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DEVELOPMENT OF MOLTEN CARBONATE FUEL CELL
POWER PLANT TECHNOLOGY

Quarterly Technical Progress Report No. 9 for the Period
October 1—December 31, 1981

Work Performed Under Contract No. AC02-79ET15440

United Technologies Corporation
South Windsor, Connecticut

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

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DEVELOPMENT OF MOLTEN CARBONATE FUEL CELL
POWER PLANT TECHNOLOGY

Quarterly Technical Progress Report No. 9
for Period October 1, 1981 to December 31, 1981

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Prepared for

DEPARTMENT OF ENERGY
UNDER CONTRACT DE-AC01-79ET15440

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FOREWORD

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ABSTRACT

This report summarizes the work performed under U.S. Department of Energy Contract No. DE-AC01-79ET15440 during the seventh quarterly reporting period from October 1, 1981 through December 31, 1981. The overall objective of this 29-month program is to develop and verify the design of a prototype molten carbonate fuel cell stack which meets the requirements of a 1990's-competitive coal-fired electrical utility central station or industrial cogeneration power plants.

EXECUTIVE SUMMARY

During this quarter, activity continued in three of the four task areas: Task 2 - cell and stack design, development and verification; Task 3 - preparation for fabrication and testing of the full-scale prototype stack; and Task 4 - development of the capability to operate stacks on coal-derived gas.

The evaluation of SrTiO_3 as a matrix filler was suspended. Chemical analysis showed strontium dissolution and cell tests showed a possible reduction in electrode activity. Cell tests with matrices that contained no added fillers functioned satisfactorily, but these matrices contained cracks when the cell were disassembled. Further testing is required.

A process for making full-scale bubble barriers was established. A suitable binder oxidation-cycle/sinter-cycle was developed. Samples have been processed at higher sintering temperatures in an attempt to eliminate sintering during cell operation. Further development of the bubble barrier fabrication process is required to eliminate voids in the part. These voids can result in an unacceptably low bubble pressure.

Heat-treat experiments with the Ni-Cr anodes have shown that a minimum temperature is required to achieve a good dispersion of chrome throughout the nickel phase. Such a treatment results in an anode which is resistant to sintering, but which still creeps at a significant rate.

A secondary heat-treating process is being developed to reduce or eliminate anode creep and progress to date is encouraging. The creep resistance of this type anode is retained during 1000 hours of exposure to electrolyte at simulated cell conditions.

Direct formed anodes have been fabricated with a narrower channel width than previously reported since structural analysis showed that better conformity would result from this configuration change. A cell containing such an anode is running well on the endurance bench. Flow channel dimensional control is improved over earlier samples, but still requires improvements for a full area cell.

A relatively coarse patterned single piece current collector was received from a production perforating vendor and demonstrated adequate cathode support in a single cell test but the cell did not exhibit good performance.

Several approaches to obtaining full scale separator plates are being investigated. For the near term, cross rolling of 24 in. wide bimetal sheet is the prime candidate. Butt welding the bilayer or using an alternative material that is available in full scale width may be more attractive for the long term.

A 4 x 4 in. cell was tested using the stack separator plate design approach instead of the normal "boiler plate" configuration in an attempt to obtain better conformity between components with time as cell components creep. This cell was subjected to six thermal cycles. Its performance was as good as that attained by the best cells tested previously and superior to most. Further testing of this concept is planned.

A cell was tested with a 0.060 in. electrolyte tile in place of the 0.018 in. tape matrices normally used. The tile holds much more electrolyte than the tape and can give up some of this electrolyte with time. Performance decay of the tile cell was similar to typical tape cells operated at 150 psia. It is concluded that the matrix thickness and total cell electrolyte volume are not major factors in performance decay.

Construction of the four pressurized single cell test stations was completed.

An Fe-Cr-Ni alloy continues to demonstrate better corrosion resistance than AISI 316 stainless steel at anode conditions; however, degradation of the protective oxide layer after 2500 hours in a severe laboratory immersion test is apparent. The material performed satisfactorily for 2900 hours in an ambient pressure cell test at anode conditions.

A test plan for individual components of the manifold seal configuration has been developed and two tests were performed with the stack simulator rig.

Teardown investigation is in progress on the 10-cell stack, originally assembled under an Electric Power Research Institute Project and continued on test under this project to a total operating time of 3010 hours.

The 10-cell subscale stack has been operated for 462 hours at pressure up to 10 atmospheres demonstrating performance levels consistent with subscale single cells. The stack experienced an uncontrolled depressurization which necessitated a shut-down for repairs to the stack and stand. Both have been completed and the stack is ready for restart.

A design review of components for the 20-cell subscale stack (DOE #2) is scheduled for January; however, the long lead time items have been identified and have been placed on order.

The design effort during this quarter was concentrated on the design of the cell package and stack hardware for DOE Stack No. 2. The stack will contain twenty cells and is scheduled for test in April, 1982. Construction drawings were completed for all long lead-time stack hardware.

An improved separator plate configuration has been designed in a parallel Niagara Mohawk Power Company program. This plate will be tested in DOE Stack No. 2.

A one-piece cathode current collector with improved deflection characteristics has been designed and fabricated. Structural tests show this component meets the design requirements.

All items for the full area short-stack test facility identified previously as requiring long lead times have been received.

Bench-scale cell tests indicate that carbon disulfide (CS_2) and carbonyl sulfide (COS) reduce the performance of molten carbonate fuel cells to the same degree that hydrogen sulfide (H_2S) does. The mathematical model of sulfur effects was modified to include gas-phase diffusional losses and a revised estimate of the poisoning of the H_2 - oxidation reaction. The results of this model are in agreement with experimental data on sulfur effects obtained at ambient pressure with fuel gases of the preliminary reference design.

INTRODUCTION

This report summarizes the work performed at the Power Systems Division of United Technologies under Department of Energy Contract No. DE-AC01-79ET15440 "Development of Molten Carbonate Fuel Cell Power Plant Technology" from October 1, 1981 through December 31, 1981. This work is separated into three tasks:

TASK 2 - DEVELOP AND VERIFY CELL AND STACK DESIGN

This task established the detailed design of a full-scale stack which meets the functional requirements of the reference power plant design selected in Task 1. Under this task, the cell and stack components required for this design are also developed. This effort culminates in the verification of the stack design by a test of a short stack of full-scale cells.

TASK 3 - DEVELOP CAPABILITY FOR FULL-SCALE STACK TESTS

This task provides the capability for manufacturing and definition of the facilities required for testing full-scale cells and the prototype stack. Task efforts include establishing a low cost manufacturing process for the electrolyte matrix based on a tape forming process, providing test plans for the prototype stack, and providing a plan for acquisition and construction of long lead time equipment for a test of the full-scale prototype stack.

TASK 4 - DEVELOP CAPABILITY FOR OPERATION OF STACKS ON COAL-DERIVED GAS

This task determines the mechanisms by which contaminants passing through the fuel gas cleanup system and those in the cathode air supply may affect the molten carbonate fuel cell. A mathematical model predicting the impact of contaminants over 40,000 hours will be developed. This model will permit definition of the impact of gas composition on cell performance and will be used to establish the cleanup system specification. The operability of molten carbonate fuel cells on coal-derived gas will be demonstrated using a mobile test unit for endurance tests of single cells at gasifier sites.

Section 1

TASK 1. ESTABLISH POWER PLANT REFERENCE DESIGN

No effort this quarter.

Section 2

TASK 2. DEVELOP AND VERIFY CELL AND STACK DESIGN

2.A Develop Electrolyte Structures (Activity 150)

Ceramic Matrix

Alternative Filler Materials - The use of SrTiO_3 as an alternative matrix filler was ruled out. Chemical analysis of electrodes used in cell 340, which contained SrTiO_3 in the matrix, showed 0.2 w/o Sr in both electrodes. This observation led to the concern that low electrode activity measured on this cell was due to SrTiO_3 dissolution products. Attempts to measure the effect of SrTiO_3 saturated electrolyte on anode activity in a half-cell test proved inconclusive. It had been previously reported in Activity 175 that SrTiO_3 is more stable at anode conditions than at cathode conditions. SrTiO_3 is currently being evaluated as a filler in anodes. Use of SrTiO_3 in the tape will be suspended pending the results of the anode tests.

