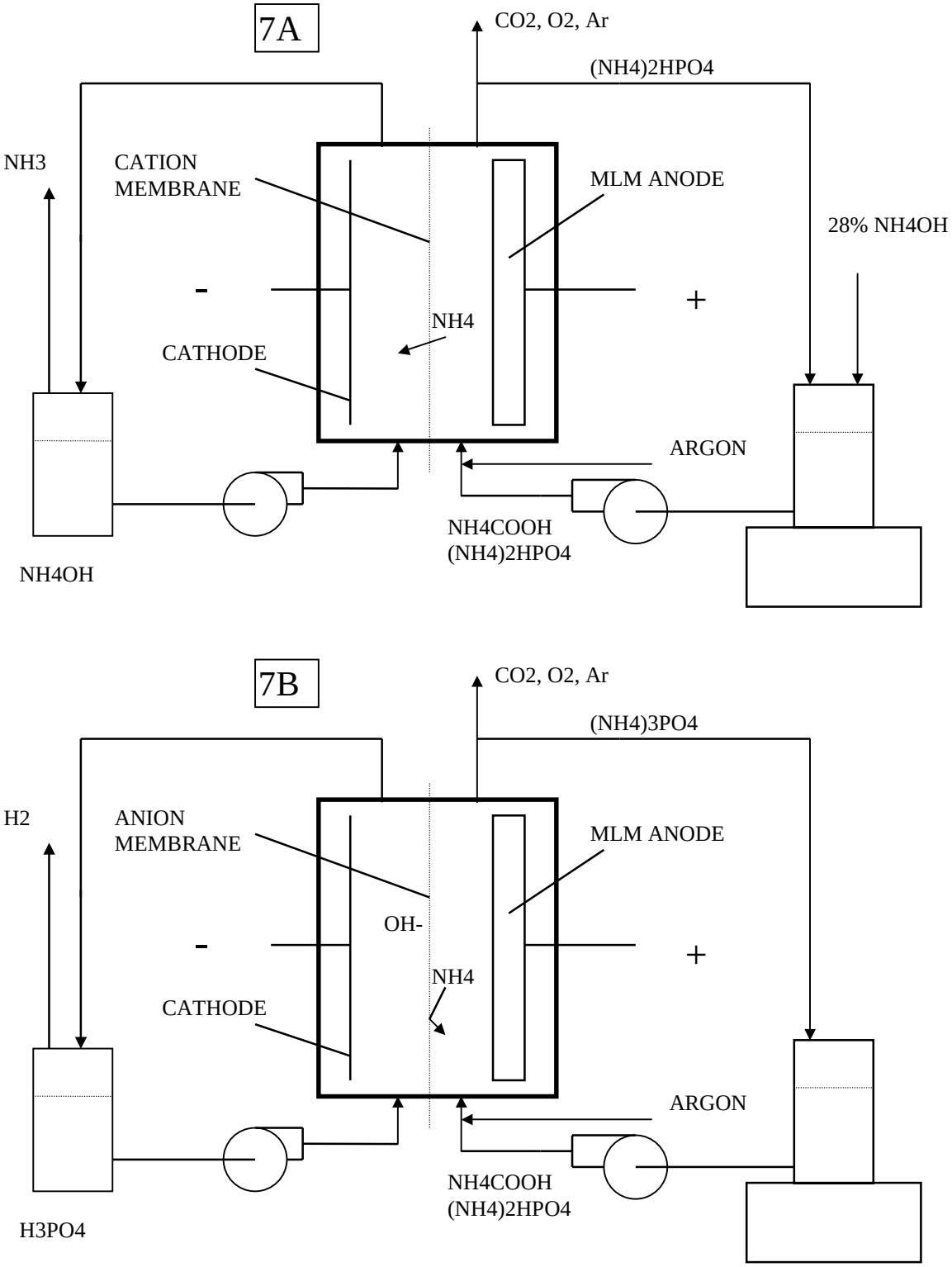


Figure 8
Pilot OD Electrolyzer

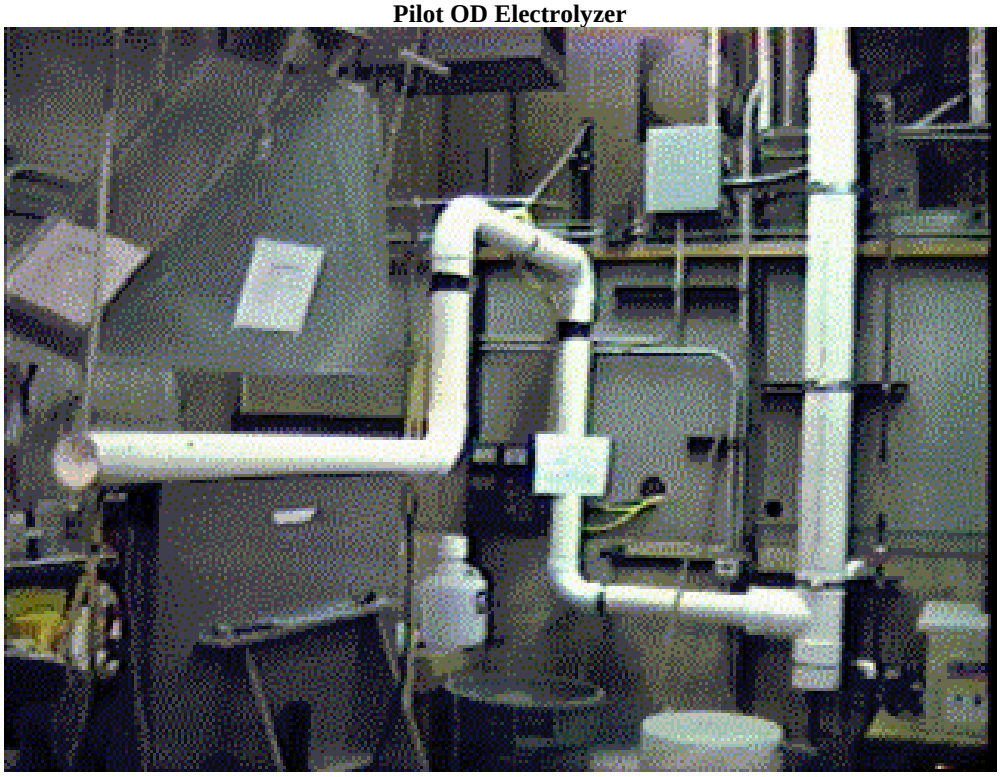


Figure 9 is a picture of two anode life test systems. See the section on long term anode life tests for a description.

Figure 9
Anode Life Test Systems

Test Results:

Synthetic Feed Tests

Cyclic Voltammetry Tests:[11]

Initial work focused on formate because it was the most abundant organic that required oxidation.
An anode is required for the oxidation of formate in an ammonium phosphate solution. A successful anode must meet two criteria. First a significant electrocatalytic activity of the anode coating for the oxidation of formate and second a sufficient lifetime for commercial viability. Several anode coatings on titanium substrates were screened using the electrochemical technique of cyclic voltammetry for their ability to oxidize formate. The lifetime criterion was initially judged based on previous experience with these anode coatings in oxygen evolving electrolytes. Later, a better definition of the lifetime was obtained by long term operation in actual phosphate/formate electrolyte.

Complications from the anode coatings and electrolyte required a modified cyclic voltammetric technique. For the usual platinum group metal oxide coatings there is a large background "capacitance" current associated with the surface area and proton exchange reaction of the oxide coating itself. Further, the reaction of interest occurs along with varying rates of oxygen evolution. The current due to the reaction of interest appears as a shoulder on the oxygen evolution current. Background corrected cyclic voltammetry (BCCV) was utilized to screen candidate coatings and to overcome these complications. This technique basically consists of acquiring a standard cyclic voltammogram with and without the presence of the species of interest, formate. The "without" curve is then digitally subtracted from the "with" curve providing a nominal formate-only cyclic.

Using the BCCV technique, six anode coatings (EC-100, EC-300, EC-600, EC-900, EC-1100, and Platinum) on sheet titanium substrates were examined for their electrocatalytic activity for formate oxidation. This report summarizes the results of this screening process.

