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HIGH-TEMPERATURE

MOLTEN-CARBONATE FUEL CELLS

TECHNICAL PROGRESS REPORT FOR THE

PERIOD JANUARY - MARCH 1979

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ENERGY RESEARCH CORPORATION

3 Great Pasture Road

Danbury, Connecticut 06810

Date Published - May 1979

Prepared for the

DEPARTMENT OF ENERGY

20 Massachusetts Avenue

Washington, D.C. 20545

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Work Performed Under Contract No. DE-AC-03-76ET11304

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EXECUTIVE SUMMARY

A pilot size (1500 cm²) cell was assembled and tested this quarter with lightweight hardware. This cell reproduced the performance of a similar intermediate size (300 cm²) cell. A power output of 120 W was achieved at 120 mA/cm² and 0.75 V. Progress in this and other task areas is summarized below.

Component Development

- Pore structures of three successively manufactured SS-screen reinforced cathodes were found uniform when examined by mercury porosimetry. This establishes the consistency within one electrode plaque as well as between different electrode plaques.
- Manufacturing procedures of 1500 cm² electrode and electrolyte tile were improved so as to reduce dimensional tolerances to less than $\pm .5\%$.
- By systematically varying the temperature and time for the reduction of nickel-cobalt hydroxide, metal powders with surface areas of 0.6 to 2 m²/g were obtained. Very fine alloy powders of Ni-Co-Cr have also been prepared using the same procedure.
- No significant effect on the lithium aluminate surface area was noticed when initial melt composition and the heat treatment temperature of in situ electrolyte powder preparation was varied. However, some effect on the allotropic composition as well as particle morphology was observed.
- Separate synthesis procedures for high surface area α -LiAlO₂ (60 m²/g), β -LiAlO₂ (30 m²/g) and γ -LiAlO₂ (30 m²/g) have been developed. The process for γ -LiAlO₂ synthesis is very attractive, particularly in connection with high-rate, electrolyte-tile manufacturing procedures.

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Cell Testing

- The performance of the laboratory-size cell (No. 131) was further improved by 20 mV, attaining 800 mV at 150 mA/cm² and 40% fuel conversion.
- The straight corrugated sheet metal current collector was tested in the intermediate-size cell (300 cm²) for 1700 hours. Post-test observations revealed no deformation of the sheet metal corrugation.
- The second pilot-size cell, assembled with the lightweight sheet metal hardware, exhibited 750 mV at 120 mA/cm² (160 A) and 40% fuel conversion. This is equivalent to 120 watts of power output from a single cell.
- Correlation of cathode polarization with the electrolyte content of the electrode shows that the optimum electrolyte inventory is 15 to 20% of the cathode pore volume.

Stack Design & Development

A second lightweight stack was designed and assembled. This stack included improved design for the bipolar plates and gas manifolds as well as auxiliary test facilities. As a result, short-circuit currents were reduced and seal efficiencies were improved, yielding 97% for both fuel and oxidant gases.

Modeling and System Analysis

MCFC system analyses were continued to evaluate cell performance with respect to different system options. This included: a) air vs O₂ blown gasifier fuel gas, b) air vs O₂ fed cathode, c) fuel and oxidant utilization, and d) CO₂ exchange schemes.

Based on these system analyses, the MCFC system model has been further improved.

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TABLE OF CONTENTS

	<u>Page No.</u>
EXECUTIVE SUMMARY	i
TASK 1 COMPONENT DEVELOPMENT	1
1.1 Electrode Structures	1
1.2 Electrolyte Powder	9
1.3 Electrolyte Tiles	21
1.4 Cell Frame and Current Collectors	23
TASK 2 CELL TESTING	26
2.1 Laboratory-Size Cell Testing	26
2.2 Intermediate-Size Cell Testing	41
2.3 Pilot-Size Cell Testing	45
2.4 Diagnostics	55
TASK 3 STACK DESIGN AND DEVELOPMENT	71
3.1 Lightweight Stack Testing	71
3.2 Manifold Seal Development	78
TASK 4 MODELING AND SYSTEM ANALYSES	82
4.1 System Analyses	82
4.2 Fuel Cell Subsystem Model	97
FUTURE WORK PLAN	98

ENERGY RESEARCH CORPORATION

LIST OF FIGURES

<u>Figure No.</u>	<u>Page No.</u>
1.1.1 Consistency in Electrode Plaque Production	2
1.1.2 Reduction of Hydroxide to Metal Powder	7
1.2.1 Scanning Electron Micrograph of VX-15 LiAlO ₂ : 23% α + 54% β + 23% γ -LiAlO ₂ recrystallized in a 37 mol% Li ₂ CO ₃ melt, 4.1 m ² /g	12
1.2.2 Scanning Electron Micrograph of VX-10 LiAlO ₂ : 27% α + 50% β + 23% γ -LiAlO ₂ recrystallized in a 42 mol% Li ₂ CO ₃ melt, 4.2 m ² /g	12
1.2.3 Scanning Electron Micrograph of VX-5 LiAlO ₂ : 37% α + 32% β + 31% γ -LiAlO ₂ recrystallized in a 46 mol% Li ₂ CO ₃ melt, 3.9 m ² /g	12
1.2.4 Electron Micrograph of TX-650 LiAlO ₂ (Final Firing at 650°C): 17% α -LiAlO ₂ , 4.9 m ² /g	14
1.2.5 Electron Micrograph of TX-665 LiAlO ₂ (Final Firing at 665°C): 16% α + 71% β + 13% γ -LiAlO ₂ 5.2 m ² /g	14
1.2.6 Electron Micrograph of Standard Process (MX-45) LiAlO ₂ (Final Firing at 680°C): 15% α + 70% β + 15% γ -LiAlO ₂ , 5.2 m ² /g	14
1.2.7 Scanning Electron Micrograph of LiAlO ₂ Prepared by Heating Pure α -LiAlO ₂ at 950°C for 5 Hours: 75% γ -LiAlO ₂ + 25% α -LiAlO ₂ , 31 m ² /g	18
1.2.8 Scanning Electron Micrograph of Stoichiometric β -LiAlO ₂ , 29 m ² /g	20
1.2.9 Scanning Electron Micrograph of β -LiAlO ₂ After Heating at 700°C for 5 Hours in Air	20
1.2.10 Scanning Electron Micrograph of 86% γ -LiAlO ₂ Obtained by Heating Stoichiometric β -LiAlO ₂ at 750°C for 5 Hours in Air	20
1.4.1 Laboratory Cell Anode Flanges	24