The option of omitting additional matrix fillers entirely was tested in four cells during this quarter. Cell 342 built for this purpose was thermal cycled six times without the bubble pressure dropping below 10 psi. Shutdown of the cell was forced at this point by anode housing corrosion. Cells 368P (a pressurized cell), 369, and 370 were tested for other purposes, but without additional fillers in the matrix. While none of the later cells were subjected to a thermal cycle 340, 368P, and 369 have been shut down and inspected. In all three cases the ceramic tape contained cracks when the cell was disassembled. This is not normally observed in matrices and a greater probability for cracking on thermal cycling may be the result of eliminating the filler material. Further testing is required to establish whether they are in fact required, but will continue to be used until this issue is resolved.

Open Circuit Voltage Depression - Three mechanisms which might explain depressed open circuit voltages (OCV's) were studied during the quarter. Oxalate ions functioning as a soluble redox couple was ruled out due to a calculated 0.1 ASF maximum current attributable to this mechanism. This is too low to cause the observed reduction in OCV. Calculation of the theoretical OCV assuming complete equilibrium (including methanation) would account for some, but not all of the discrepancy. An electrochemical short across the seal caused by O₂ reduction on the sides of the flange and the edge of the bubble barrier was calculated to produce a current of the required magnitude assuming it was limited only by the inplane resistance of the matrix. Tests are planned in which the external surfaces of a 4 x 4 in. single cell will be exposed to a reducing gas in order to check this hypothesis.

Matrix Process Development - Process development was initiated to form the 17 mil tape in one or two plies rather than the four plies used previously. This would reduce processing time and costs. A trial to produce a two-ply tape resulted in settling of the matrix filler within the ply and resulted in an unacceptable degree of stratification. Increasing viscosity might reduce settling but conflicts with other equipment limitations. Four plies will continue to be used for the present.

Bubble Barriers

Bubble Barrier Process Development - Development of a continuous process to form bubble barriers was continued and the initial full size (18 x 36 in.) parts were produced. The general processing steps consists of:

- (1) Formation of a bubble barrier tape.
- (2) Heat-treatment in a two-stage cycle in which the polymeric binder is burned-out in air and then the powder is sintered in a reducing atmosphere.
- (3) Roll compacting to the desired porosity/thickness.
- (4) Annealing.

The tape forming operation results in a uniform thickness tape with a thickness value of 12 ± 1 mils. X-ray inspection of the tape showed the presence of numerous internal voids. Some progress was made in reducing the number of voids by lowering the viscosity of the tape precursor and by extending the tape drying time; but additional development is required. These voids result in large pores in the compacted part and result in aqueous bubble pressures of 2.0 to 3.5 psi versus a desired minimum value of 7.0 psi.

Examination of used bubble barriers from cell tests have shown that the barrier continues to sinter within the cell and this sintering results in an increase in pore size and a corresponding reduction in bubble pressure with time. The use of a high temperature heat treatment step is being evaluated to improve long term bubble barrier stability. Laboratory heat-treat cycles were run on several samples that were then filled with electrolyte and aged in a fuel atmosphere for 250 hours at 1300°F. The samples are currently being examined for evidence of improved sintering resistance.

2.B Develop Anode (Activity 155)

Optimization of Anode Stability - Evaluation of the higher temperature treated nickel-chrome anodes was continued out to 2200 hours of exposure to electrolyte at 1300°F. The stability of these anodes is compared to anodes sintered at lower temperatures in Figure 2-1. The following conclusions can be drawn:

- (1) Samples sintered at the higher temperature show an initial growth in volume which increases as the Cr content increases. Subsequent volume shrinkage of approximately 0.5% per 1000 hours is observed.
- (2) Samples sintered at lower temperatures show a significant shrinkage with time, ranging between 4% to 10% volume shrinkage per 1000 hours.
- (3) Replacing nickel with a non-shrinking ceramic filler reduces the shrinkage in proportion to the volume of filler used.

Tests have shown that anodes sintered at high temperature still creep at an unacceptable rate. This activity is being curtailed in-lieu of developments reported under advanced materials. That work begins with a Ni-Cr anode sintered at high temperature that was developed in this activity.

Advanced Concepts for Anode Stabilization - Results previously reported have shown that of the conventional strengthening techniques: precipitation hardening, dispersion hardening, and solid solution strengthening, are the most effective and practical approaches to improve the creep strength of porous nickel anodes. As a result, during this reporting period, strengthening the anode by these various techniques was examined.

Samples prepared by one technique all exhibited an order of magnitude improvement in the initial creep strength (Figure 2-2) over the standard Ni-Cr anodes in a short term test. The test consisted of subjecting the samples to a static load of 100 psi at 1300°F for up to 1000-hours under a saturated fuel gas environment. On the basis of these preliminary results, the nickel-chromium system was selected for further optimization. However, since the secondary heat treatment process has

Figure 2-1. Anode Shrinkage Stability vs Time at 1300°F

not produced consistent results thus far, a search for more effective techniques were continued.

Since encouraging results were obtained, a series of tests were conducted in which both temperature and exposure time were varied in an attempt to optimize the process. Short-term creep tests showed that all of these samples exhibited good initial creep properties compared to a control sample which was not subjected to the added processing step (A thru D in Table 2-1). The samples exposed to the high temperature/short time cycles exhibited the best initial creep strength. Compatibility testing of these samples is continuing.

Table 2-1. Creep Resistance of Anode Samples

Process Cycle	Calculated Porosity, %	Creep Strength After MCO_3 Exposure @ 1400°F, Δt , %*			
		0 Hr.	250 Hr.	500 Hr.	1000 Hr.
None	74	-28	-28	-34	-28
A	69	+0.3	-1.2	-1.3	-1.8
B	70	0	-1.2	-1.2	-1.8
C	69	-2.0	-13.1	-3.9	-2.9
D	65	-1.5	-19.7	-3.8	**

* Δt , % = percent change in thickness after 16 hour/1300°F/100 psi.

** Sample lost in test.

Figure 2-2. Short Term Creep of Ni-Cr Anodes

Although results to date indicate that a suitable anode structure can be obtained by the added heat treatment step in controlled laboratory studies, the method now used is not considered a practical production technique. As a result, full-scale retort treatment of Ni-Cr samples was investigated. The microstructures obtained from laboratory preparations were used as models for the retort studies.

Metallographic examination of the retort prepared Ni-Cr samples showed them to be uniform. Short-term (16 hour) creep testing of these samples show a definite improvement in creep strength over standard Ni-Cr samples but, because of the low inherent porosity of the Ni-Cr samples, the improvement is not as dramatic as that observed in the higher porosity samples. The creep properties of various Ni-Cr samples as a function of porosity was shown in Figure 2-2. These data indicate that regardless of the technique a significant improvement in the initial creep strength can be obtained. Retention of creep strength after exposure to molten carbonate for prolonged periods of time will continue to be investigated.

The improved creep resistance of the presently developed anode is compared to earlier anodes in Figure 2-3. Future anode development will focus on optimizing and verifying the properties of the structure. Other advanced anode work will be discontinued.

Direct Formed Anodes

One of the full-scale formed anodes fabricated last quarter was fabricated through the rolling step, trimmed to 18 x 40.5 inches, and cut into 36 sections 4.5 inches square for detailed uniformity measurements. Multiple readings were taken on each section, then averaged. The results, shown in Table 2-2, are as follows:

- o Total thickness which is controlled by the rolling operation is within the desired range, varying only 1.6 mils over the entire anode.
- o Channel depth uniformity is improved over the previously reported 12 x 12 inch formed anode, varying by less than 6 mils. Further improvements in the channel depth uniformity are being made by improving tolerances in the molding equipment.