Experimental:

The glass cell used is depicted in Figure 10. The various anode samples were clamped to the O-ring joint which provided a geometric surface area of 1.0 sq cm. The glass reference probe was fixed approximately 2 mm from the anode surface. A commercial saturated calomel electrode (SCE) was the reference electrode. The measured potentials were not compensated for residual IR. The counter electrode was an EC-600 coated 3.2 mm diameter titanium rod. The electrolyte was prepared as a saturated solution of $(NH_4)H_2PO_4$. All experiments were done at room temperature

The anode to be tested was clamped to the cell and the cell was filled with 13.0 ml of the phosphate solution. The reference chamber was also filled with 13.0 ml. A series of cyclics at three different scan rates (20,50, and 100 mV/sec) were taken. A repeat of the 50 mV/sec and 100 mV/sec scans were done to verify reproducibility. If necessary a third scan was taken. Aliquots (2.0 ml) of the formate/phosphate solution were added to the cell and new scans acquired. Typically four separate, but incremental, aliquots were added. The final concentration of formate was calculated based on total anode chamber volume. The 50 mV/sec scans were used for all of the results discussed below.

Results:

An example of the data set and the subtraction results is presented in Figure 11. Shown are the curves for the background, background + formate, and formate-only cyclics for the EC-1100 coating at 26 mM formate concentration. The distinct peak produced as a result of the subtraction is attributed to the oxidation of formate, presumably to CO_2.

[11] Private communication, Cyclic Voltammetric Screening of Electrodes for the Oxidation of Formate, by Ken. L. Hardee, ELTECH Research Corp., 12/7/93.

Figures 12-14 show the resultant BCCV curves for selected anode coatings at different formate concentrations. Figures 15-17 are selected plots of the current peak height vs. formate. In general, the responses are linear, except for the Pt/Ti sample. Here, changes in the Pt surface may be responsible for the non-linearity.

All of the DSA® coatings appear to oxidize formate at about the same potential, ca. 1.1 V vs SCE. However, the response of the EC-1100 appears to provide the maximum current. EC-300 (not shown) is intermediate between EC-100 and EC-1100. Since the platinum group metal components of EC-100, EC-300, and EC-1100 are Ru, Ru/Ir, and Ir respectively, it appears Ir may be the critical component for good electrocatalytic activity. This activity also matches the order of stability (EC-100<EC-300<EC1100) for these coatings operating under oxygen evolving conditions.

From the cyclic data it appears oxidation of formate on DSA coatings will occur near oxygen evolution. The efficiency of oxidation should be high, but because the operating potential is near the potential of oxygen evolution, the anode will probably require an oxygen evolving coating. Pt/Ti appears to offer operation at a significantly lower potential than the DSA coatings. However, there may be surface problems with the Pt, indicated by the relatively low current peak heights (compared with EC-1100, Figures 16 and 17), the non-linear response, and the broadness of the peaks. The literature also indicates poisoning of the formate oxidation reaction is a concern for platinum electrodes. Long term stability of this coating is also much poorer than EC-1100, based on previous accelerated life testing.

All of the coatings tested showed some capability to oxidize formate in a phosphate electrolyte. However, the product of the oxidation (CO or CO_2) was not identified. Based on the good cyclic volammetric response and the expected stability of EC-1100, it was the coating recommended for further studies.