ENERGY RESEARCH CORPORATION

LIST OF FIGURES
(continued)

<u>Figure No.</u>	<u>Page No.</u>
2.1.1 Performance of a State-of-the-Art Cell (No. 131)	31
2.1.2 Cell Performance Resulting from Improved Compatibility of Fuel Cell Components	32
2.1.3 Influence of Electrolyte Inventory in Cathode on its Performance	33
2.1.4 Mechanical Integrity of the Post-Test Cathode Structures Reinforced with SS-Screen	36
2.3.1 Components of a Pilot-Size Lightweight Hardware Cell (S15-1)	49
2.3.2 Assembly and Test Facility - Pilot-Size Cell	50
2.3.3 Power Output of a Lightweight Hardware Pilot- Size Cell as a Function of Operating Cell Potential (Cell S15-1)	51
2.3.4 Performance of a Pilot-Size Lightweight Hard- ware Cell with the Standard and Noble Oxidant (Cell S15-1)	52
2.3.5 Scale-Up of a Staggered Pattern Lightweight Hardware to the Pilot-Size	53
2.4.1 Pore Volume Distribution Curves for Pre- and Post-Test Anode of Cell S7-3	59
2.4.2 Pore Volume Distribution Curves for Pre- and Post-Test Cathode of Cell S7-3	60
2.4.3 Electron Micrograph of Ni-Anode Before Test (Cell S7-3)	61
2.4.4 Electron Micrograph of Ni-Anode After 1900 Hr. of Operation (Cell S7-3)	62
2.4.5 Electron Micrograph of LiAlO_2 (Batch B-112) Prior to Use in Cell S7-3. (25% α + 60% β + 15% γ)	65
2.4.6 Electron Micrograph of LiAlO_2 After 1900 Hr. Test in Cell S7-3. (40% α + 35% β + 25% γ)	65

ENERGY RESEARCH CORPORATION

LIST OF FIGURES
(continued)

<u>Figure No.</u>	<u>Page No.</u>
2.4.7 Pore Volume Distribution Curves for Pre-(B-108) and Post-Test Matrix of Cell 118	66
3.1.1 Assembly and Test Facility for the Lightweight Stack Testing	74
3.1.2 Performance of a Lightweight Stack with the Standard Oxidant and Noble Oxidant	75
3.1.3 Comparison of Performance of Individual Cells in a Lightweight Stack (STK7-2)	76
3.2.1 Schematic of Test Facility for the Manifold Seal Development	79
4.1.1 Effect of Feedstock Composition on Fuel Cell Performance	84
4.1.2 Polarization Curves with O ₂ Blown Coal Gasifier Fuel	87
4.1.3 Effect of Fuel Utilization on Cell Performance	90
4.1.4 Schematic of MCFC Subsystem with CO ₂ PED	94

ENERGY RESEARCH CORPORATION

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1.1.1	Consistency and Reproducibility in Nickel Electrode Manufacturing	3
1.1.2	Complete Qualitative Spectrographic Analysis of Mixed Hydroxide Powders	5
1.1.3	Ni-CO Powder Preparation Procedures	8
1.2.1	Effect of Melt Composition on the Reaction Product of $\gamma\text{-Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3$ in $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ Mixtures	10
1.2.2	Conditions of Heat Treatment of $\alpha\text{-LiAlO}_2$ and Resulting Yields of $\gamma\text{-LiAlO}_2$	16
1.3.1	1500 cm^2 Electrolyte Tile Manufacturing	22
2.1.1	Laboratory-Size Cell Testing - Details of Components	27
2.1.2	Laboratory-Size Cell Testing - Summary of Performance	28
2.1.3	Mechanical Integrity of Cathode Structures	35
2.1.4	Cell Potential at 117 mA/cm^2 with Different Cathode Gas Mixtures	40
2.2.1	Intermediate-Size Cell Testing - Details of Components	42
2.2.2	Intermediate-Size Cell Testing - Summary of Cell Performance	43
2.3.1	Pilot-Size Cell Testing - Details of Components	47
2.4.1	Electrolyte Inventory and Distribution in the Porous Components of Cells 118 and S7-3	56
2.4.2	Structural Stability of Electrodes	56
2.4.3	Phase Stability of LiAlO_2 Matrix in Cell S7-3	64
2.4.4	Structural Stability of LiAlO_2 Matrix	64

ENERGY RESEARCH CORPORATION

LIST OF TABLES
(continued)

<u>Table No.</u>		<u>Page No.</u>
3.1.1	Lightweight Hardware Stack Testing - Details of Components	72
3.2.1	Manifold Seal Development for Lightweight Stack	80
4.1.1	O ₂ -Blown Coal Gasifier Fuel Composition	83
4.1.2	Performance Comparison of Air-Blown and O ₂ - Blown Gasifier Fuel Cases	83
4.1.3	Material and Energy Balance (O ₂ -Blown Coal Gasifier Fuel - Air [CO ₂] Oxidant)	86
4.1.4	Material and Energy Balance (O ₂ -Blown Coal Gasifier Fuel - O ₂ [CO ₂] Oxidant)	89
4.1.5	Effect of Fuel Utilization on System Parameters	91
4.1.6	Effect of O ₂ Utilization on System Parameters	93
4.1.7	Comparison of System Performance for CO ₂ PED and Burner Cases	95
4.1.8	Material and Energy Balance (CO ₂ PED - 100% Efficiency)	96

ENERGY RESEARCH CORPORATION

TASK 1 COMPONENT DEVELOPMENT C. Herscovici, L. Paetsch,
A. Pigeaud, and D. Dharia

1.1 Electrode Structures

1.1.1 Electrode Sintering Procedures

• 300-cm² Electrodes

To test the consistency of ERC's electrode sintering technique, a brief study was made of a number of characteristics. Table 1.1.1 shows the data obtained on three consecutive electrode plaques reinforced by SS screen. They are designated 27R (#6, 7, and 8), each of which measured approximately 8 in. x 10 in. Furthermore, three small samples cut from Plaque 27R-6 were analyzed to examine uniformity of an electrode plaque. The pore volume distribution curves are plotted in Figure 1.1.1. It is evident from Table 1.1.1 and Figure 1.1.1 that deviations lie well within acceptable limits, both with respect to within-plaque uniformity as well as between-plaque reproducibility. Thus it may be concluded that ERC electrode manufacturing procedures yield sufficiently uniform electrode structures.