TEMP = 1300°F

P = 100 PSI

FLAT SAMPLES

ANODE HEIGHT .065 in.
(NORMALIZED)

Ni - Cr - 55% POROSITY

PREFILLED 50% W/ELECTROLYTE

Figure 2-3. Anode Creep Data

- o Channel width varied by less than 11 mils. These variations are due to non-uniform shrinkage during the secondary sinter step, and can be reduced by optimizing the furnace operating conditions. The immediate emphasis will be to minimize non-uniform shrinkage in the 1 ft² pieces which are to be cut from full-scale parts sintered at high temperature for use in the next development stack.

Table 2-2
Inspection Results from Sectioning Full-Scale
Direct Formed Anode S/N 2

Property	Units	<u>4.5 x 4.5 Inch Section</u> ¹ Range of Variation
Total Thickness	mils	1.6
Channel Depth	mils	6
Channel Width	mils	11
Porosity	%	3
Mean Pore Size	microns	0.6
Weight/Area	g/in ²	0.51

NOTE: Anode was cut into 36 sections, 4.5 inches square, which were individually measured. Reported variations are from 4.5 x 4.5 inch averages.

Structural analysis of the direct formed anode from cell 322, which exhibited a 1-2 mil sag in the web area, predicts a larger web deflection for the formed anode than for a previously tested machined anode which exhibited no sag after 4 x 4 inch cell testing. A new half-scale formed anode mold was therefore fabricated to make formed anodes with a closer rib spacing. Three 1-ft² anodes with this geometry were made and dimensional uniformity information is being generated from data obtained from two of these parts. These parts exhibit average (based on 4.5 x 4.5 inch sections) channel width variations of about 5 mils, and average channel depth variations of about 6 mils. This data is being analyzed further, to generate uniformity maps of the channel dimensions. An additional modification is being made to the molding facility to improve mold cavity tolerances prior to fabricating the formed anodes for the next subscale stack.

Formed Anode 4 x 4 Inch Testing

Cell 365 is being tested to evaluate performance and stability using a high temperature treated anode and bubble barrier. The anode is a direct formed Ni-Cr composition with the wider than desired wide channel geometry. The cell has exhibited good performance with almost no decay following 958 hours of testing. Output voltage at 160 amps/ft² has remained at 0.730 volts and the test is continuing.

Cell 373 is being tested to evaluate an alternative ceramic filler material in a direct formed anode with the narrower inch channel geometry. The anode in this cell was also stabilized by secondary heat treating. After 300 hours, cell performance remains at 0.730 volts at 160 amps/ft² and the test is continuing.

2.C Develop Cathodes (Activity 160)

Process Scale Up - Evaluation of the four half-scale cathodes fabricated in September indicated that 1 ft² parts of the desired porosity and mean pore diameter could be obtained with minor modifications to the cycle used to fabricate these sinters. Preliminary evaluation of weight per area variations indicated that further improvements in mold cavity tolerances were required before a full-scale (18 x 36 inch) cathode could be fabricated with acceptable uniformity.

Full-scale cathode trials were resumed after shim adjustments were made to the powder molding table to improve mold cavity uniformity. Maximum to minimum mold machine cavity variations were reduced from 18 mils to 9 mils. The resulting full-scale sinters exhibit typical thickness variations of about 10 mils, and are acceptable for fabricating 1 ft² parts. An additional structural modification was initiated to the molding machine in December to correct mold cavity non-uniformity caused by bowing of the lower support plate. Mold trials will be conducted to assess this uniformity improvement during the next quarter.

Parts Fabrication - Full-scale cathode fabrication was continued with the objective of fabricating 1 ft² cathodes for the DOE 20 cell stack and for a parallel EPRI sponsored program. Process trials were conducted to optimize mold plate treatment, mold weight, and furnace cycle. After completing process trials, a total of 145 1-ft² cathodes were made from 80 full-scale (18 x 36 inch) sinters, for a yield of 60%. Average nickel cathode properties are within ± 2 mils in thickness; $\pm 1\%$ in geometric porosity; and within ± 0.9 microns in average mean pore diameter.

2.D Separator Plate Development (Activity 165)

Single-Piece Current Collector - A production perforating vendor delivered samples of an 0.090 x 0.250 in. slot single piece current collector in a straight pattern as opposed to the 0.060 x 0.250 in. staggered pattern previously tested. The part was found to have reasonable deflection and spring back characteristics and adequate strength. A 400 hour single cell test showed poor performance with poor inter-component conformity as a possible cause. A relatively light loading on the cell of 10 psi may have contributed to this. No evidence of excessive cathode deformation due to the relatively coarse pattern was observed upon disassembly and photomicrographs of the tape-cathode interface are being taken. An order was placed to have a set of these plates fabricated for the second DOE stack should additional single cell testing confirm its acceptability.

The perforating manufacturer has indicated that all near-term orders, including those of full scale cells, can be manufactured using the existing tooling at costs competitive with the folded sheet metal material.

Separator Plate Processing and Process Development - Several approaches for manufacturing full scale separator plates in sizes up to 36 x 36 in. are under consideration as noted below and shown in greater detail in Figure 2-4.

- 1) Join two sheets to a narrow back up strip. (a)

- 2) Butt weld two 18 in. wide coils at the mill to obtain a 36 in. wide coil with a compatible center strip. (b)
- 3) Cross roll 24 in. wide material to 36 in. (c)
- 4) Use an alternative non bi-layer material that is available in the desired width.

The first two approaches represent minimal investment and are being pursued on a sample basis. The cross rolling effort is being paced by a material shipment delay due to a manufacturing error by the cladding vendor which forced a slip in the shipment date.

A significant development effort will be required to commercially butt weld coils. A proposal was prepared by the cladding manufacturer to determine the optimum approach for obtaining a full scale width coil that is metallurgically compatible in the weld regions and amenable to large scale production. Alternative separator plate materials covered in Section 175 are available in sheets or coils in the widths desired.

67-211

Figure 2-4. Approaches for Manufacturing Full Scale Separator Plates

2.E Single Cell Test Summary (Activity 114)

Fifteen 4 by 4-in. cells were tested this quarter in support of component development activities and determination of cell performance characteristics at reference design condition in Task 2, and for sulfur and other impurities tolerance evaluation in Task 4. Cells 342, 351, 353 and 357 were tested as part of the matrix development effort; Cells 346 and 370 were tested to evaluate alternative separator plate materials; and Cell 345 was tested to evaluate cell tolerance to sulfur. Cells 365, 373 and 380 were tested as part of the anode development effort; Cell 369 was tested to evaluate an alternative cathode current collector configuration and Cell 362 was tested to evaluate the functional characteristics of cells in a modified cell housing design. Cell 354 was tested to evaluate a stack fill/startup procedure for its effect on performance. These cells and their testing are summarized in Table 2.3.

Cells 349 and 368 were tested to provide performance and decay characteristics at reference design condition. Diagnostic testing of previous cells indicated that decay could be attributed to loss of electrolyte from the cell package. The objective of both cell tests was to verify this finding.

Cell 349 was built with a tile to provide a greater electrolyte inventory in the cell package. A tile has greater thickness and porosity than a tape matrix and hence, contains more electrolyte. During the first 1000 hours of operation at pressurized conditions, the decay rate was equivalent to a tape cell, 30 mV/1000 hours, but the rate accelerated after this period and the cell was terminated at 1940 hours. The cell lost a total of 136 mV at 160 ASF. It was concluded that the decay characteristics of this cell were not significantly different from a tape matrix cell. Post test analyses are being performed to determine the electrolyte quantity and distribution.

Cell 368 contained an anode with one of the two previously investigated stabilizer materials absent. This stabilizer material reacted with the electrolyte and was responsible for the bulk of the total short term electrolyte loss from earlier cell

packages. If electrolyte loss from the cell package is a significant contribution to cell decay, then this cell would have had lower decay. The cell started at ambient pressure and had good typical performance. While the cell was stabilizing at ambient pressure (prior to pressurization) the cell voltage suddenly dropped and the cell went to open circuit automatically. The cause of the problem was traced to an improper fuel gas mixture. Upon returning to load after the gas composition was corrected, the cell began to decay rapidly. The decay did not respond to a change in operating variables and the cell test was terminated.