Figure 10 Electrochemical Cell for Cyclic Voltammetry

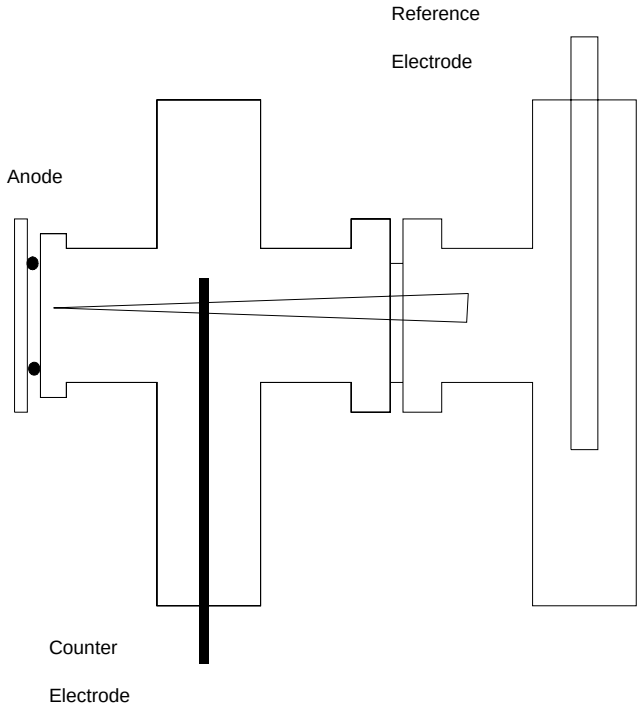


Figure 11

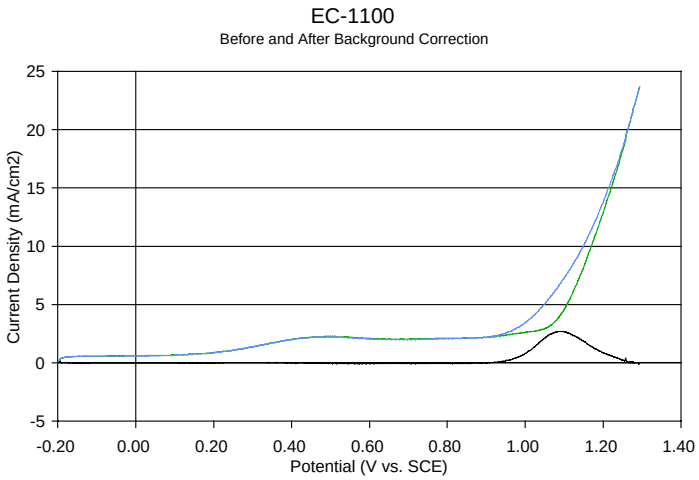


Figure 12

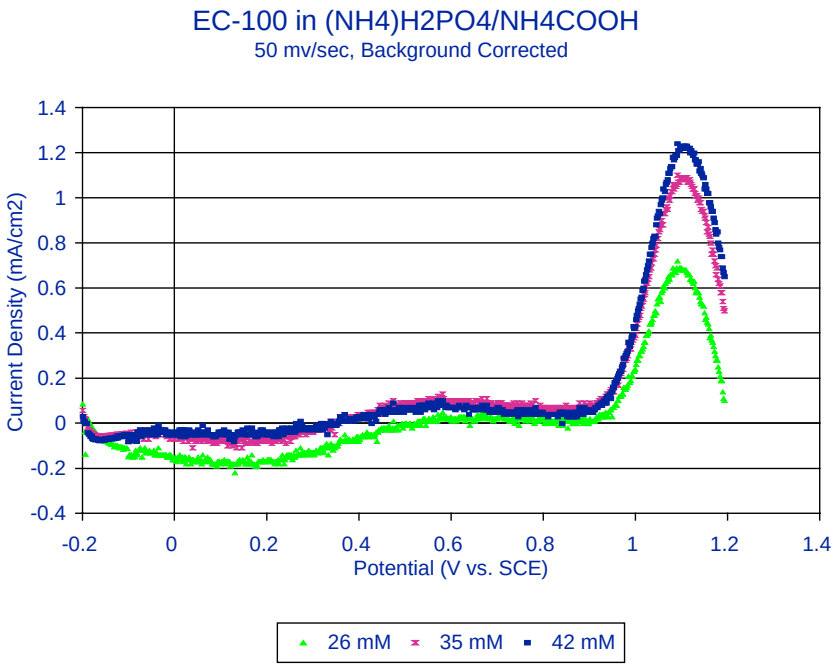


Figure 13

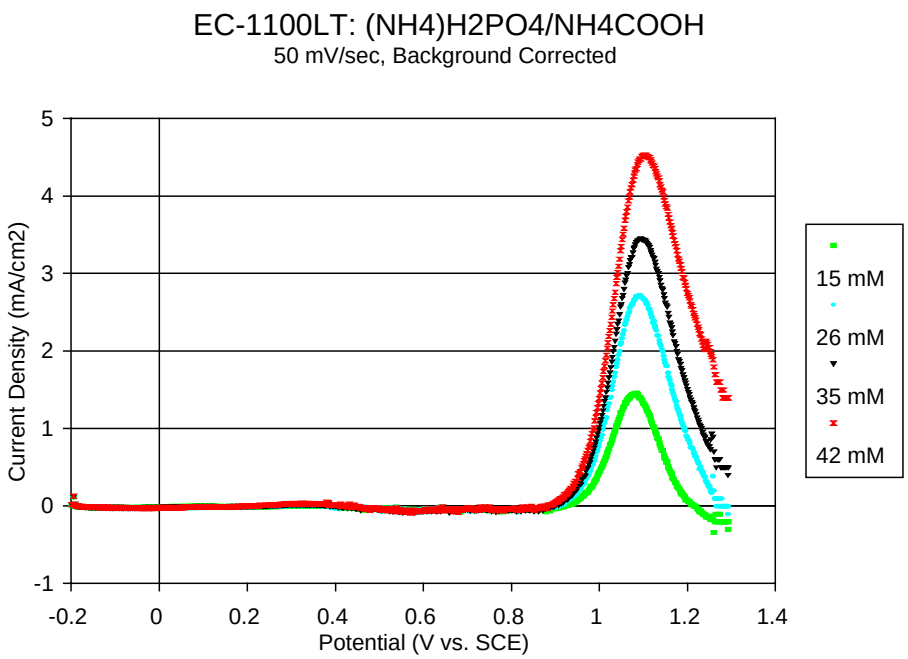


Figure 14

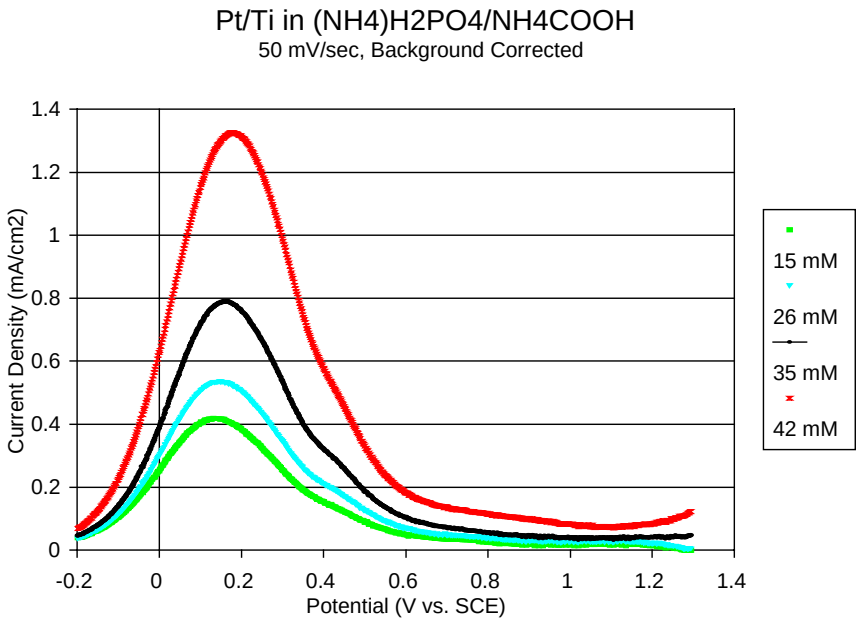


Figure 15 EC-100 Cyclic Peak Height vs Formate Concentration

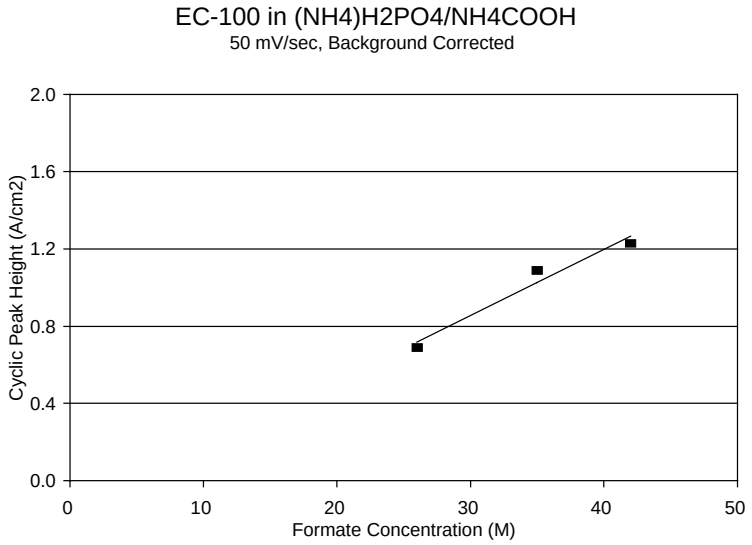


Figure 16 EC-1100 Cyclic Peak Height vs Formate Concentration

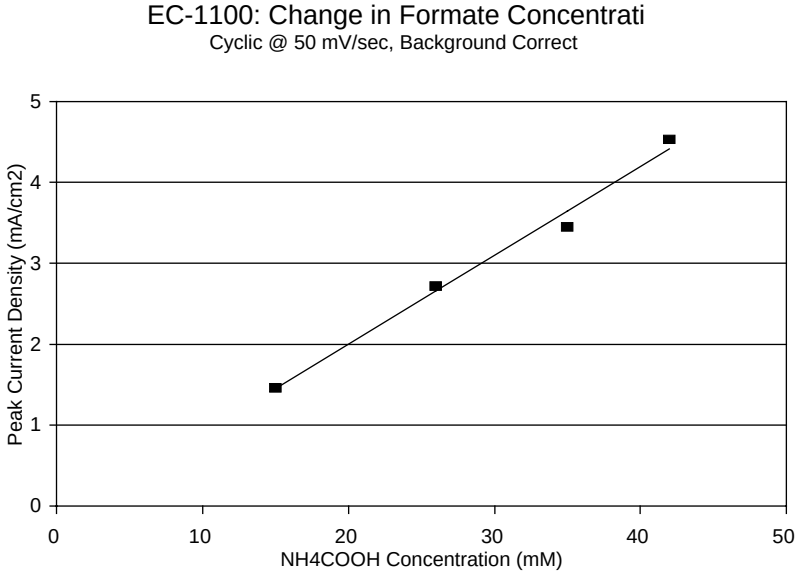
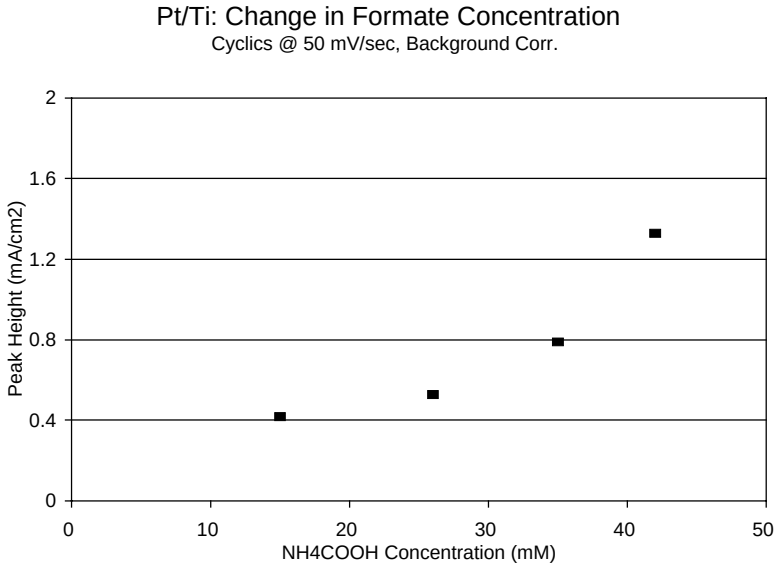


Figure 17 Pt/Ti Cyclic Peak Height vs Formate Concentration



A literature review[2] conducted in preparation for the cyclic voltammetry tests indicated oxidation of formate might be enhanced at near neutral pH, decreasing at pH extremes. Results discussed later tended to support this claim.

Multilayer Mesh (MLM) Anode vs Single Layer Anode

Two tests were conducted to determine if a MLM anode would achieve higher efficiency than a single layer anode under the same conditions. Nafion 450 separated cell tests (Figure 7A) were conducted at 78 ASF. The catholyte temperature was 40°C and the anolyte temperature was 65°C. The catholyte was 3% NH_4OH. Tests were conducted with actual plant feed between approximately 8.5 and 1.0 wt % formate and oxalate combined. The cell with the MLM achieved 100% efficiency (based on Draeger tube CO_2) and the single layer anode achieved only 50% efficiency.

Bench Scale Feasibility Tests

The first four bench scale tests were conducted on synthetic Stream 2 solution in an 18 sq inch unseparated electrolyzer (Figure 4) in a batch mode (Figure 6) using 3 liters of electrolyte. The feed contained approximately 1 wt% ammonium formate and 0.5 wt % ammonium oxalate. Anodes coated with EC-600 and EC-1100 were tested with feed near 5.7 and 2.9 pH and at 78 (EC-600) and 63 ASF (EC-1100). Steel cathodes were used. Formate and oxalate concentrations were determined using ion chromatography. Table 2 summarizes the results.