Development efforts were continued to decrease the cathode thickness to less than 15 mil and to incorporate stainless steel instead of nickel reinforcement in it. Because of the greater stiffness of SS screen (which is also not as easily stress-relieved as nickel screen), flatness problems have been encountered in the reinforcement causing uneven distribution and poor screen-to-plaque adherence when the green powder structure is rapidly heated in our H₂-furnace. Progress continues to be made in solving these problems using different mesh screens and various stress relieving and mold-filling techniques. Consequently a 15 mil thick 300-cm² cathode has recently been produced which has uniform thickness and a narrow pore size distribution (average 12.2 μ m). It incorporates a SS screen reinforcement of 80 x 80 mesh of 3.7 mil diameter wires and is 7 mil thick at the crossover points. The

a) Within one electrode plaque

b) Between electrode plaques

FIGURE 1.1.1 CONSISTENCY IN ELECTRODE PLAQUE PRODUCTION

TABLE 1.1.1 CONSISTENCY AND REPRODUCIBILITY IN NICKEL ELECTRODE MANUFACTURING

Electrode Plaque (SS-reinforced)	Sample, #	Thickness, mil	Calculated		Hg-Porosimetry Measurements				BET Surface Area, m ² /g
			Density, g/cc	Porosity, %	Porosity, %	Pore sizes(μm) for pore volumes of			
						10%	50%	90%	
27R-6	1	20.0	2.30	74.2	70.0	26	9.4	0.01	0.117
	2	19.0	2.18	75.5	72.9	49	11.3	6.7	0.117
	3	19.5	2.24	74.8	72.5	34	10.0	3.6	0.116
27R-7		21.0	2.26	74.6	73.8	33	10.5	6.3	—
27R-8		22.0	2.30	74.2	72.2	28	9.8	5.0	0.109

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pore size distribution of this electrode is similar to the Ni-screen reinforced thicker electrode. Initial cell performance with this cathode is quite satisfactory, as discussed in Section 2.

• 1500-cm² Electrodes

Thickness variations of 2 to 5 mils have been encountered in producing large electrode plaques for both anode and cathode use in our pilot-scale test program. To evaluate the most successful packing techniques developed so far, two pilot-size electrodes, one reinforced with nickel screen and the other with SS screen, have been produced. They are currently being tested in the pilot cell, Test 2, as described in Task 2. By pressing, this plaque was successfully reduced to the required ± 1 mil thickness variation with desired porosities of 71% and 77%.

The production of large thin cathodes reinforced with SS screen has been much more problematic since these procedures are still being developed for bench-scale size electrodes.

1.1.2 Stabilized Anode Structures

• Hydroxide Powder Preparation

One pure (Ni) and two mixed (Ni-Co and Ni-Co-Cr) hydroxide powders recently precipitated and spray dried and also one standard comparison sample (that originally produced 90 mol% Ni + 10 mol% Co hydroxide of Batch #52) have been analyzed for elemental purity. Table 1.1.2 shows the qualitative spectrographic analysis of the samples with some estimates of the quantities involved. The sample letters correspond to the hydroxide batches as follows: A - 100 mol% Ni; B - 90 mol% Ni + 10 mol% Co; C - 85 mol% Ni + 10 mol% Co + 5 mol% Cr. From this analysis, it appears that no important metallic contamination occurred which could have any significant effect on sintering rates. The possibility of some synergistic effects, however, cannot be ruled out.

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TABLE 1.1.2

COMPLETE* QUALITATIVE SPECTROGRAPHIC ANALYSIS
OF MIXED HYDROXIDE POWDERS(Letters are quantitative estimates in percentages)[†]

Element	Sample			
	A	B	C	#52
Nickel	Major	Major	Major	Major
Cobalt	---	Major	Major	Major
Chromium	---	---	Major	---
Potassium	.0y	.0y	.x	.x
Magnesium	.00x	.00x	.00x	.00y
Calcium	.000y	.000y	.000y	.00x
Manganese	---	---	.000y	---
Iron	.00y	.000y	---	---
Copper	.00x	.00x	.00x	.000y
Aluminum	.00x	.00x	.00x	---
Silicon	.00x	.00x	.00x	.00x

* Elements checked on each sample but not detected include:
Li, Na; Be, Sr, Ba; Ti, Zr; V, Nb; Mo, W; Zn, Cd; B, Ga,
In; Ge, Sn, Pb; P, Sb, Bi.

† x indicates a number between 1 and 3
y indicates a number between 3 and 7

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• Reduction of Hydroxide to Metallic Powder

Reduction of the above hydroxides to high surface area (HSA) metal powders was performed under a flowing, H₂-gas atmosphere. All four powders were reduced during the same experimental run in a large, airtight, Inconel box which, if required, can be heated to approximately 1000°C by insertion into a normal box furnace. Temperature vs time inside the box and the evolution of total water of reaction from the 4 samples were closely monitored. Average rate of heating of the powders was about 90°C/hr. The average rate of reduction of the samples as a function of total water generated is shown in Figure 1.1.2. Similar to thermogravimetric experiments which are also temperature and time dependent, this figure shows that the overall process goes through several stages of reaction. The following three reactions have been tentatively assigned to the three waves observed:

- 1) 25 to 250°C range: loss of water of adsorption and the water of hydration associated with the dry powders. (Approximate agreement with theoretical estimates of water of hydration was obtained.)
- 2) 250 to 390°C range: reduction of one hydroxyl radical resulting in the monohydroxide powder:

(The small deviation due to 5 mol% chromium trihydroxide in Sample C is probably not noticeable.)