Cell 362 consisted of a typical tape matrix cell package housed in modified hardware. The design allows load follow-up on the active cell area as the anode thickness changes because of possible shrinkage and creepage. Another benefit is that the dimensional tolerances on the cell components can be relaxed while achieving adequate conformity between the cell components. The cell start-up and operation at ambient pressure was normal. After stabilization, the cell was subjected to a test procedure designed to assess whether or not adequate conformity exists between cell components. Cell 362 was subjected to this test procedure six times over its 1200 hour lifetime. Its response was as good as the best cells in "boiler plate" hardware and superior to most. The effect of cell follow-up pressure on this response was also investigated. The ram pressure was reduced from 75 psi to 25 psi and the diagnostic test was repeated. The cell lost 160 mV from the beginning of test to end of test when returned to the same temperature. The ram pressure was raised to 75 psi and the performance recovered 140 mV. This response to ram pressure was as expected for the configuration function intended.

Because of the success of this cell, additional cell tests are planned in similar hardware. It should result in a more meaningful assessment of individual components.

Discussions of the remaining cells listed in Table 2-3 are presented under the appropriate activity in this report.

Construction of the four pressurized single cell test stations was completed and are now being pressure and flow tested.

TABLE 2-3. SUMMARY OF CELL CONFIGURATION, TEST OBJECTIVES, AND PERFORMANCE

Cell	Operating Time, Hours	Description	Cell Performance mV @ 160 amp/ft ²	Cell iR mV @ 100 amp/ft ²	Peak Performance mV @ 160 amp/ft ²	Test Purpose
342	1850 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -alternative design on cathode	510	59	716	Evaluation of alternative matrix configuration.
345	2236 (Terminated)	Anode-Flat Cathode-thick Matrix-std. C/C-folded sheet metal on anode -perforated plate on cathode	711 @100 amps/ft ²	61	611 (O ₂ -blown Texaco fuel)	Evaluation of cell tolerance to sulfur
346	2836 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	603	50	690	Evaluation of alternative anode side materials
349	1940 (Terminated)	Anode-reference design Cathode-thick Matrix-0.060-in. tile C/C-reference design on anode -perforated plate on cathode	680 (O ₂ -blown Texaco fuel)	59	816 (O ₂ -blown Texaco fuel)	Evaluation of thick matrix effects at high pressure.

TABLE 2-3. SUMMARY OF CELL CONFIGURATION, TEST OBJECTIVES, AND PERFORMANCE
(Continued)

Cell	Operating Time, Hours	Description	Cell Performance mV @ 160 amp/ft ²	Cell iR mV @ 100 amp/ft ²	Peak Performance mV @ 160 amp/ft ²	Test Purpose
351	1130 (Terminated)	Anode-reference design Cathode-thick Matrix-tape-alternative fabrication C/C-reference design on anode -perforated plate on cathode	555	50	725	Evaluation of matrix fabri- cated by alternative process.
353	2160	Anode-fat Cathode-thick Matrix-alternative material in bubble barrier C/C-folded nickel sheet metal on anode -perforated plate on cathode	711	37	736	Evaluation of matrix bubble barrier with high stabilizer content.
354	1984 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	734 @100 amp/ft ²	61	741	Evaluation of stack electro- lyte fill and startup procedures.

TABLE 2-3. SUMMARY OF CELL CONFIGURATION, TEST OBJECTIVES, AND PERFORMANCE
(Continued)

Cell	Operating Time, Hours	Description	Cell Performance mV @ 160 amp/ft ²	Cell iR mV @ 100 amp/ft ²	Peak Performance mV @ 160 amp/ft ²	Test Purpose
357	1257 (Terminated)	Anode-reference design Cathode-thick Matrix-tape-alternative fabrication C/C-reference design on anode -perforated plate on cathode	628	39	747	Evaluation of matrix fabricated by alternative process.
362	1260 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	738 @100 amp/ft ²	61	710	Evaluation of bench scale single cell hardware modification.
365	1006 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	757	28	757	Evaluation of anode fabricated by low cost process
368	320 (Terminated)	Anode-flat Cathode-thick Matrix-std. C/C-folded nickel sheet metal on anode - perforated plate on cathode	618 @50 amp/ft ²	27	721	Evaluation of anode with reduced stabilizer materials at reference design condition.

TABLE 2-3. SUMMARY OF CELL CONFIGURATION, TEST OBJECTIVES, AND PERFORMANCE
(Continued)

Cell	Operating Time, Hours	Description	Cell Performance mV @ 160 amp/ft ²	Cell iR mV @ 100 amp/ft ²	Peak Performance mV @ 160 amp/ft ²	Test Purpose
369	386 (Terminated)	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -alternative design on cathode	632	44	649	Evaluation of low cost cathode current collector
370	477	Anode-reference design Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate, alternative material on cathode	734	29	741	Evaluation of alternative cathode side material
373	310	Anode-reference design, alternative stabilizer Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	725	20	737	Evaluation of alternative anode stabilizer material

TABLE 2-3. SUMMARY OF CELL CONFIGURATION, TEST OBJECTIVES, AND PERFORMANCE
(Continued)

Cell	Operating Time, Hours	Description	Cell Performance mV @ 160 amp/ft ²	Cell iR mV @ 100 amp/ft ²	Peak Performance mV @ 160 amp/ft ²	Test Purpose
380	142	Anode-reference design, alternative pretreatment Cathode-thick Matrix-std. C/C-reference design on anode -perforated plate on cathode	824 @100 amp/ft ²	37	824 @100 amp/ft ²	Evaluation of anode stabilizer pretreatment process.

C/C - Current Collector

Std. Cathode - 0.015-in. thickness

Std. Matrix - 0.018 - 0.022-in.

Cell performance at H₂ utilization of 96%, CO₂ utilization of 30%, O₂ utilization of 21%

Dry Vol. %	Fuel		Oxidant	
	H ₂	- 71.5	CO ₂	- 0.18
	CO	- 13.8	O ₂	- 0.13
	CO ₂	- 14.7	N ₂	- 0.69

2.F Stack and Cell Materials Development (Activity 175)

Separator Plate Materials

Tests to determine the corrosion resistance of candidate separator plate materials at -850 and +30 mV were continued. The test potentials represent conditions duplicating cell anode and cathode environments, respectively, during high pressure operation. The results are shown in Table 2-4. An Fe-Cr-Ni alloy continues to demonstrate greater corrosion resistance than AISI 316 stainless steel at anode conditions and corrosion resistance equivalent to AISI 316 at cathode conditions.

The material has, however, begun to show appreciable oxidation at anode conditions in the form of layers, with outer layers discontinuous, cracked and spalling. A sample currently in test for 2700 hours will be continued to 5000 hours and will be analyzed.

Cell 346, an ambient pressure cell which contained an Fe-Cr-Ni alloy insert on the anode side, completed 2900 hours of testing. Metallographic examination of the insert showed a tight adherent oxide 0.0008 inch thick at the cell inlet and 0.0016 inch thick at the cell outlet. IR of this cell was normal and did not change significantly during the test; so, in addition to being relatively passive, the surface oxide is also conductive. The apparent discrepancy between the cell test and the immersion corrosion tests could be explained by a difference in potential. The anode potential in the ambient pressure cell is -930 mV versus a standard CO_2/O_2 reference whereas the corrosion test is -850 mV. Corrosion sweeps on this material show that this potential difference is important. The -850 mV condition is representative of the exit condition of a cell operating at stack "B" conditions. This material will be evaluated in a single cell at conditions equivalent to the stack B exit.

The laboratory test in which the Fe-Cr-Ni alloy is exposed to a simulated cell cathode environment completed 4150 hours of testing. The alloy was found to have a 0.002 inch thick oxide layer present when examined after 3000 hours of testing.