Table 2 First Four Bench Scale OD Results

First Four Bench Cell Tests												
	Active Area sq inches			18								
	Volume of Electrolyte L			3								
	Expected Formate Feed gpl			8.625								
	Expected Oxylate Feed gpl			4.26								
Run No. 1												
Anode: EC600							Theo	Formate	Oxalate			
		Current	Amp	Formate	Oxalate		gmoles/min	gmoles/min	gmoles/min	Current	Cell	
Sample No.	Time Min.	Amps	minutes	gpl	gpl		/sq M	/sq M	/sq M	Effic. %	Volts	pH
1	0	9.72	0	6.75	3.38		NA	NA	NA	NA	2.81	5.82
2	120	9.72	1166.4	3.71	2.23		0.260	0.142	0.028	65.5	3.04	
3	240	9.72	1166.4	1.12	0.52		0.260	0.121	0.042	62.7	3.08	
4	360	9.72	1166.4	0.24	0.25		0.260	0.041	0.007	18.4	3.08	5.4
									Avg CE	48.8		
Run No. 2												
Anode: EC1100							Theo	Formate	Oxalate			
		Current	Amp	Formate	Oxalate		gmoles/min	gmoles/min	gmoles/min	Current	Cell	
Sample No.	Time Min.	Amps	minutes	gpl	gpl		/sq M	/sq M	/sq M	Effic. %	Volts	pH
1	0	7.85	0	5.84	2.84		NA	NA	NA	NA	2.56	5.54
2	120	7.85	942	1.98	0.73		0.210	0.181	0.052	110.5	2.91	
3	240	7.85	942	2.34	0.18		0.210	-0.017	0.013	-1.6	3.17	
4	360	7.85	942	1.26	0.18		0.210	0.051	0.000	24.1	3.21	5.99
									Avg CE	44.3		
Run No. 3												
Anode: EC600							Theo	Formate	Oxalate			
		Current	Amp	Formate	Oxalate		gmoles/min	gmoles/min	gmoles/min	Current	Cell	
Sample No.	Time Min.	Amps	minutes	gpl	gpl		/sq M	/sq M	/sq M	Effic. %	Volts	pH
1	0	9.72	0	8.73	4.39		NA	NA	NA	NA	2.86	2.91
2	120	9.72	1166.4	3.88	1.23		0.260	0.227	0.077	116.9	3.14	
3	240	9.72	1166.4	1.4	0.5		0.260	0.116	0.018	51.5	3.27	
4	360	9.72	1166.4	0.32	0.25		0.260	0.051	0.006	21.8	3.28	3.07
									Avg CE	63.4		
Run No. 4												
Anode: EC1100							Theo	Formate	Oxalate			
		Current	Amp	Formate	Oxalate		gmoles/min	gmoles/min	gmoles/min	Current	Cell	
Sample No.	Time Min.	Amps	minutes	gpl	gpl		/sq M	/sq M	/sq M	Effic. %	Volts	pH
1	0	7.85	0	4.21	2.17		NA	NA	NA	NA	2.48	2.88
2	120	7.85	942	3.51	0.48		0.210	0.033	0.041	35.3	2.85	
3	240	7.85	942	2.54	0.18		0.210	0.045	0.007	25.1	3.06	
4	360	7.85	942	0.87	0.18		0.210	0.078	0.000	37.2	3.09	3.06
									Avg CE	32.5		

Current densities were selected based on the area of the two anodes and an estimated limiting current density of 4 ASF (based on z=2, D=0.000002, and sigma=0.001).

$$I_{limiting} = zFDAC_b/\eth \text{ (Bockris/Reddy, '77')}$$

Where: z = number of electrons per equivalent, 1
F = Faraday's constant, 9.65 $x10^4$ amp seconds
D = Diffusion Coefficient, estimated at ~$2x10^{-6}$ cm^2/sec for formate
A = Electrode area, basis of 1 sq cm
Cb = formate concentration, moles/cc
ð = diffusion layer thickness, estimated at $1x10^{-3}$ cm

The EC-600 MLM anode had 26 layers for 2800 sq inches per sq foot while the EC-1100 anode had 21 layers for 2260 sq inches per sq foot. Taking the area of the anodes into account, the projected current density was 77.8 ASF for the EC 600 anode and 62.8 ASF for the EC-1100 anode. Current efficiencies of 48.8, 44.3, 63.4, and 32.5% were achieved, based on ELTECH IC analyses, between ~6 and 0.5 gpl formate.

High pH test

Tests with simulated Stream 3 feed at pH 12 showed 10-22% current efficiency for formate oxidation but the oxalate was untouched (Ref. Table 3). This was significantly different from the results obtained during bench scale feasibility tests discussed above which achieved higher efficiencies for formate and oxalate oxidation and a preference for oxalate oxidation. It is suspected these results may be in agreement with literature claims of reduced current efficiency at pH extremes[2]. Further evidence supporting this agreement is presented in the Feed Preparation Electrolyzer.

Table 3 Formate/Oxalate Destruction - Stream 3
Single Acid Simulated Feed, pH 12
18 sq inch electrolyzer, MLM Anode w EC 1100 coating, Unseparated
3 liters total solution, 60°C
Batch Operation

Run No.	Time Min.	Current Amps	Current Density ASF	Formate gpl	Oxalate gpl	Cell Voltage V	Current Efficiency %
1	0	0	0	3.92	362	0	NA
	360	7.85	62.9	2.59	369	2.51	10
2	0	0	0	4	387	0	NA
	300	3.92	31.4	2.89	424	2.04	20.2
3	0	0	0	4.24	416	0	NA
	360	1.96	15.7	3.52	438	1.9	21.9

Individual Tests Oxalate, Formate, Formamide - Separated OD Bench Tests

Three tests (runs 31, 32, and 33) were conducted each using synthetic feed in a 25 sq inch separated cells (Figure 7A) with one organic added to simulate Stream 1 concentrations. Table 4 summarizes the runs. Run 31 showed oxalate was oxidized from 3.7 gpl to 0.6 gpl with the current efficiency dropping from 94 to 24% based on Draeger CO_2 analyses. Based on 2 L/min Ar purge, 4.45 vol % CO_2 would correspond to 100% efficiency based on formate and 8.52 vol % CO_2 based on oxalate. Run 32 showed formate was oxidized from 47.1 gpl to below detection at 89% current efficiency based on Draeger CO_2 analyses. Run 33 showed no decrease in formamide concentration, and no CO_2 evolution. It wasn't oxidized.

Table 4 Separated OD Bench Tests - Individual Tests Oxalate, Formate, Formamide
(Common Parameters: 77 ASF, 2 L/min Ar, 2 liters electrolyte, 26 layer anode)

					%	CO2	CELL
	Run	FORMATE	OXALATE	Formamide	CO2	CE %	V
Run No.	Hrs	GPL	GPL	GPL			
13765-31	0		3.7				
	35min				8	93.9	4.2
	50min				2	23.5	4.2
	1		0.662		0		4.2
13675-32	0	47.1					3.8
	2				4	89.9	3.7
	3				4	89.9	3.7
	4				4	89.9	3.8
	5	<100ppm			4	89.9	3.9
13675-33	0			0.3			
	30min				0		4.2

Actual Feed Tests

Separated OD Bench Tests

As with the Separated OD Bench Tests conducted with synthetic feed above, the same tests with actual feed showed initial efficiencies of 85% or above based on TOC or CO_2 content of the off-gas. Efficiencies based on IC analyses of formate and oxalate were lower. This could indicate organics in addition to formate and oxalate were being oxidized (or transported across the membrane). Again, oxalate appeared to be preferentially oxidized. Table 5 provides a summary.

Table 5 Separated OD Bench Tests
(Actual Feed, Nafion 450 Membrane, 77 ASF, 2 L/min Ar)

								TOC		IC
	Run	ANOLYTE	FORMAT	OXALATE	TOC	%	CO2	ORG	CELL	ORG
Run No.	Hrs	LITERS	GPL	GPL	%	CO2	CE %	CE%	V	CE%
13675-21	4	3	70.1	3.5	4.4	4	89.9		7.5	
	24.5	3	20.6	<100mg/l	2.2	300ppm		108	7.4	66.7
13675-23	4	2				4.5	101.1		6.2	
	5.5	2				1	22.5		5.8	
	6	2							5.8	
13675-25		2	107.3	1	4.3					
	4	2				5	112.4		7.4	
	8	2				4	89.9		5.9	
	12	2				3.5	78.7		5.9	
	12.43	2	71.1	104.4mg/l	3.2			58.6		
	16.57	2	43.4	36.6mg/l	2.2	4	89.9	160	5.3	
	16.57	2	36.8	32mg/l	1.79			225		75.6
13675-29	0	2	46.5	0.455	5.13			84		
	17	2	31.2	92 mg/l	1.72			101.7	4.84	
	18.1	2				4	89.9		4.68	
	21.13	2	8.87	<38 mg/l	0.81			103	5.1	
	24.4	2	3.25	<38 mg/l	0.47			96.7	5.1	

LC results provided by DuPont for Run 29 re shown in Table 6. Current efficiencies declined from 94.9 to 33.1% as formate and oxalate dropped from 8.95 & 0.458 wt % to 0.446 & 0 wt % respectively. However, CO2 and TOC efficiencies (Table 6) remained high. Since CO2 efficiencies remained high, at least a portion of the higher efficiency was probably due to oxidation of other organics. All of the higher efficiency could not be attributed to transport across the membrane.