- 3) 390 to 600°C range: reduction of the last hydroxyl radical resulting in pure metal powder:

Evidence of these consecutive reaction zones with reference to temperature and time helps to explain the problems encountered originally with our attempts to consistently produce HSA powders (> 1.5 m²/g) in ERC's industrial-size hydrogen furnace. It is now clear that very critical control must be exercised over the

FIGURE 1.1.2 REDUCTION OF HYDROXIDE
TO METAL POWDER

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speed with which the samples travel through the furnace as well as over the peak temperature encountered in the hot zone. The reason is that too short an exposure time or low final temperature may result in only a partial reduction of the powders which will then remain too high in surface area and cannot be suitably consolidated into electrode plaques with no surface cracking. On the other hand, too long a period of heating or too high a peak reaction temperature which goes beyond the simple reduction of the second hydroxyl radical will result in some presintering activity. This will then yield clumpy, low surface area powders which are difficult to level or pack and will result in low surface area plaques as was illustrated earlier. A similar but smaller retort was originally used before the large Inconel box was put into operation, although no temperature-time-water profiles were recorded. However, the data from these earlier runs did illustrate (as shown in Table 1.1.3) that a significant decrease in surface area occurred (i.e., a presintering tendency was shown) when the ultimate reaction temperature or time of reaction was increased, with all else remaining constant.

TABLE 1.1.3
Ni-Co POWDER PREPARATION PROCEDURES

Temperature, °C	Time, minutes	Theoretical Yield, %	Surface Area, m ² /g
560	60	99.4	1.95
600	60	99.0	1.61
600	120	100.0	1.10
650	60	99.4	0.64

Using this data as a guide, 500 g batches are now being produced in the large box in order to have sufficient powder available for our anode sintering experiments. More tests are also in progress to better characterize the exact conditions required to speed up the reduction process so that it will be compatible with continuous batch production in our large hydrogen furnace.

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1.2 Electrolyte Powder1.2.1 Electrolyte Preparation: In Situ Method

The standard electrolyte powder used for hot-pressing tiles at ERC is prepared by the in situ method. This method produces a LiAlO_2 matrix/alkali carbonate electrolyte mixture by multiple heating, grinding and blending of a $\gamma\text{-Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ mixture. Identification of process variables which influence the lithium aluminate surface area and hence the interparticulate pore structure is presently the principal development objective. The effects of such variables as carbonate composition and heat treatment temperature on aluminate characteristics are discussed in the following sections.

• Effect of Carbonate Composition

As discussed in the previous quarterly report*, a series of in situ electrolyte batches was processed to determine the effect of carbonate melt composition on product LiAlO_2 . The X-ray, SEM and BET characterization data received during this interim is discussed below. The X-ray and BET surface area results are presented in Table 1.2.1.

In our standard process (e.g., MX-45), high conversion of the primary reaction product, $\alpha\text{-LiAlO}_2$, is accomplished by recrystallization at 650 to 680°C in a 30 mol% Li_2CO_3 melt; in this lithium-deficient environment, transformation to $\beta\text{-LiAlO}_2$ is predominant. It is apparent from the results in Table 1.2.1 that, as the Li_2CO_3 concentration increases, the degree of alpha transformation to the beta phase decreases. This was also observed by others.** This trend may be rationalized in terms of the solubility of $\alpha\text{-LiAlO}_2$ in the melt. It is conceivable

* ERC Technical Progress Report, SAN/1196-11, Oct.-Dec. 1978.

** Mason, D. M. and Van Drunen, C. J., U.S. Pat. 3,998,939, Dec. 21, 1976.

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TABLE 1.2.1

EFFECT OF MELT COMPOSITION ON THE REACTION
 PRODUCT OF γ - Al_2O_3 + Li_2CO_3 in Li_2CO_3 + K_2CO_3 MIXTURES

Batch Identification No.	Melt* Composition, mol% Li_2CO_3	Product LiAlO_2 Phase Composition, %			LiAlO_2 Surface Area, m^2/g
		α	β	γ	
MX-45	30	14	73	13	5.2
VX-15	37	23	54	23	4.1
VX-10	42	27	50	23	4.2
VX-5	46	37	32	31	3.9

* After reaction of Al_2O_3 + Li_2CO_3

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that the solubility of α -LiAlO₂ is high at low lithium concentrations and thus transformations to the beta and gamma phases are accelerated via a solution-precipitation mechanism.

It is also evident that, as the carbonate melt becomes richer in Li₂CO₃, the β/γ ratio decreases. The observation of an increase in yield of γ -LiAlO₂ accompanying an increase in Li₂CO₃ is in agreement with that of Semenov[†]. He reported that Li₂CO₃ is a mineralizer that accelerates transformation of an $\alpha \rightarrow \gamma$ -LiAlO₂ and that the effect is proportional to the Li₂CO₃ content.

Scanning electron micrographs of the LiAlO₂ products from the three batches with non-standard compositions are presented in Figures 1.2.1 through 1.2.3. The figures illustrate that the yield of elongated, rod-like particles is proportional to the β -LiAlO₂ content, with the most developed rods forming in the most Li₂CO₃-deficient melt. Although higher yields of agglomerated, submicron particles appear to correspond with higher α -LiAlO₂ contents, this observation is not supported by the BET surface area results which are in a narrow range for the three batches.

• Effect of Heat Treatment Temperature

In our standard process of carbonate/aluminate powder production, the α -LiAlO₂ initially formed at 525° and 650°C is recrystallized for 40 hours at 680°C in a 30 mol% Li₂CO₃ melt. The carbonate composition is subsequently adjusted to the final electrolyte composition by an appropriate addition of Li₂CO₃. The lithium aluminate matrix thus produced typically contains 70 to 80% rod-like β -LiAlO₂ with surface areas in the range of 5 to 6 m²/g.

During this reporting period, two otherwise standard batches (identified as TX-650 and TX-665) were given the 40 hour

[†] Semenov, N. N., Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim, Nauk 1, 1967.