Table 2-4. Corrosion Test Results of Separator Plate Candidates

Time (hr)	Simulated Anode Conditions -850 mV*		Simulated Cathode Condition +30 mV*	
	Weight Change (%)	Oxide Thickness (mils)	Weight Change (%)	Oxide Thickness (mils)
<u>FE-Cr-Ni Alloy</u>				
0	-	-	0	0
250	+0.40	0.9	-0.14	1.0
500	-0.30	2.0	-0.30	1.5
1000	+0.80	3.0	-0.11	1.6
2500	+1.01	10.0 Maximum	-	-
3000	-	-	-0.52	2.0
<u>Ferritic Stainless Steel C</u>				
0	-	-	-	-
250	+0.02	<1	-	-
500	+0.01	<1	-	-
1000	0.00	<1	-	-
3000	+0.04	<1	-	-
5000	-0.05	<1	-	-
<u>AISI 316 Stainless Steel</u>				
0	-	-	0	-
250	-1.90	1.0	+0.40	0.4
500	-3.70	1.2	+0.60	0.6
1000	-29.60	Severe	+1.20	1.3
3000	-	-	+1.50	1.6
<u>Type 201 Nickel</u>				
0	-	-	-	-
250	+0.02	<1	-	-
500	-0.74	<1	-	-
1000	+0.13	<1	-	-

*Versus Au reference electrode with 67% CO₂/33% O₂ at 1 atmosphere. Electrolyte composition 62 mole % Li₂CO₃/38 mole % K₂CO₃
 Temperature: 1400°F, except type 316 stainless steel, 1200°F at -850 mV.

AISI 316 similarly tested developed a 0.0016 inch thick oxide after 3000 hours. A single cell test, where the Fe-Cr-Ni alloy is being tested as a cathode current collector, has begun.

Laboratory tests to identify acceptable material systems for use in wet seal areas were also continued. Aluminized 201 nickel and AISI 316 were exposed to simulated wet seal environments for 3000 hours. The aluminizing coating prevented corrosion of both the nickel and 316 and will be effective as long as defects are not present in the coating. Two aluminum containing ferritic stainless steels, ferritic stainless steels A and B, which were previously evaluated for separator plates will also be evaluated in simulated wet seal environments. The advantage of using these alloys is that they will continue to form a protective oxide if defects are introduced during processing. Also, electronic conductivity is not required in the wet seal area which was a limitation with these materials as separator plates candidates.

Matrix Fillers

Tests to determine the stability of SrTiO_3 , Li_2SnO_3 and Li_2TiO_3 ceramic materials continue toward 3000 hours at anode conditions. No new data were collected this period; however, samples were removed for analysis.

Work Planned for Next Reporting Period

- o Continue testing Fe-Cr-Ni alloy separator plate material.
- o Continue evaluating the Fe-Cr-Ni alloy from the 3000 hour endurance cell.
- o Initiate testing of aluminum containing ferritic stainless steel at simulated wet seal conditions.
- o Initiate testing of a new Fe-Cr-Ni alloy at simulated anode and cathode conditions.
- o Continue testing SrTiO_3 , Li_2SnO_3 and Li_2TiO_3 matrix filler materials.

2.G Develop Stack Hardware (Activity 180)

The test plan for evaluation of the seal configuration consists of determining leakage rates at cross-pressures up to 30" H₂O at room temperature and at 1200°F. After cooling, the sequence will be repeated until three sets of room temperature and two sets of 1200°F data are obtained. Subsequently, the blow-out cross-pressure at temperature for each seal configuration will be established.

Evaluations will be run on dry gasket configurations and gaskets filled with electrolyte. Additionally, a voltage will be put across the manifold seal and ionic currents across the configuration will be measured.

Two seal tests were performed with the one foot by three foot stack manifold seal test rig. The first test cycle, containing a dry seal, was terminated when heater failure prevented heatup to 1200°F. The initial cold leakage at 5 in. H₂O cross-pressure was 4 pph. This agreed with the predicted leakage rate for the seal configuration used.

The second test cycle, also containing a dry seal was terminated after the leakage rate at 1200°F was measured to be an order of magnitude higher than that predicted. Upon cool-down and disassembly, the seal was found ruptured in one corner. This is the first occurrence of this type failure necessitating that the rig be rebuilt to determine whether this result was a test anomaly or whether the gasket seal material used was deficient in strength. If strength is found to be a problem, an improved gasket geometry using the same seal material has been identified for future testing.

The 10-cell stack tested initially under an Electric Power Research Institute Project and continued to 3010 hours under this activity has been disassembled. Two observations made prior to disassembly are significant. The first concerned an electrical resistance measurement that showed cells No. 8 and 10 were partially shorted. Figure 2-5 tabulates the measured values and shows the tendency toward low electrical resistance across the last four cells on the negative end of the stack

with Cells No. 8 and 10 having the lowest resistances. These low ohmic values are believed to be due to manifold corrosion products (positive ions of iron oxide) precipitating at the negative end of the stack under the manifold seal. This is the only area where corrosion products were concentrated, and once removed, the resistances of these four cells were increased to values approaching those of the remaining cells. This observation explains qualitatively (since the measurements were made while the stack was at room temperature) the deteriorating open circuit voltages of Cells No. 8 and 10 during the final 1000 hours of the test. We believe that this problem can be eliminated with either manifold corrosion protection or by the use of alternative manifold materials. These approaches will be evaluated in subsequent stack tests.

CELL POSITION	ELECTRICAL RESISTANCE (Ω)	
1	> 1500	}
2		
3		
4		
5		
6		
7	500	
8	0.5	
9	2.25	
10	0.01	59-75

Figure 2-5. Stack Resistance Measurements

The second observation confirmed the predicted behavior of stack height throughout the test. Figure 2-6 is a plot of stack compressive movement averaged on a per-cell basis and normalized using a scale that places the zero-point at the cell deflection required to remove the "pinch" built into each cell at assembly. The round symbols in the figure show that the height of this tape-matrix stack remained fixed following the measurement made during the first thermal cycle at 529

hours (projected back to a much earlier time based on the brief period required to achieve internal seals), compared to the square symbol data obtained on a tile stack also tested under the Electric Power Research Institute Project that continued to show compressive movement through 1940 hours of operation. This desirable characteristic of a tape-matrix stack allows the design advantages of the "fixed-height" compressive loading system in simplifying reactant gas containment.

Figure 2-6. Stack Cell Compression Data

The teardown analysis of components used in this stack is being performed under the EPRI project and has been expanded in scope to include several endurance issues that are currently important to United's pressurized stack development effort. These issues for the cell packages include:

- a) Cathode dissolution,
- b) electrolyte loss and distribution,

- c) stability of component thickness and conformity to other components,
- d) chemical stability of cell materials,
- e) metallurgy of the separator plate,
- f) end cell differences, and
- g) corrosion protection of the separator plate seal surfaces.

Issues for the manifolds and exhaust pipes include:

- a) manifold flange corrosion protection,
- b) stability and electrolyte content of the manifold gaskets, and
- c) evidence of electrolyte in the reactant exhaust system.

Sample preparation has been completed and post-test analysis is in progress. The results will be shared with the Department of Energy once the analysis is complete.

2.H Conduct Subscale Stack Test and Analysis (Activity 115)

Stack testing was started on 10/19/81. A heatup schedule similar to that used for previous stacks was followed until acceptable internal seal leakage was achieved. Following a 12.9 hour hold at 1100-1200°F, the stack was pressurized to 5 atmospheres and stack manifold seal leakage levels were measured to be < 1% of design flows. Internal cell crossover was too low to measure. The stack was then operated at 100 ASF and average cell performance improved from an initial value of 0.79 volts/cell to 0.84 volts/cell, a level consistent with good subscale cells as shown on Figure 2-7. Individual cell calibration data obtained at that time is shown in Figure 2-8. The reactants used for this test simulate a system with an O₂-blown Texaco coal gasifier (Table 2-5). Average cell iR levels during Run 1 ranged from 26-30 mV/100 ASF with excellent uniformity as shown in Table 2-6.