Table 6 Run 13675-29 - Summary LC Analyses

Volume liters		2											
SG		1.3											
Area sq in		25											
CD ASF		77											
Summary of Run 13675-29								Theo	Theo	Theo	Actual		
		wt%	wt%	wt%	wt%	g Oxidized	g Oxidized	A-sec	A-sec	A-sec	A-sec	CE	
Time hrs	pH	Oxalate	Maleate	Formate	Formamide	Oxalate	Formate	Oxalate	Formate	Total	Total	%	
0	5.43	0.458	0.011	8.948	0.197	NA	NA	NA	NA	NA	NA	NA	
17	5.75	0.005	0.006	2.22	0.074	11.778	174.9	25831	750247	776078	818125	94.9	
21.13	6.14	0.003	0.005	0.911	0.103	0.052	34.0	114	145968	146082	198756.25	73.5	
24.4	5.62	0	0.003	0.446	0.172	0.078	12.1	171	51853	52024	157368.75	33.1	

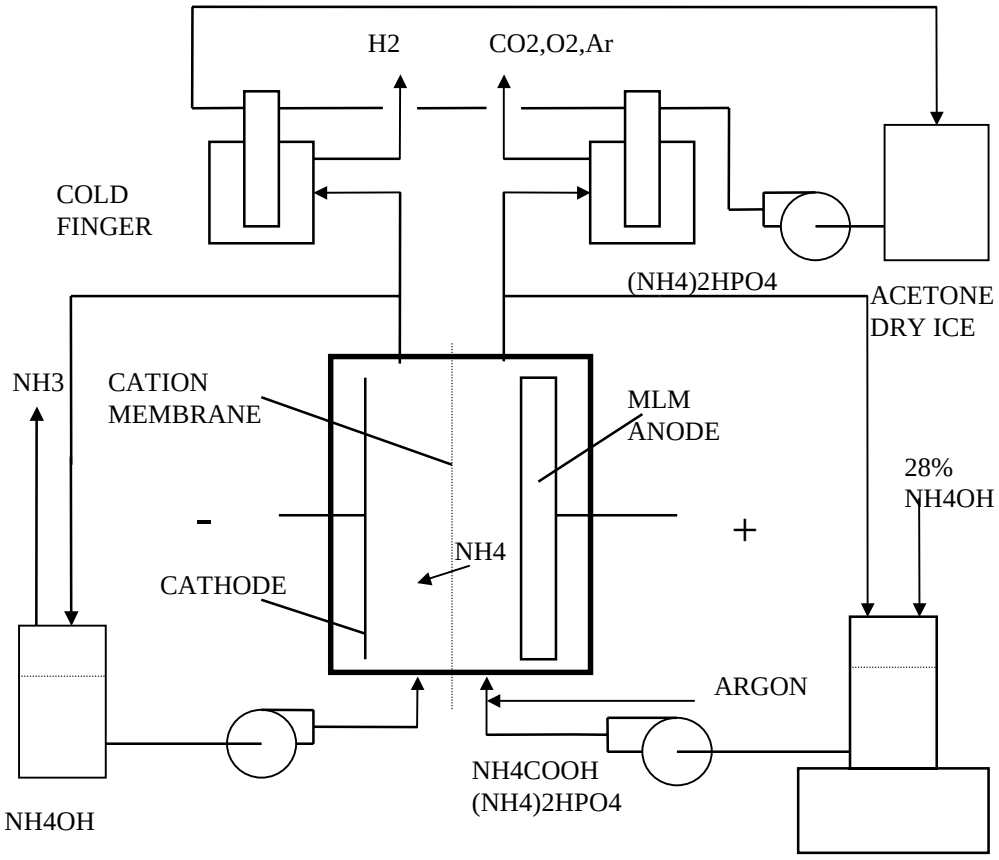
Solution Preparation for Corrosion Test

Four liters of actual Stream 4 solution was treated through an unseparated 25 sq inch OD cell at 150 ASF, Figures 5 and 6. Formate was lowered from 22.6 to 4.7 gpl and oxalate was lowered from 12.1 to 0.07 gpl with an overall current efficiency of 63.5%.

First Reduction Products Tests

The objective of these tests was to determine if organics were being reduced at the cathode to produce unwanted or volatile by-products. Two series of reduction products tests were conducted. The first was with a separated bench cell, an argon purge, and acetone dry ice traps on the anolyte and catholyte vent gas streams. Figure 18 provides a block flow diagram.

Figure 18 First Reduction Products - Block Flow Diagram



No condensate was observed in either of the traps. Draeger tests for formaldehyde were negative and no interferences were observed.

Table 7 is a summary of the analytical results obtained on the anolyte and catholyte during the first test. There was reasonable agreement between the ELTECH and DuPont labs. Oxalate was quickly oxidized at the anode from 0.45 to 0.04 wt % while at the cathode it decreased from 0.48 to 0.39 wt %. Formate was also oxidized at the anode, from 8.8 to 4.75 wt % while at the cathode it decreased from 8.9 to 6.1 wt %. This decrease of formate in the cathode is probably due to transport across the membrane into the anode compartment. Both DuPont and ELTECH TOC's were lower than anticipated based on DuPont LC and ELTECH IC results.

Table 7 First Reduction Products Tests

File: REDPROD.XLS										
	DuPont	ELTECH	DuPont	DuPont	ELTECH	DuPont	DuPont	ELTECH	DuPont	ELTECH
	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Predicted	Predicted
Hours	Oxalate	Oxalate	Meleate	Formate	Formate	Formamide	TOC	TOC	TOC	TOC *
0	0.45	0.51	0.02	8.8	7.83	0.16	3.16	3.78	4.87	4.32
2	0.3	0.31	0.02	8.7	9.93	0.15	3.1	3.84	4.77	5.38
4	0.21	0.18	0.02	8.72	8.84	0.15	3.18	3.5	4.76	4.76
6	0.1	0.08	0.02	7.16	6.94	0.12	2.76	3	3.89	3.72
8	0.04	0.03	0.02	4.75	5.54	0.12	1.83	2.42	2.58	2.96
	DuPont	ELTECH	DuPont	DuPont	ELTECH	DuPont	DuPont	ELTECH	DuPont	ELTECH
	Catholyte	Catholyte	Catholyte	Catholyte	Catholyte	Catholyte	Catholyte	Catholyte	Predicted	Predicted
Hours	Oxalate	Oxalate	Meleate	Formate	Formate	Formamide	TOC	TOC	TOC	TOC *
0	0.48	0.47	0.02	8.93	7.5	0.12	3.11	3.6	4.93	4.13
2	0.45	0.47	0.02	8.6	8.5	0.11	3.04	3.7	4.75	4.66
4	0.33	0.29	0.01	6.09	6.4	0.11	2.18	2.44	3.37	3.49
6	0.35	0.3	0.01	6.04	6.5	0.113	2.16	2.25	3.35	3.55
8	0.39	0.33	0.01	6.09	6.8	0.16	2.17	2.7	3.40	3.72
Note: All results are weight %. ELTECH's numbers have been converted from gpl assuming a SG of 1.2										
* Doesn't include formamide or meleate.										

Second Reduction Products Tests

Description of Second Reduction Products Tests

For the second series of tests an unseparated bench cell (Figure 5) was used with the vent gasses being combined, diluted with argon below the lower explosive limit, and passed through three scrubbers, n-butanol, dinitrophenylhydrazine, and 5% NaOH. N-butanol was intended to trap organics that could be analyzed by GC/MS. DNPH was to trap carbonyls which would be converted to hydrizones and analyzed using a UV method. The NaOH scrubber was to trap CO_2. Gas samples were also collected for GC analyses. Figure 19 is a picture of the second reduction products test system.

Nine runs were conducted in three groups of three. Runs 1 to 3 were conducted at 150 ASF using 1.5 L of feed with the objective to destroy 90% of the formate and oxalate. Runs 4 to 6 were conducted at 77 or 75 ASF using 1.5 L of feed with the objective to destroy 90% of the formate/oxalate. Runs 7 to 9 were conducted at 150 ASF using 3 L of feed with the objective to oxidize the oxalate to 100 ppm. Run duratins of 7, 14, and 4 hours respectively were selected in order to achieve the desired organics oxidation. Table 8 summarizes the run conditions and the scrubbers used.