15,000X

PO132

FIGURE 1.2.1

Scanning Electron Micrograph of
VX-15 LiAlO_2 : 23% α + 54% β + 23%
 γ - LiAlO_2 recrystallized in a 37 mol%
 Li_2CO_3 melt, $4.1 \text{ m}^2/\text{g}$

15,000X

PO133

FIGURE 1.2.2

Scanning Electron Micrograph of
VX-10 LiAlO_2 : 27% α + 50% β + 23%
 γ - LiAlO_2 recrystallized in a 42 mol%
 Li_2CO_3 melt, $4.2 \text{ m}^2/\text{g}$

15,000X

PO134

FIGURE 1.2.3

Scanning Electron Micrograph of
VX-5 LiAlO_2 : 37% α + 32% β + 31%
 γ - LiAlO_2 recrystallized in a 46 mol%
 Li_2CO_3 melt, $3.9 \text{ m}^2/\text{g}$

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heat treatment at reduced temperatures of 650° and 665°C respectively. Results of lithium aluminate product characterization by X-ray phase analysis, BET surface area and scanning electron microscopy are presented in Figures 1.2.4 and 1.2.5. Characterization data of a standard batch, MX-45, is given in Figure 1.2.6 for comparison.

The anticipated effect of increase in surface area with decrease in temperature was not observed. As indicated in the figure captions, reduction of final heat treatment temperature from 680° to 650°C had no significant effect on LiAlO_2 surface area. There is evidence of an increase in very fine crystallites with a decrease in firing temperature and a broader particle size distribution in the experimental lower temperature preparations. Regarding the particle morphology, high yields of rod-like $\beta\text{-LiAlO}_2$ are observed in each micrograph and it appears that larger aspect ratios correspond with lower firing temperatures. The phase composition of the final products seems insensitive to firing temperature in the range investigated. (The exact β and $\gamma\text{-LiAlO}_2$ content in TX-650 could not be determined because of an anomalous peak intensity for the $\alpha\text{-Al}_2\text{O}_3$ used as an internal standard.) A selection of the best final firing temperature will require additional information from thermomechanical testing and cell testing of the tiles.

1.2.2 Electrolyte Preparation: Synthesis Method

Methods are being developed at ERC for producing LiAlO_2 free of excess reagents (i.e., Li_2CO_3 , LiOH). The synthesis of pure LiAlO_2 with desirable characteristics is of interest for subsequent development of alternate matrix fabrication techniques. The synthesis of a high surface area $\gamma\text{-LiAlO}_2$ is of particular interest because of the apparently greater stability of this allotrope. Two approaches to the production of pure $\gamma\text{-LiAlO}_2$ have been investigated: transformation of pure $\alpha\text{-LiAlO}_2$ at temperatures above 900°C and transformation of pure $\beta\text{-LiAlO}_2$ at temperatures above 700°C. Details of these syntheses

7500X

PO135

Figure 1.2.4: Electron Micrograph of TX-650 LiAlO_2 (Final Firing at 650°C): 17% α - LiAlO_2 , $4.9 \text{ m}^2/\text{g}$

7500X

PO136

Figure 1.2.5: Electron Micrograph of TX-665 LiAlO_2 (Final Firing at 665°C): 16% α + 71% β + 13% γ - LiAlO_2 , $5.2 \text{ m}^2/\text{g}$

7500X

PO137

Figure 1.2.6: Electron Micrograph of Standard Process (MX-45) LiAlO_2 (Final Firing at 680°C): 15% α + 70% β + 15% γ - LiAlO_2 , $5.2 \text{ m}^2/\text{g}$

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and the results of product characterization are discussed in the following sections.

• LiAlO₂ Production From a Stoichiometric Mixture of
γ-Al₂O₃ + Li₂CO₃:

Previous work performed at ERC showed that complete conversion of Al₂O₃ to LiAlO₂ occurred when heat-treated with excess Li₂CO₃ at 600°C for 60 hours. The α-LiAlO₂ thus produced has a clump-like particle morphology with a BET surface area of 58 m²/g. During this reporting period, the process was repeated using a 1:1 molar mixture of γ-Al₂O₃ (Degussa-C) and Li₂CO₃. Various additional heat treatments of the product α-LiAlO₂ at 920° and 950°C were also performed to promote solid state transformation to γ-LiAlO₂. The absence of a liquid phase during the high temperature firing is desirable to limit crystallite growth.

Weight loss measurements on a 1:1 molar mixture of γ-Al₂O₃ + Li₂CO₃ powder heated at 600°C indicated 94% theoretical weight loss after 60 hours. This is in close agreement with the X-ray analysis which indicated 3% unreacted Al₂O₃ in the heat-treated product. Further heating at 650°C for 20 hours produced no further weight loss, indicating that the reaction rate had become impracticably slow. Thus subsequent high temperature firing was performed on this 94% α-LiAlO₂ powder.

Heat treatment of this α-LiAlO₂ was performed in air at 920° and 950°C for various time intervals to induce transformation to γ-LiAlO₂. The remaining α-LiAlO₂ content in the fired product was analyzed gravimetrically using concentrated HCl as solvent. The heat treatment conditions and corresponding yields of γ-LiAlO₂ are shown in Table 1.2.2.

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TABLE 1.2.2

CONDITIONS OF HEAT TREATMENT OF α -LiAlO₂
AND RESULTING YIELDS OF γ -LiAlO₂

Temperature, °C	Time, Hours	% γ -LiAlO ₂
920	1	41
920	2	57
920	5	59
920	10	49
950	2	53
950	5	75

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As shown, a maximum yield of 75% γ -LiAlO₂ was obtained from the 5 hour, 950°C firing. This heating schedule was then repeated for a larger batch of α -LiAlO₂ (120g) and a similar yield of 70% γ -LiAlO₂ was obtained. The residual 25 to 30% α -LiAlO₂ may be acceptable for matrix application and thus this product was submitted for surface area and particle morphology analyses. The results are presented in Figure 1.2.7.

As illustrated, this LiAlO₂ consists of agglomerates of globular primary particles. There appears to be a narrow particle size distribution, with primary particle diameters of 0.1 to 0.2 μ m. This high surface area powder (31 m²/g) shall be tested for structural stability in a molten carbonate fuel cell environment. If testing indicates instability due to the high surface area and/or residual alpha content, heat treatment time can be increased to obtain higher yields of γ -LiAlO₂.