Table 2-5. Molten Carbonate Stack Test Gases

Reactant Gas Compositions (simulating system with O ₂ - blown Texaco coal Gasifier)				
<u>GF-1</u>	-Fuel-	<u>%</u>	<u>ROX-1</u>	-Oxidant-
				<u>%</u>
H ₂		14.1	CO ₂	18.05
CO		20.8	O ₂	8.8
CO ₂		2.2	N ₂	65.8
H ₂ O		62.9	H ₂ O	7.35

Figure 2-7. Stack Performance at 5 Atmosphere Test Conditions (GF-1 and ROX)

Figure 2-8. Stack Calibration Data at 5 Atmospheres

Table 2-6. Cell iR (mV/100 ASF)

Hot Time	Cell #	1	2	3	4	5	6	7	8	9	10
13 Hours *		28	28	30	32	34	33	30	28	24	26
125 Hours *		26	26	26	28	28	28	27	24	22	22
173 Hours **		29	28	28	28	28	28	24	24	24	***

* 5 Atmospheres

* 10 Atmospheres

*** Instrumentation Problem - Cell 10

At 125 hours hot time, the cell stack was depressurized and the containment vessel removed to correct several stack and facility problems. Following repressurization, it was determined that the cathode exhaust manifold leakage had increased. However, cell performance levels were unaffected and testing continued.

At 150 hours hot time, the cell stack operating pressure was increased from 5 to 10 atmospheres and at 200 hours a calibration was run to 160 ASF. The results of this calibration are shown on Figure 2-9. Average performance agreed well with pre-test predictions and individual cell uniformity is shown in Table 2-7 at both 5 and 10 atmospheres.

Table 2-7. Individual Cell Performance

	Cell #	1	2	3	4	5	6	7	8	9	10
*** 160 amps/ft ²	.807	.803	.799	.783	.778	.787	.785	.792	.770		*
*** 100 amps/ft ²	.874	.878	.873	.862	.859	.864	.864	.869	.856		*
** 100 amps/ft ²	.854	.862	.851	.845	.841	.847	.847	.854	.836	.835	

* Instrumentation problem - cell 10

** 5 Atmospheres

*** 10 Atmospheres

Figure 2-9. Stack Performance at 10 Atmosphere Test Conditions (GF-1 and ROX-1)

The stack underwent a shutdown cycle at 258 hours to investigate the cause of an increase in cathode exhaust gas leakage. Inspection showed that the seal on the cathode exit manifold was missing along one entire edge. Additionally, it was observed that some ceramic spacers were interfering with stack compressive movement. These spacers had been used to keep loose insulation from contracting the stack. Stack height measurements confirmed the interference; specifically, the corner which had the maximum interference had compressed 0.052 in. while the non-interference corner had compressed 0.093 in. These spacers were eliminated from the rebuild.

Resistance measurements taken during the rebuild showed a partial short across cell No. 10. Black deposits found in the fuel exit corners of this cell were determined to be precipitates of iron oxide believed resulting from manifold corrosion. The short was minimized by removal of the black deposits which produced an increase in electrical resistance from 5 Ω to > 1000 Ω across cell No. 10.

Long-term corrosion protection of the manifolds will be controlled by aluminizing the manifolds and, if required, with a change in seal material. Aluminized flange manifolds were not available in time for this rebuild.

Table 2-8 shows a comparison of individual cell performance levels for runs No. 1 and No. 2 (before and after the thermal cycle). With the exception of end cells, which are affected by thermal cycles and corrosion products bridging cell No. 10 causing minor electronic shorting, performance levels were generally higher than run No. 1. IR levels of interior cells were essentially unchanged from run No. 1, as shown in Table 2-9.

Table 2-8. Comparison of Cell Performance Run No. 1/Run No. 2

Hot Time	Cell No.	1	2	3	4	5	6	7	8	9	10
(Voltage at 100 amps/ft ²)											
220 Hrs											
(Run No. 1)		.874	.878	.873	.862	.859	.864	.864	.869	.856	*
350 Hrs											
(Run No. 2)		.836	.880	.879	.885	.885	.890	.892	.887	.873	.818

Table 2-9. Comparison of Cell iR (MV/100 ASF) - Run No.1/Run No. 2

Hot Time	Cell No.	1	2	3	4	5	6	7	8	9	10
173 Hrs											
(Run No. 1)		29	28	28	28	28	28	24	24	24	*
370 Hrs											
(Run No. 2)		52	29	29	28	28	36	26	26	24	43

* Instrumentation Problem - Cell No. 10

At 370 hrs a diagnostic program was run to re-examine a temperature sensitivity problem which had been observed on Cell No. 6 during run 1. The problem is characterized by an abnormally high performance loss during down-power transients and is believed to be associated with a temporary "gap" formation with a loss of cell area and increased iR. Figure 2-10 shows the performance of Cell Nos. 6 and 4, (a normal cell) during the excursion. This phenomenon has been observed in isolated cells during operation of several stacks and is believed understood and is the subject of intensive investigation.

The results of fuel and oxidant utilization diagnostic programs are shown in Figures 2-11 and 2-12. In the case of the oxidant utilization, the response of individual cells is very uniform with a change from 11.7% to 41.7% utilization with the exception of Cell No. 10. The Cell No. 10 difference is most likely due to the local shorting caused by the buildup of corrosion products observed following Run No. 1. The fuel utilization sweep from 35 to 58% shows above average responses for Cell Nos. 1, 3 and 10. Again, in the case of Cell No. 10, this is most likely due to localized shorting. Cell No. 3 is most likely not receiving its nominal share of fuel, probably due to field dimensions, and Cell No. 1 may be abnormally utilization sensitive due to a reduced temperature (heat loss) also accounting for its increased iR level.

Overall, during 462 hours of operation this stack can be characterized as having stable and above predicted performance levels, and crossover too low to measure. A time log of the average performance of Cells No. 2 through 9 is shown on Figure 2-13. The end cell problems are most likely the result of the thermal cycle in the case of Cell No. 1; and shorting due to corrosion product accumulation in the case of Cell No. 10.

After a total test time of 462 hours, the test stand's fuel inlet line ruptured which subjected the stack to an instantaneous crosspressure of up to 135 psi. At the time of this event, the stack was running at 100 ASF and a pressure of 10 atmospheres. Immediately after replacing the ruptured line it was determined that the high crosspressure incident caused an additional fuel side leak inside the containment vessel necessitating that the stack be shutdown for inspection.

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Figure 2-10. Stack Temperature Sensitivity

Figure 2 11. Stack Fuel Utilization Response

Figure 2-12. Stack Oxidant Utilization Response

Figure 2-13. Stack Endurance Log

Upon removal of the dome and stack insulation, it was found that the manifold seal on the fuel exit manifold was ruptured. The stack and containment vessel were removed from the stand for further inspection and for upgrading the stand's reactant gas lines.

Analysis of the fuel inlet line revealed that 321SS tubing had been installed in place of the welded 304SS schedule 40 pipe that was specified. Failure analysis of the ruptured tube showed grain growth, internal voids (cracking) at grain boundaries, and heavy oxidation; indicative of excessive temperature and/or stress.

Seal material imploded over a large area of the fuel exit side of the stack. The fuel exit face was cleaned as were the gas channels of individual cell anodes. A room temperature crossover check revealed no measurable crossover in the stack indicating that the pressure upset did not cause any internal rupture of the stack repeating components.

Stack height measurements showed that the high to low spread in compression was reduced to 0.026 in. compared to the 0.041 in. spread when the ceramic spacers interfered with the stacks compressive movement. The measurements also showed that the stack had compressed an additional 0.023 in. (average) since the shut-down at 258 hours.

Corrosion products were again removed from the negative end of the stack producing resistance measurements of $> 1000 \Omega$ per cell prior to installing the manifold. Aluminized manifolds intended to control corrosion and minimize precipitates, were installed on this rebuild.

The stack and containment vessel were mounted in the stand and prepared for restart in early January.