Figure 19 Second Reduction Products Test System

Table 8 Second Reduction Products - Run Conditions

Run No.	Objective	ASF	Feed Volume liters	Duratn Hours	Scrubber
1	Oxidize 90% of formate/oxalate	150	1.5	7	Butanol
2	Oxidize 90% of formate/oxalate	150	1.5	7	DNPH
3	Oxidize 90% of formate/oxalate	150	1.5	7	2N NaOH
4	Oxidize 90% of formate/oxalate	77	1.5	14	Butanol
5	Oxidize 90% of formate/oxalate	75	1.5	14	DNPH
6	Oxidize 90% of formate/oxalate	75	1.5	14	2N NaOH
7	Oxidize Oxalate to 100ppm	150	3	4	Butanol
8	Oxidize Oxalate to 100ppm	150	3	4	DNPH
9	Oxidize Oxalate to 100ppm	150	3	4	2N NaOH

Butanol Scrubber Results

Samples of n-butanol before and after scrubber tests were analyzed by GC. Impurities found in butanol scrubber samples before and after scrubbing were of the same magnitude (25-150 ppm) and character indicating that the butanol did not pick up any significant amount of scrubbed or by-product organics from the organic destruction electrolyzer. Similar analyses on the feed and product electrolyte showed no significant changes in impurities.

Dinitrophenylhydrazine Scrubber Results

GC/MS analysis of the dinitrophenylhydrazine scrubbers showed no accumulation of stripped organics.

Sodium Hydroxide Scrubber Results (CO_2 in Purge Gas)

The objective of the sodium hydroxide scrubbers was to trap the CO_2 from the electrolyzer, convert it to carbonate and quantify it by acid titration. Both the remaining NaOH and the Na_2CO_3 could be determined by titration with acid. The amount of CO_2 absorbed based on the increase of carbonate and the decrease of sodium hydroxide could be compared against that expected based on formate and oxalate analyses and against GC and Draeger tube analyses of the purge gas. Runs 3, 6, and 9 were conducted with sodium hydroxide scrubbers. Table 9 compares the five CO_2 vent gas concentrations (NaOH loss, carbonate gain, Draeger tube, ELTECH GC, and ELTECH IC.)

Table 9 Summary of CO_2 Purge Gas Analyses/Estimates

								Avg. mole %	Avg. mole %			
			Feed				CO2 grams	CO2 in 2 l/min	CO2 in 2 l/min			Form/Oxa
Run			Volume	Duratn	CO2 grams	CO2 grams	ELTECH IC	Argon	Argon	Draeger	ELTECH GC	ELTECH IC
No.	Objective	ASF	liters	Hours	NaOH Basis	Base 2 Basis	Form/Oxa	NaOH Basis	Base 2 Basis	% CO2	% CO2	% CO2 Avg.
3	90% all	150	1.5	7	69.2	70.5	146.7	2.1	2.13	10-7	<2	8.16
6	90% all	75	1.5	14	63.47	80.3	144.7	6.73	8.51	6-4	4.3-3.1	4.2
9	100ppm ox.	150	3	4	49.39	45.9	130.68	2.99	2.77	8.5-6	5.6-5	12.2

There appears to be reasonably good agreement between the NaOH loss and the carbonate gain for the three runs. However, runs 3 and 9 show the CO_2 based on the NaOH scrubber is significantly lower than from the other three methods and Run 6 shows the CO_2 based on the NaOH scrubber to be higher than the other three. Run 6 took a 100 cc/min slip stream of vent gas, measured with a small metering pump, and scrubbed it in series through three 150 ml scrubbers. Runs 3 and 9 took the entire vent gas stream (2 L/min Ar) and passed it through two one gallon scrubbers. Possibly the efficiency of the scrubbers was better for Run 6 because of the lower flow rate of vent gas. It is suspected the gallon jug scrubbers were not as efficient as desired. The second gallon scrubber in series accumulated a significant amount of CO_2 which had to pass through the first scrubber. The second gallon scrubber was expected to be equally inefficient.

In the final analysis, the caustic scrubber tests were not as accurate as desired because of poor efficiency of the gallon jugs and possible difficulty in maintaining an accurate slip stream flow for the 150 ml scrubbers.

In further analysis of the CO_2 in the vent gas from: NaOH scrubbers, Draeger tubes, GC, and IC results, Run 9 IC results show a higher CO_2 concentration in the vent gas than for GC and Draeger tube analyses. This may be explained by the greater than 100% efficiency obtained for Run 9 based on IC and TOC, see Table 12. Since vapor loss of formate or oxalate has been all but ruled out by acetone, n-butanol and dinitrophenylhydrazine scrubber analyses (see below), possibly the formate and oxalate are catalytically destroyed initially (while at relatively high concentration) or they are absorbed onto the anode and then oxidized later. These possibilities warrant further study.

GC Results

Unfortunately many of the gas bulbs leaked or analytical procedures allowed air contamination, and results of gas samples with high N_2 had to be rejected. Table 10 shows the results obtained by ELTECH on the GC analyses of gas samples. The possibility that ammonia was being reduced to N_2 should be investigated.

Table 10 ELTECH GC ANALYSES

DuPont Victoria Feed Organic Destruction Tests									
Unseparated Cell									
Argon Flow 2 l/min									
							ELTECH	ELTECH	ELTECH
			Feed				VENT	VENT	VENT
Run			Volume	Duratn			SAMPLES	ANALYSIS	SAMPLES
No.	Objective	ASF	liters	Hours	Comment	%CO2 Drg	NB 13675	% CO2 GC	WITH N2
1	90% all	150	1.5	7	1st Hr	9	50-13-1	11.2	
1	90% all	150	1.5		last Hr	8.8	50-19-2	8.8	
2	90% all	150	1.5	7	1st Hr	6.1	52-13-2	4.2	XXX
2	90% all	150	1.5		last Hr	8	52-19-1	8.8	XXX
3	90% all	150	1.5	7	1st Hr	10	57-11-2	<2	XXX
3	90% all	150	1.5		last Hr	7	57-18-2	<2	XXX
4	90% all	77	1.5	14	1st Hr	0.5	49-13-1	6.2	
4	90% all	77	1.5		last Hr	3.8	49-32-1	<2	XXX
5	90% all	75	1.5	14	1st Hr	1.2	54-14-1	4	XXX
5	90% all	75	1.5		last Hr	3	54-32-1	<0.5	XXX
6	90% all	75	1.5	14	1st Hr	6	60-11-1	4.3	XXX
6	90% all	75	1.5		last Hr	4	60-32-1	3.1	XXX
7	100ppm ox.	150	3	4	1st Hr	7.8	53-15-1	12.5	
7	100ppm ox.	150	3		last Hr	8.4	53-17-1	11	
8	100ppm ox.	150	3	4	1st Hr	11	51-15-1	10.7	
8	100ppm ox.	150	3		last Hr	12	51-17-1	10.2	XXX
9	100ppm ox.	150	3	4	1st Hr	8.5	56-11-2	5.6	
9	100ppm ox.	150	3		last Hr	6	56-14-1	5	XXX

TOC Results

Table 11 summarizes TOC results obtained for runs 1, 4, and 7.

Table 11 TOC and Current Efficiency - Second Reduction Products Tests

			Feed			DuPont	DuPont
Run		CD	Volume	Duratn		TOC wt%	TOC
No.	Objective	ASF	liters	Hours	Comment	Range	% CE
1	90% all	150	1.5	7	1st Hr	4.13/4.54	137.7
1	90% all	150	1.5		last Hr	1.34/1.86	
4	90% all	77	1.5	14	1st Hr	4.78/4.94	120.5
4	90% all	77	1.5		last Hr	2.02/1.77	
7	100ppm ox.	150	3	4	1st Hr	4.14/4.07	320
7	100ppm ox.	150	3		last Hr	2.93/2.75	

LC, IC, and Efficiency Summary

Table 12 summarizes the DuPont liquid chromatography results, the ELTECH ion chromatography results, and efficiencies calculated based on both.