• LiAlO₂ Production From a Stoichiometric Mixture of γ -Al₂O₃ + LiOH:

An alternate approach to the production of electrolyte-free γ -LiAlO₂ is the synthesis of stoichiometric β -LiAlO₂ followed by high temperature induced transformation to γ -LiAlO₂. Kinoshita, et. al.* have shown that essentially pure β -LiAlO₂ may be prepared from a stoichiometric mixture of Al₂O₃ + LiOH by relatively mild firing in air. We have adapted this method to prepare a fine-particled β -LiAlO₂ precursor and have begun to study the effect of subsequent firing temperature on yield of γ -LiAlO₂.

The β -LiAlO₂ precursor was prepared by physically mixing stoichiometric quantities of γ -Al₂O₃ (Degussa-C) and LiOH (-100 mesh jar-milled powder) and heat-treating in air at 465°C

* "Advanced Fuel Cell Development," Progress Report No. ANL-78-16 for October-December 1977, prepared for DOE by Argonne National Laboratory, Argonne, IL.

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15,000X

P0110

 $1\mu\text{m}$

FIGURE 1.2.7

SCANNING ELECTRON MICROGRAPH OF LiAlO_2 PREPARED
BY HEATING PURE $\alpha\text{-LiAlO}_2$ AT 950°C FOR 5 HOURS:

$75\% \gamma\text{-LiAlO}_2 + 25\% \alpha\text{-LiAlO}_2, 31 \text{ m}^2/\text{g}$

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for 2 hours. Subsequent X-ray analysis of this product detected no unreacted Al_2O_3 and indicated a phase composition of 94% $\beta\text{-LiAlO}_2$ + 6% $\alpha\text{-LiAlO}_2$. A scanning electron micrograph of this $\beta\text{-LiAlO}_2$ powder (Figure 1.2.8) shows that the fine $\beta\text{-LiAlO}_2$ crystallites ($29 \text{ m}^2/\text{g}$) exist as clump and rod-shaped particles.

Samples of this $\beta\text{-LiAlO}_2$ were subsequently heated in air, each for 5 hours, at temperatures of 700° , 750° , 800° and 850°C . It was qualitatively observed that the 700°C firing caused practically no change in the powder bulk density while all other firings resulted in significant powder densification. X-ray analysis of the 700°C fired powder indicated no change from the phase composition of the original 94% $\beta\text{-LiAlO}_2$ precursor; X-ray analysis of the 750°C fired material, however, indicated a phase composition of 2% α + 12% β + 86% $\gamma\text{-LiAlO}_2$. Because a high yield of $\gamma\text{-LiAlO}_2$ was obtained under these conditions, further X-ray analyses of the 800 and 850°C fired powders were not performed.

Scanning electron micrographs depicting the particle structures of the 700° and 750°C fired powders are compared in Figures 1.2.9 and 1.2.10, respectively. Figure 1.2.9 shows that the 700°C heat treatment resulted in no significant change in particle size, and it appears that the clump-like morphology was essentially preserved. On the other hand, heating at 750°C for 5 hours (Figure 1.2.10) resulted in phase transformation and dramatic particle growth: large ($\sim 0.7 \mu\text{m}$) polyhedral particles of $\gamma\text{-LiAlO}_2$ are clearly evident. Future experiments will focus on transformation temperatures between 700°C and 750°C to identify the lowest possible temperature needed for high β to $\gamma\text{-LiAlO}_2$ transformation in a practical time interval.

It is of interest to note that a 75% transformation of α to $\gamma\text{-LiAlO}_2$ required a 5-hour, 950°C firing in air while an 86% β to $\gamma\text{-LiAlO}_2$ transformation required only 5 hours at

15,000X

PO138

Figure 1.2.8: Scanning Electron
Micrograph of Stoichiometric
 β -LiAlO₂, 29 m²/g

15,000X

PO139

Figure 1.2.9: Scanning Electron
Micrograph of β -LiAlO₂ After Heating
at 700°C for 5 Hours in Air

15,000X

PO140

Figure 1.2.10: Scanning Electron
Micrograph of 86% γ -LiAlO₂ Obtained
by Heating Stoichiometric β -LiAlO₂
at 750°C for 5 Hours in Air

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750°C in air. The lower temperature required for β -LiAlO₂ transformation is probably due to the closer similarity in the atomic arrangement characteristic of the beta and gamma allotropes. In spite of the lower process temperatures, however, the surface area of γ -LiAlO₂ by the latter method is expected to be less than the 31 m²/g, obtained by the first method (because the surface area of the starting β -LiAlO₂ was only 29 m²/g compared with about 60 m²/g for α -LiAlO₂).

1.3 Electrolyte Tiles

1.3.1 300-cm² Tiles

For some time the question has existed whether our standard production tiles are always uniformly packed and whether in low density areas hairline cracks could exist as precursors to the formation of large cracks. The facilities of Argonne National Laboratory were made available to us through the courtesy of Dr. Kim Kinoshita who offered to have one of our normal production 7 in. x 7 in. tiles tested by X-ray radiography. No density variation was observed in the tile submitted nor could any crack be detected in the tile.

The 300-cm² tiles necessary for cell testing (Task 2) were manufactured. No problems were encountered for this bench-scale tile manufacturing.

1.3.2 1500-cm² Tiles

The pilot-size tile manufacturing procedures were improved to reduce the thickness variations. Various powder doctoring methods, tile pressing procedures and dimensional tolerances of the pressing assembly were examined. As a result, tile thickness variations have been reduced from $\pm 10\%$ to $\pm 5\%$ (Table 1.3.1). Further effort will be continued to reduce this thickness variation to $\pm 2\%$.

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Table 1.3.1

1500 cm² Electrolyte Tile Manufacturing

Tile No.	Thickness (mils)			Variation	
	Lowest	Highest	Medium	(mils)	%
15 T-19	98	119	108.5	21	$\pm$ 9.7
15 T-20	63	74	68.5	11	$\pm$ 8.0
15 T-21	92	111	101.5	19	$\pm$ 9.3
15 T-22	99	113	106.0	14	$\pm$ 6.6
15 T-23	99.5	110.5	105.0	11	$\pm$ 5.2
15 T-24	65	73	69.0	8	$\pm$ 5.8
15 T-25	61	71	66.0	10	$\pm$ 7.6
15 T-26	63.5	71.5	67.5	8	$\pm$ 5.9
15 T-27	69.0	80	74.5	11	$\pm$ 7.4
15 T-28	78	82	80.0	4	$\pm$ 2.5
15 T-29	71.5	79.5	75.5	8	$\pm$ 5.3
15 T-30	70.5	77.0	73.7	6.5	$\pm$ 4.4

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1.4 Cell Frame and Current Collectors

1.4.1 Comparison of Anode Flanges

As mentioned in an earlier discussion of anode flange deterioration*, wet-seal corrosion involves parasitic currents flowing between the reduction and oxidation sites that exist respectively at the outer and inner edges of the anode flange. These reactions are sustained by the presence of reducible oxygen and oxidizable fuel at the respective edge areas. However, these gases cannot rapidly penetrate into the actual wet-seal interfacial areas; therefore the oxidation reaction at the metal/tile contact surface occurs mainly with the metal itself. Thus, particularly with unprotected anode surfaces, corrosion of the contact area should occur closer to the outer edge (where the opposing oxygen reduction reaction takes place) than to the inner edge.