2.1 Manufacture Non-Repeating Components and Provide Subscale Stack for Test and Analysis (Activity 182)

All preparatory work on the first subscale stack was completed and the stack was delivered to test. This work consisted of completing installation of the stack voltage, temperature and current instrumentation remaining from the prior reporting period.

Three LVDTs - devices which convert displacement to a linear voltage signal - were installed. One device was mounted off the stack pressure plates, inside the thermal insulation, allowing a continuous measurement of stack movement due to temperature change and component creep. LVDTs were also mounted on the center of each compressive load bar to obtain direct measurement of compressive load change. Stack compressive load was transferred to the external follow-up system at 65 psi equivalent active area loading. Experience has shown that approximately 15 psi of this load will be lost due to compression of the stack insulation during the first 100 hours of testing.

Measurements of the load bar deflection were taken during the initial loading procedure for a baseline curve to be used in conjunction with monitoring LVDT deflection changes.

A photograph of the stack mounted in the stand, with the vessel dome not yet in place is shown in Figure 2-14.

A design review of non-repeating components for the upcoming 20-cell subscale stack (DOE #2) is scheduled for January. In advance of the review, the long lead time materials were identified and ordered.

(WCN-9228)

Figure 2-14. Stack Mounted in Test Stand

2.J Analytical Design of Cell and Stack Component (Activity 116)

The design effort during this quarter was concentrated on the design of the cell package and stack hardware for DOE Stack No. 2. The stack will contain twenty cells and is scheduled for test in April 1982.

The objectives of the stack are listed below:

Configuration Development

- o Evaluation of Improved Separator Plate
- o Evaluation of Low Cost Single Sheet Cathode Current Collector

Process Development

- o Evaluation of Matrices Formed by the Tape Process
- o Evaluation of Bubble Barriers formed by the Tape Process
- o Evaluation of Direct Formed Anodes
- o Evaluation of Electrode Cut from Full-Scale Parts

Material Development

- o Evaluation of Stabilized Anode
- o Evaluation of Corrosion Resistant Flange Materials
- o Evaluation of Pack Aluminization of Flanges

Stack Hardware Development

- o Evaluation of Components to Eliminate Cell Shorting
- o Evaluation of Negative End Plate Corrosion Protection
- o Evaluation of End Cell Compressible Flange Design
- o Evaluation of Alternative Manifold Seal

Construction drawings for the stack are scheduled for completion early in the next quarter. Construction drawings were completed for all long lead-time-items such as end-plates, manifolds, manifold load bars, and compressive loading system hardware.

Analytical design effort was concentrated on an alternative separator plate configuration, elastic analysis of direct formed anodes, load deflection tests of new cathode current collectors and selection of corrosion resistant materials to prevent external shorting of stack cells.

A new separator plate design is planned for the second DOE stack since the separator plate configuration and fabrication process in the first DOE stack could not meet the dimensional control required for large scale cells. Two alternative separator plate configurations with the potential for meeting the dimensional requirements were identified in the parallel Niagara Mohawk Power Corporation Program. Design and process development effort during the quarter was devoted to providing a basis for the selection of a design for evaluation in DOE Stack No. 2. Analytical design studies, fabrication trials, and out-of-cell component tests were conducted to qualify the design which appeared to be the simplest to manufacture. The design is not described in this report in order to protect subject patent rights under the parallel NMPC development contract.

Single sheet cathode current collectors are being developed to replace the two piece current collector. The new design was selected for lower cost, and at the same time, provide better compressive deflection and springback properties. The design requirements of this component were established with the aid of a finite element structural analysis computer program. Early samples fabricated by one vendor were not fabricated exactly to the design requirements. The sample, however, was tested in Cell 341 for 1500 hours for an early evaluation of the concept. The test indicated satisfactory function of the component as indicated by stable internal resistance and a favorable post-test inspection.

During the quarter, vendor provided samples which matched the requirements specified in the construction drawings. The deflection and springback characteristics were measured at room temperature and at 1300°F to determine the maximum strength before collapse. The structural data are shown in Figures 2-15(a) and 2-15(b). The room temperature deflection data presented in Figure 2-15(a) compares the 8 mil and 12 mil versions of the single sheet current collector with the two piece folded sheet metal and perforated plate current collector used in the present stack. The data indicates a considerable improvement in deflection and springback properties for the 8 mil thickness relative to the 12 mil thickness and the former two-piece design. The structural tests indicate that the as-received and annealed versions of the 8 mil current collector suffered some compressive

Single Sheet Cathode Current Collector

Figure 2-15(a). Room Temperature Pressure vs. Deflection Test

Figure 2-15(b). 1300°F Collapse Test

collapse beyond 8 mils of total deflection at pressures of 250 psi and 139 psi, respectively, at the test temperature of 1300°F. This allows sufficient margin for operation at the design compressive load of 50 psi. Samples of the single sheet current collector will be qualified further in single cell tests planned for the next quarter.

The direct formed anode described in Activity 155 has been selected for evaluation in DOE Stack No. 2. The direct forming process was developed as a low cost process for manufacturing full-scale parts. During the early development of this component, a post-test examination of a direct formed anode run in a subscale cell test revealed a wavy interface between the anode and the tape matrix. This was not observed in cell tests with the machined ribbed anodes used prior to the development of the direct formed process. We suspected that the difference in distortion was due to the greater channel width used in the direct formed anode compared to the channel width of the machined anode. A finite element structural analysis was set up to model the deflection of the components of the cell package assuming a compressive load of 50 pounds-per-square-inch of active area. The results predicted that the waviness was due to non-uniform deflection and that the channel width was an important design variable. The analysis showed better load distribution at the anode-tape interface for the narrow channel design compared to the wide channel design. The deflection at the tape interface for the narrow channel design was calculated to be approximately one-half that of the wide channel design. As a result of this analysis, the direct formed anodes with narrow channels were selected for the stack.

Provisions were included in the stack design to eliminate the source of corrosion products which deposit at the negative end of the stack. The deposits result in an electronic short at the edges of the cells near the negative end plate. The manifold flange and separator plate flanges will be aluminized to provide corrosion protection. In addition, an alternative material with excellent corrosion resistance has been selected for a portion of the separator plate flanges. A new end plate configuration with improved corrosion resistance has also been selected for evaluation in the next stack.

Work Planned for Next Quarter

- o Conduct design review for the next subscale stack (DOE Stack 2).
- o Complete construction drawings for DOE Stack No. 2.
- o Run qualification cell tests for the one-piece metallic cathode current collector.
- o Estimate mechanical load distribution of DOE Stack No. 2.
- o Estimate electrolyte life of DOE Stack No. 2.

2.K Provide Full-Scale Short-Stack Test Facility (Activity 98)

The pressure vessel base and dome were received previously. The transport cart which enables the base/dome/stack to be moved from the assembly area to the test stand was completed during this reporting period, including the cart leveling device.

The lifting fixture which is necessary to properly handle the large hardware items (stack, vessel, and dome) was received and installed in the stand now being used to test the subscale stack in Activity 115.

The electrical load box, capable of controlling stack current from 0 to 2000 amps, had been received in a previous reporting period. No new effort is planned at this time.

Section 3

TASK 3 - DEVELOP CAPABILITY FOR FULL-SCALE STACK TESTS

3.A Identify Full-Scale Manufacturing Equipment Requirements (Activity 121)

Modifications are being made to the molding table used to make the direct formed anodes to improve uniformity. Installation of a pneumatic lock system on the electrode molding bench is partially completed. The locks will give more uniform support to graphite electrode molds and reduce thickness variations.

Planned Work for Next Reporting Period

- o Complete installation of the pneumatic locks.
- o Produce components as required for scheduled stack builds.