Table 12 LC, IC, and Efficiency Summary

DuPont Victoria Feed Organic Destruction Tests										
Unseparated Cell										
Argon Flow 2 l/min							SG = 1.3	SG = 1.3		
			DUPONT	DUPONT	DUPONT	DUPONT	ELTECH	ELTECH		
			ANAL.	ANAL.	ANAL.	ANAL.	ANAL.	ANAL.	DuPont	ELTECH
Run			Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	form. ox.	form. ox.
No.	Objective	Comment	Oxalate	Maleate	Formate	Formamide	Formate	Oxalate	CE %	CE %
1	90% all	1st Hr	0.317	0.017	8.64	0.111	9.32	0.28	95.1836	106.128
1	90% all	last Hr	0.004	0.02	1.757	0.285	1.61	0.01		
2	90% all	1st Hr	0.293	0.016	8.549	0.097	8.94	0.26	95.3286	103.837
2	90% all	last Hr	0.004	0.018	1.643	0.309	1.38	0.01		
3	90% all	1st Hr	0.287	0.013	8.449	0.1	8.53	0.26	99.916	102.257
3	90% all	last Hr	0.003	0.016	1.201	0.528	1.09	0.01		
4	90% all	1st Hr	0.355	0.019	9.331	0.123	10.22	0.3	83.5093	93.9909
4	90% all	last Hr	0.004	0.021	1.897	0.187	1.8	0.01		
5	90% all	1st Hr	0.292	0.015	8.239	0.081	8.55	0.27	76.4599	82.1474
5	90% all	last Hr	0.003	0.018	1.597	0.359	1.39	0.01		
6	90% all	1st Hr	0.311	0.013	8.834	0.104	8.64	0.28	83.7876	83.5852
6	90% all	last Hr	0.003	0.016	1.551	0.435	1.35	0.01		
7	100ppm ox	1st Hr	0.278	0.015	8.285	0.078	8.95	0.26	139.848	185.667
7	100ppm ox	last Hr	0.032	0.015	6.34	0.092	6.31	0.04		
8	100ppm ox	1st Hr	0.305	0.017	8.599	0.099	8.96	0.27	153.202	156.492
8	100ppm ox	last Hr	0.038	0.016	6.467	0.091	6.76	0.04		
9	100ppm ox	1st Hr	0.275	0.015	8.334	0.084	8.5	0.25	184.051	224.046
9	100ppm ox	last Hr	0.026	0.014	5.736	0.079	5.29	0.03		

The DuPont and ELTECH analyses and efficiencies agree reasonably well. Runs 1 through 3 have efficiencies very near 100%. Runs 4 through 6 have efficiencies averaging near 85%. Runs 7 through 9 have efficiencies averaging near 175%. It is speculated that higher current density (150 vs 75 ASF) may improve organic oxidation efficiency based on comparing runs 1-3 and 7-9 at 150 ASF with runs 4-6 at 75 & 77 ASF. It is also speculated the efficiencies over 100% for runs 7-9 may be due to volatilization of organics or catalytic decomposition. Volatilization may be more significant in these runs because of the short duration and high organic concentration. However, reduction products tests discussed previously all but rule out volatilization of the organics. This needs to be resolved.

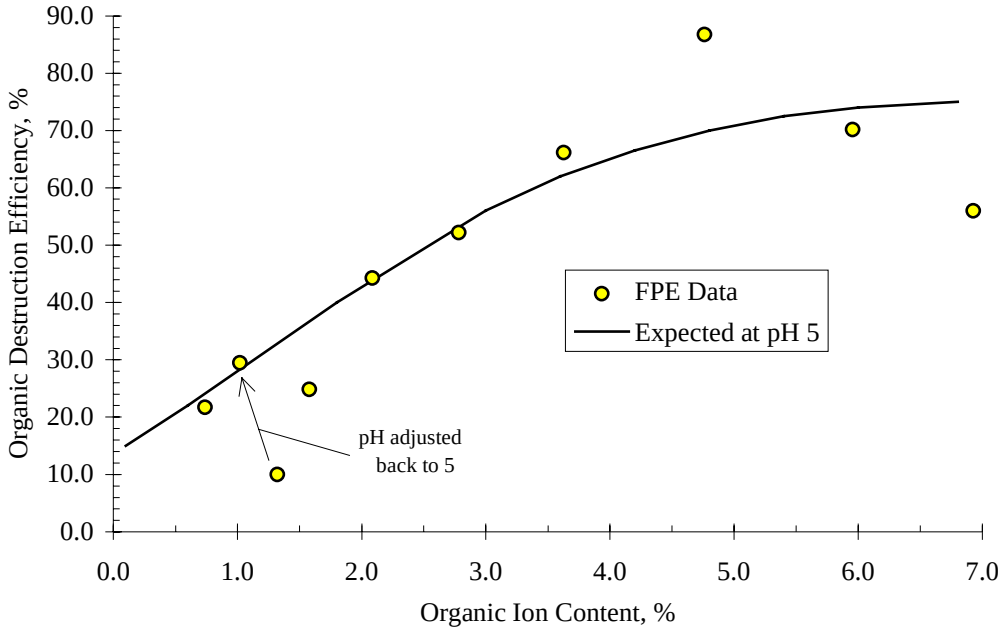
Feed Preparation Tests

Actual Stream 1 solution needed to be treated to lower the formate and oxalate to simulate steady state Stream 2 conditions. The 4.2 sq ft, separated, pilot cell was run at 50 ASF. Actual solution was circulated as anolyte to oxidize the organics from approximately 12 to 1%. A 3.5 wt% ammonium hydroxide (saturated) solution was not conductive enough to pass current so 1% sodium hydroxide was used as the catholyte. The cell was equipped with a high surface area anode, a stainless steel cathode, and a Nafion 350 cationic membrane to separate anolyte and catholyte.

Forty-four gallons (168 liters) of DuPont Victoria Plant Feed was diluted with deionized water at a 75:25 ratio to discourage crystal formation. The resulting 224 liters of electrolyte (Stream 1 solution) containing 87.6 gpl formate and 1.06 gpl oxalate was treated a total of 220.5 hours at 200 A. All of the oxalate was oxidized in less than 48 hours and the final formate concentrations was 8.0 gpl. Periodic anolyte pH adjustments with ammonium hydroxide made to the electrolyte during and at the end of treatment controlled the anolyte pH to near it's original 5.4 value. The ammonium oxalate was destroyed to below detection and the ammonium formate concentration was reduced to 1% ammonium formate. Organic destruction efficiency vs organic ion concentration results are shown in Figure 20.

During the operation of the FPE, the efficiency was found to be better near a pH of 5. A curve is shown in Figure 20 that corresponds to the expected efficiency a pH near 5. Operation with unseparated OD destruction of organics is expected to be similar to this curve.

Figure 20 Organic Destruction Efficiency Feed Preparation Tests



99% Oxidation of Formate and Oxalate

The feed electrolyte treated by the FPE was used for this test. The objective was to reduce the ammonium organics concentration from 1.0 wt% to 0.1 wt%. An unseparated 28.8 sq inch OD open-tank cell with high surface area anodes and stainless steel cathodes was used.

The feed electrolyte treated by the FPE was used for this test. The objectives of this test were to reduce the ammonium organics concentration in the feed solution from 1.0 wt% to 0.1 wt% and to establish operational parameters to satisfy these conditions. An unseparated, 28.8-sq inch OD open-tank cell with high surface area anodes and stainless steel cathodes was used

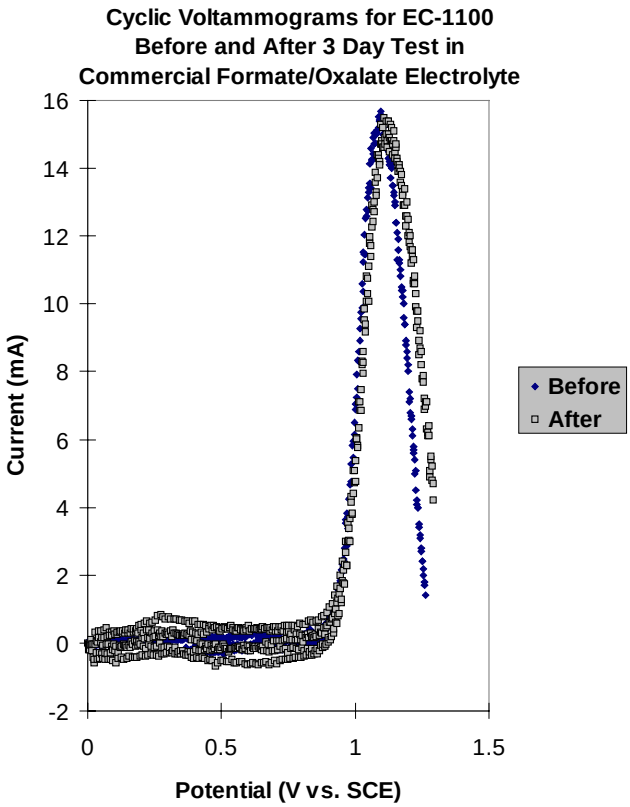
The OD efficiency was lower than anticipated; 15% to reduce the NH_4COOH concentration from 1.0 wt% to 0.1 wt%. Similar batch tests with synthetic feed achieved 40% current efficiency.