While this is true in most cases, occasionally the situation is reversed, particularly when edges close to the site where fuel gas exits from the cell are considered. In these areas, the relative reducing and oxidizing potentials of the gases on the inside and outside of the wet seal may be opposite to what normally exists.

It was originally stated (but not illustrated with an actual example) that this conclusion is closely corroborated by many of our observations which show that severe attack of the wet-seal area generally starts at the outer edge. An example illustrating this phenomenon with two 8.5 cm² laboratory cell flanges is shown in Figure 1.4.1. The slightly enlarged figure shows the usual corrosive attack that occurs on an unprotected flange (A) and also the absence of severe corrosion on an aluminum coated flange (B). These macrographs pertain to two cells that have each logged an average of 3000 hours of endurance testing.

* ERC Technical Progress Report SAN/1196-10, July-Sept. 1978, Figure 1.4.6.

FIGURE 1.4.1 LABORATORY CELL ANODE FLANGES

- (A - 316 SS unprotected;
- B - protected by coating
- with aluminum

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Although the seals on both cells did not fail before termination, a heavy crust of porous oxide had replaced the metal shown corroded away on the unprotected flange (A). No such severe corrosion occurred on the aluminum coated, diffusion-bonded flange. Thus the figure, besides showing how corrosion is often initiated at the outer edge, also illustrates that our recent aluminum coating procedures are quite effective against one of the most severe types of corrosion found in the MCFC system.

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TASK 2 CELL TESTING A. Leonida, C. Shah,
P. Patel and D. Dharia

The main areas investigated under this task include:

- a) Improving the compatibility of cell components,
- b) Increasing the mechanical integrity of cathode structures,
- c) Evaluating various electrolyte tile structures,
- d) Testing lightweight hardware,
- e) Scale-up of lightweight hardware from intermediate-size (300 cm²) to pilot-size (1500 cm²).

Cell performance was further improved by an increased compatibility of electrolyte tile with electrode structures (Cells 126 and 131). Higher mechanical strength and uniformity in cathode structure were observed with SS screen reinforcement than with nickel screen reinforcement. Performance of different electrolyte structures made by the aqueous slurry method was evaluated. With an improved cathode design, a straight pattern lightweight hardware cell (S7-5) displayed better performance than the earlier cell (S7-4). The lightweight material with straight corrugations was found satisfactory after 1750 hours of endurance. The lightweight hardware was successfully scaled-up from intermediate-size to pilot-size (Cell S15-1). Performance level achieved in the lightweight hardware scaled-up cell was comparable to sub-scale cells having similar components.

Stability of cell components in laboratory-size Cell 118 and intermediate-size Cell S7-3 was analyzed.

2.1 Laboratory-size Cell Testing

Areas investigated in this subtask include improvement in the compatibility of fuel cell components, increase in mechanical strength of cathode, and continued evaluation of various electrolyte tile structures. Tables 2.1.1 and 2.1.2 represent detailed

TABLE 2.1.1 LABORATORY-SIZE CELL TESTING - DETAILS OF COMPONENTS

CELL NO.	ELECTRODES						ELECTROLYTE					PURPOSE OF CELL TEST
	ANODE			CATHODE			COMPOSITION	BATCH NO.	TILE DENSITY g/cm ³	% OF THEOR. DENSITY	THICKNESS OF TILE (mil)	
	THICKNESS (mil)	MEAN PORE SIZE (μm)	POROSITY (%)	THICKNESS (mil)	MEAN PORE SIZE (μm)	POROSITY (%)						
126	25	3.0	72	22	12.0	81	40/60: S/L 50/50: Li/K	KI-3	2.43	95.7	81	Improvement in cell performance. Electrode pair being the same as Cell 112.
127	26	2.6	65	19	10.5	75	40/60: S/L 62/38: Li/K	KI-6	2.48	96.3	40	To test thin tile
128	20	2.6	67	20	10.5	75	40/60: S/L 50/50: Li/K	KI-3	2.44	95.3	36	Components same as Cell 126 except for a thinner tile and stored electrolyte in anode.
129	24	3.2	65	21	9.5	72	45/55: S/L 68/32: Li/K	EC-3	2.39	98.5	77	Lithium rich electrolyte composition
130	21	3.2	64	21	9.5	75	std.*	EC-1	2.36	96.4	76	Reference cell for electrolyte composition study - standard composition.
131	23	3.2	66	22	9.5	74	40/60: S/L 50/50: Li/K	KI-3	2.41	95.0	63	State-of-the-art cell
132	26	3.5	69	22	9.5	75	std.*	KI-1	2.42	95.1	59	Electrolyte made by modified <u>in situ</u> method having 22 m ² /g surface area.