Section 4

TASK 4 - DEVELOP CAPABILITY FOR OPERATION OF STACK ON COAL-DERIVED GAS

4.A Establish Tolerance to Sulfur (Activity 124)

In the last quarterly report, data were presented on the effect of H_2S on the performance of ambient pressure bench-scale Cells 324 and 345 while operating on three different fuel gas compositions. Those gas compositions were all in shift equilibrium and correspond to Stack "A" inlet, Stack "B" inlet, and Stack "B" exit composition of the preliminary reference design. These compositions were presented in Tables 4-1 and 4-2 of that report. The purpose of those tests was to determine H_2S effects in the absence of any effects of poisoning of the water-gas-shift reaction. The experimental results of those tests were presented in Table 4-3 of that report and are repeated here in graphical form in Figure 4-1.

During this quarter, Cell 345 was run using simulated stack "A" inlet fuel containing 0.7 and 1.3 ppm CS_2 . These CS_2 levels correspond to bulk molar sulfur to H_2 ratios of 2.1×10^{-6} and 4.0×10^{-6} , respectively. Steady state performance losses at 100 amp/ft² with 10% fuel (H_2 and CO) utilization were 17 ± 3 mV and 30 ± 5 mV, respectively. In addition to these experiments, the cell was operated on the same fuel gas containing 0.9 ppm COS (2.8×10^{-6} molar ratio of S to H_2) at the same current density and fuel utilization. This resulted in a cell performance loss of 6 ± 2 mV.

These experimental performance data with CS_2 and COS were added to Figure 4-1 as a function of $P_S^0/P_{\text{H}_2}^0$, where P_S^0 is the partial pressure of sulfur-bearing compounds after conversion to H_2S and $P_{\text{H}_2}^0$ is the partial pressure of H_2 . This ratio is equal to the molar ratio of S to H_2 . The superscript zero indicates that these partial pressures are the pressures in the gas cavity behind the anode and not within the anode where concentration gradients may change these values. The close agreement between the effects of H_2S , CS_2 , and COS, when plotted in this manner in Figure 4-1, indicates that CS_2 and COS are probably converted primarily to H_2S within the cell, as would be predicted thermodynamically.

Figure 4-1. Effect of H_2S , CS_2 and COS on Cell Performance
(All Data Pertain to 100 ASF With H_2S Unless Otherwise Noted)

Because the coverage of nickel catalyst by sulfur is dependent on the ratio of the local H_2S partial pressure to the local H_2 partial pressure, gas-phase diffusional losses were included in the anode mathematical model so that the value of this ratio based on the bulk gas composition could be related to the local value. The gradient of H_2S was assumed to be small because the rate of consumption (or production) in an anode is small. However, the hydrogen partial pressure gradient can be significant as indicated by the poor anode performance when operating on Stack "B" exit gas as reported last quarter.

With the inclusion of these gas-phase diffusional losses in the model, it includes an estimate of all the known performance effects of H_2S in the concentration range of interest. These are the poisoning of the H_2 -oxidation and water-gas-shift reactions and the partial conversion of the carbonate electrolyte to sulfate. Any SO_2 or SO_3 present in the cathode gas is considered to come to equilibrium with the electrolyte to form sulfate which diffuses to the anode to produce H_2S . The effect

of poisoning of the H_2 -oxidation reaction is taken into account using a correlation of data reported in Quarterly Report No. 7. Poisoning of the water-gas-shift reaction is accounted for by assuming that the fraction of water-gas-shifting in an increment of the anode depends on the fraction of surface coverage of H_2S in that increment. Surface coverages were obtained from Figure 4-4 of Reference 1. A better estimate of the poisoning effect on this reaction could be obtained by measuring the rate of this reaction in a molten carbonate fuel cell in the presence of various levels of H_2S . These data, however, are not available. The effects of H_2S on the conversion of the carbonate electrolyte to sulfate are based on free energy and concentration polarization measurements previously reported under this contract.

The results of the mathematical model were compared to the experimental data obtained with the three fuel mixtures in the last quarter. These data allow an evaluation of performance loss other than the poisoning of the water-gas-shift reaction. The agreement between the predicted and measured loss was found to be poor due to the fact that the estimate of poisoning the H_2 -oxidation reaction was an extrapolation of data obtained using the rotating Ni wire. Data could not be obtained in that rig at sulfur levels as low were evaluated in the bench-scale cell tests. The extrapolation of data used was based on the equation shown in Figure 4-4 of Quarterly Report No. 7.

Good agreement was obtained, however, by modifying the extrapolated effect on the rate of the H_2 -oxidation reaction as shown in Figure 4-2. The comparison between the calculated and experimental results using this correction is shown in Figures 4-3(a) and (b). For all three fuel gas compositions, the effects of H_2S on performance are in good agreement. The poisoning of the H_2 -oxidation reaction is the primary reason for the performance loss.

The mathematical model was then compared with performance loss results reported previously on the effect of H_2S on an ambient pressure cell operating on simulated Texaco O_2 -blown gas at 85% ($H_2 + CO$) utilization. These experimental results

Figure 4-2. Correction to Rate of the H_2 Oxidation Reaction

(a) Stack Inlet

(b) Stack Exit

Figure 4-3. Comparison Between Model and Experimental Data

were previously reported in Quarterly Report No. 5 and are presented here in Figure 4-4. In this series of tests, each cell experienced a small performance loss upon introducing H_2S to the fuel inlet gas. Performance remained stable for a period of time, and then dropped off suddenly. The times to these performance losses are shown in Figure 4-4. Analyses of the fuel effluents indicated that it was deficient in H_2 , indicating that the water-gas-shift reaction was being poisoned. The times to the sudden performance losses agree approximately with the length of time necessary for the anode catalyst to become completely covered by a monolayer of sulfur.

Figure 4-4. Effect of H_2S on Cell Performance

The mathematical model, being a steady-state model, predicts for 1.0 and 0.1 ppm H_2S that insufficient hydrogen is present in the inlet fuel to sustain 160 ASF current due to poisoning of the water-gas-shift reaction. This was observed experimentally for these cases. However, for 0.01 ppm H_2S in the fuel gas, the degree of poisoning is so small that a negligible performance loss occurs. This means that 0.01 ppm H_2S can be tolerated on a steady state basis under these conditions of fuel composition and utilization.

The mathematical model provides a method for estimating the effect of sulfur on the performance of molten carbonate fuel cells. The performance loss is a function of the fuel gas composition and fuel utilization. The model also allows an estimate to be made of the effect of sulfur compounds in the oxidant, although this effect has not been verified experimentally. More work is also needed to compare model results with the ambient pressure data obtained with fuels richer in hydrogen and to investigate the effects of sulfur under pressurized cell conditions.

This study indicates that molten carbonate fuel cells are very intolerant to sulfur. However, higher levels of sulfur can be tolerated by periodic cell purification such as can be achieved by open circuit operation. Such techniques are possible since all of the performance loss mechanisms, except for nickel sulfidation at high sulfur concentrations, are thought to be reversible. More studies are needed to investigate purification techniques.

Inspection of components from bench-scale cells used in this study indicate that low levels of sulfur compounds in the fuel gas do not lead to accelerated material degradation on the anode side of the cell. More studies are needed of the effect of sulfur oxides on cathode components.

One technical paper and one technical note have been submitted for publication in the "Journal of the Electrochemical Society". They are, respectively:

"The Effect of Sulfur on the Anodic H_2 (Ni) Electrode in Fused Li_2CO_3 - K_2CO_3 at $650^\circ C$ " by W. M. Vogel and S. W. Smith.

and

"The Equilibrium Constant for the Reaction $H_2S + 3H_2O + (Li_{0.66}K_{0.34})_2 CO_3 \rightleftharpoons 4H_2 + CO_2 + (Li_{0.66}K_{0.34})_2 SO_4$ at Elevated Temperature" by S. W. Smith and S. M. Kapelner.

An Extended Abstract was also submitted for presentation at the Electrochemical Society Meeting in Montreal, Canada, on May 9 to 14, 1982. This presentation is entitled:

"Effects of Sulfur on Molten Carbonate Fuel Cells", by S. W. Smith, H. R. Kunz, W. M. Vogel, and S. J. Szymanski.

¹ Steam Reforming Catalyst, by J. R. Rostrup-Nielsen, Teknisk Forlag A/S (Danish Technical Press, Inc.) Copenhagen, 1975