Short-Term Stability Test for EC-1100 for Formate/Oxalate Destruction

A sample of EC-1100 (mesh) was tested for 3 days in actual Stream 1 solution. The test was conducted in a batch cell (Figure 9, ca. 2.5 L volume) with a geometric anode area of about 10 sq cm. The test was run at 4 ASF, based on the geometric area without taking into account the void area of the mesh. This is a slightly higher current density than that of a single mesh layer in the pilot cell. The temperature of the electrolyte was 60^{o}C. Cyclic voltammograms showing formate oxidation were made before and after the test and the coating loading was monitored using TEFA (Tubular Excited Fluorescence Analysis).

Figure 21 compares the cyclic voltammograms. No change in the peak height or position were found, indicative of no deterioration in the electrocatalytic nature of the anode surface. The TEFA spectra (peak height for the platinum group metal) was also unchanged. Based on this short term test, no immediate poisoning or deterioration of the EC-1100 coating was anticipated.

Figure 21 Cyclic Voltammograms for EC-1100 Before and After 3 Day Test in Commercial Formate/Oxalate Electrolyte



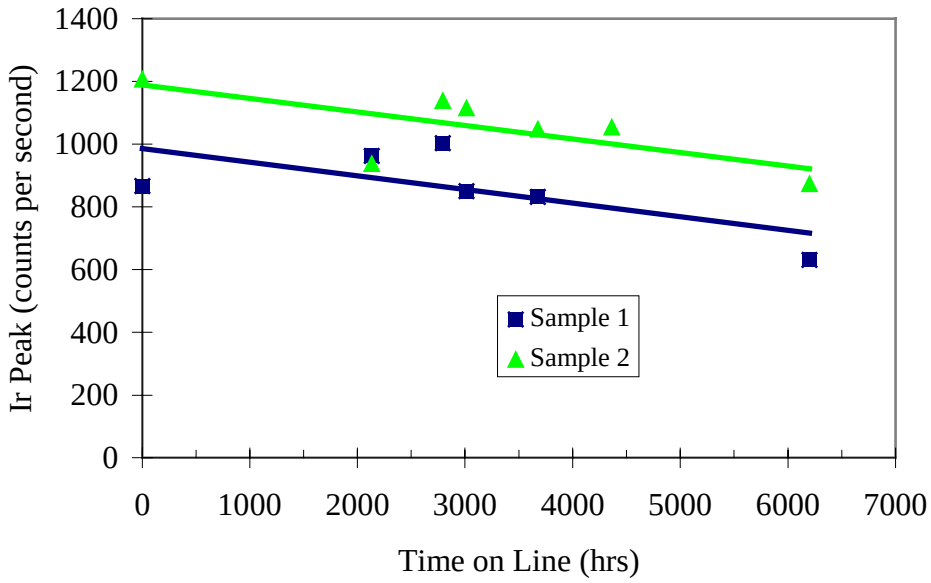
Extended Anode Life Tests

Two samples of EC-1100 on fine mesh, as used in the MLM anode, were operated in batch electrolysis cells using Solution 1 electrolyte to determine if there were any detrimental effects to the anode. The anodes were pulled periodically and examined by TEFA for coating loss, and by cyclic voltammetry for activity for formate oxidation. AC Impedance measurements were run initially and after termination of the tests. During the life test the cell voltages were monitored both by computer and manually. Water was added to the cells automatically as needed. Formate and oxalate were periodically added based on IC analysis of the concentrations in the individual cells. The electrolyte was replaced with fresh feed solution about mid-way through the test. The electrolyte temperature was maintained at 60 °C ± 5°C and the current density was 5 mA/cm^2, based on geometric (shadow) area of the sample. This current density represents the equivalent of one layer of the multi-layer full electrode.

The tests were terminated after 6201 hours with the anodes still functional. The cell voltage was about 2.2 V ± 0.2 V during the course of the tests with no trend towards passivation detected. AC impedance measurements indicated no sign of the growth of a passivation layer.

X-ray fluorescence analysis during the course of the test indicated a slow loss of Ir as seen in figure 22.

Figure 22. EC-100 Life test in Victoria Feed.



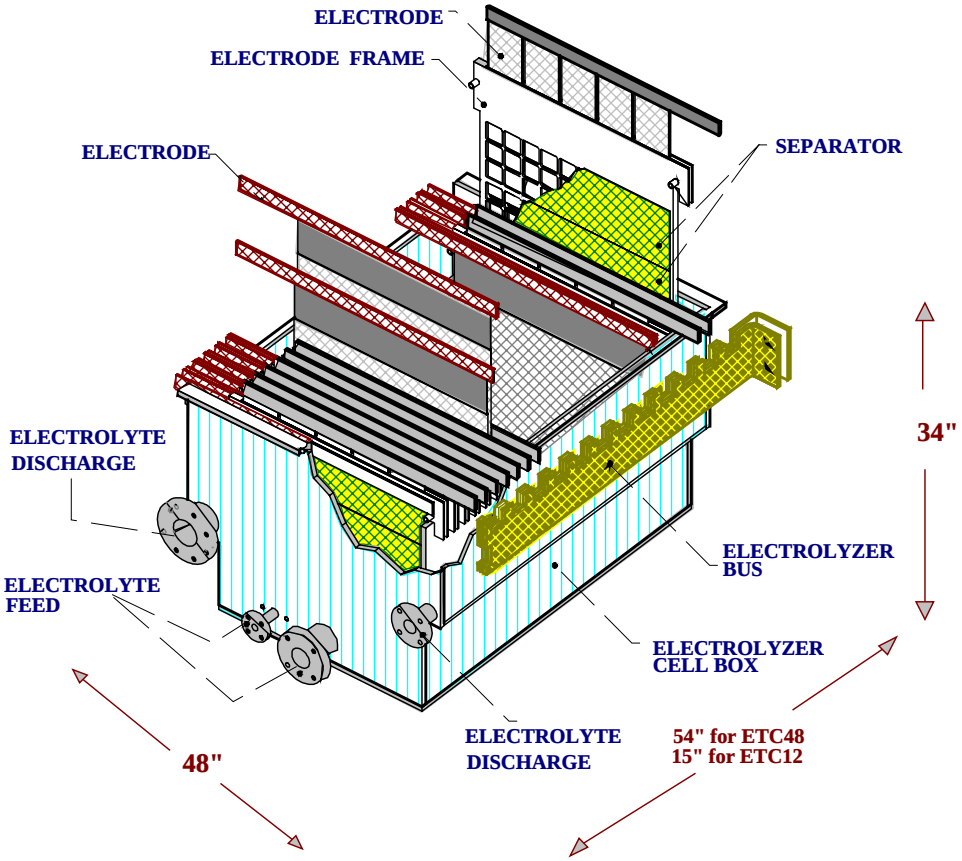
The life tests on the EC-1100 coating did not indicate any catastrophic failure of the anode coating when operated in the actual Solution 1 electrolyte. However, there appears to be a gradual loss of Ir from the coating which, if it continues, would ultimately limit the anode life. A one year life was demonstrated and a significantly longer life is anticipated.

Commercial System

A system to oxidize 4 lb/hr of formate and 2 lb/hr of oxalate at 2 and 1 wt% respectively was needed by DuPont. One commercial ETC 48 electrolyzer would require a minimum current efficiency of 17% at 75 ASF to have the required capacity. Previous tests indicated actual efficiencies of 63.5% (Solution Preparation for Corrosion Tests, pg 19) and 40% (Organic Destruction Efficiency Feed Preparation Tests, Fig. 20) could be anticipated. This indicated a full size electrolyzer would have significantly higher capacity than needed. However, because of the lack of long term pilot scale data (and the high cost of obtaining it), it was decided to install a full size ETC-48 system.

Two systems are presently being engineered for installation in early 1997. Although all of the details of how the system will perform have not been determined in the lab and pilot tests, enough evidence has been obtained to know the system being designed will meet or exceed the organic destruction, by-product, and anode life requirements. Since the systems are relatively small, it was decided to install oversized full scale commercial systems rather than pilot systems which would cost nearly the same. These commercial systems can be used to demonstrate and optimize the systems for use in other DuPont plants.

Figure 23 - Commercial ETC System



Conclusions:

1. Oxidation of formate and oxalate is feasible for the four streams tested producing carbon dioxide as the major by-product.

2. A titanium anode with a EC-1100 coating is a good candidate for long electrode life and high current efficiency.

3. Current utilization (current efficiency) is a function of solution pH, organics concentration, and anode coating. A maximum efficiency was observed at approximately 5.5 pH with an EC 1100 coated anode while efficiency declined as organics concentration decreased.

4. A multiple layer mesh electrode provides higher current efficiency than a single layer mesh electrode.

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