* Std: 55 wt% Liq. carbonates, 45 wt% LiAlO₂
 Li₂CO₃ - K₂CO₃/50-50 mol%

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TABLE 2.1.2 LABORATORY-SIZE CELL TESTING - SUMMARY OF PERFORMANCE

CELL NO	ENDURANCE (hr)	IR CORRECTED VOLTAGE AT 1A (117 mA/cm ²) (V)	R (mΩ)	WET SEAL EFFICIENCY EXIT GAS AS % OF INLET		COMMENTS
				ANODE	CATHODE	
126	431	809	41	100	100	The cell having the same pair of the electrodes as Cell 112 but higher surface area lithium aluminate displayed a better performance.
	813	856	109	99	100	
	1475	870	110	80	100	
127	171	797	32	—	—	The cell with a higher content of α -LiAlO ₂ in the electrolyte tile displayed lower performance. The OCV of this thin tile cell was also low due to a crossover from oxidant chamber to the fuel chamber.
	383	792	52	96	92	
	555	833	63	97	95	
128	194	602	22	100	100	Performance with a thinner tile is not better than Cell 126. The cell displayed high A & C polarizations.
	386	840	60	100	91	
	671	777	77	—	—	
	1029	534	96	—	—	
129	73	712	105	—	—	Lithium-rich electrolyte tile displayed low performance and poor electrolyte retention characteristics.
	118	625	105	—	—	
	166	686	86	73	107	
131	48	856	26	90	94	As expected, improved compatibility of electrolyte tile displayed a better performance than Cell 126.
	123	902	32	88	97	
	170	933	37	86	99	
132	238	480	60	93	51	The cell assembled with higher surface area matrix tile than Cell 131 displayed a lower performance and high polarizations, probably due to dry electrodes.
	404	557	67	91	52	
	550	505	45	97	48	

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summaries of these tests. Post-test observations on the integrity of SS screen reinforced cathode structures have been compared.

2.1.1 Compatibility of Cell Components

Efforts in the area of improving cell performance have been divided into two stages: 1) improve cell performance by increasing compatibility of the electrodes with respect to an electrolyte tile structure and 2) with this pair of electrodes, further improve electrolyte tile structure to achieve better performance. Earlier reports* described an evaluation of the compatibility of different electrode structures with an electrolyte batch, B-108. Last quarter, efforts were aimed at further improving the compatibility of the electrolyte tile structure. As discussed in the previous quarterly Technical Progress Report, a higher surface area lithium aluminate and a higher liquid content tile displayed an improved performance (Cells 126 and 112).

• Cell Performance Improvement

During the present reporting period, work continued on further improving electrolyte tile compatibility. Cell 131 was assembled with a thinner tile (63 mil) to reduce ohmic polarization and an electrode pair similar to the one in Cell 126. The anode in Cell 131 was sintered from a scaled-up Ni-Co powder batch and had $0.22 \text{ m}^2/\text{g}$ surface area. As expected, the cell displayed a lower ohmic resistance ($223 \text{ m}\Omega\text{-cm}^2$), as detailed in Section 2.1.3. However cell performance at 150 mA/cm^2 improved by only 20 mV as compared with the anticipated improvement of 30 mV. The anode and cathode polarizations were comparable in both cells. The limited improvement in cell performance can be explained by the lower surface area of the Ni-Co anode in Cell 131 ($0.22 \text{ m}^2/\text{g}$) as compared with that of Cell 126 ($0.33 \text{ m}^2/\text{g}$).

* ERC Technical Progress Reports No. SAN/1196-8, 9, & 10, 1978.

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Performance of Cell 131 is presented in Figure 2.1.1. The polarization curve for this state-of-the-art cell was obtained with higher gas flows to minimize flow and conversion effects. At 200 mA/cm² with the standard oxidant (air-CO₂), the cell displayed 740 mV; with the noble O₂-CO₂ mixture as oxidant, a 105 mV gain was observed.

Figure 2.1.2 summarizes the improvement in cell performance achieved by the increased compatibility of components during the past four quarters.* Cell 131 displayed a lower ohmic resistance (223 mΩ-cm²) and a higher performance than the rest of the cells. A further improvement in cell performance is anticipated by increasing the surface area of the anode (from 0.2 to 0.3 m²/g or more) and further reducing tile thickness (from 63 to 50 mil).

Electrolyte Inventory and Electrode Performance

The electrolyte inventory in the electrode influences its polarization and thus cell performance. Initial results of cell tests conducted to relate the electrolyte inventory of the electrodes with their respective polarizations were reported earlier.** The observed trend is presented in Figure 2.1.3. As shown, the cathode polarizations[†] for a large electrolyte inventory (> 40 to 50%) "flooded" electrode are high. The polarization reduces with the reduction in the electrolyte inventory, yielding an improved performance of up to approximately 20 to 25%. However, further reduction below this point results in an increased polarization. Thus, it is clear that a non-optimum electrolyte inventory in the cathode could become a performance-limiting factor. The above analysis is useful for arriving at the optimum

* SAN/1196-8, 9, 10 & 11, 1978.

** SAN/1196-10.

† Characterized by O₂-CO₂ gain

FIGURE 2.1.1 PERFORMANCE OF A STATE-OF-THE-ART CELL (No. 131)

Cell Temperature: 650°C
Electrode Area: 8.56 cm²
Anode Gas: 74.2% H₂, 18.5% CO₂, 7.3% H₂O, 3A Flow
Cathode Gas: 15% O₂, 30% CO₂, 55% N₂, 3A Flow

FIGURE 2.1.2
CELL PERFORMANCE RESULTING FROM IMPROVED COMPATIBILITY
OF FUEL CELL COMPONENTS

SAN/11304-12

FIGURE 2.1.3 INFLUENCE OF ELECTROLYTE INVENTORY IN CATHODE ON ITS PERFORMANCE

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amount of electrolyte content. Electrolyte distribution modeling among the active cell components* can then be used to design the electrodes and electrolyte tile structures for the desired electrolyte inventory.

Currently, compilation of similar data for anode inventories is in progress. The analysis and conclusion will be presented after accumulating sufficient data to establish a trend.

2.1.2 Mechanical Integrity of Cathode Structures

Conventional nickel screen reinforced cathodes lose mechanical integrity upon in situ oxidation. In particular, the structural instability of a nickel screen reinforced cathode becomes unacceptable in conjunction with the use of lightweight hardware.** Furthermore, small thickness variations along the electrode surface increase contact resistance which could worsen upon thermal cycling.

During the last quarter, efforts were initiated to improve the integrity of the cathode structure. A SS screen was selected as an alternative to nickel screen for this purpose. Post-test observations of various cell tests conducted with SS screens have been compared with those conducted with the nickel-screen reinforcement in Table 2.1.3. It can be concluded from these observations that the SS screen reinforcement imparted better structural strength than the nickel screen. Figure 2.1.4 illustrates the integrity of the SS screen reinforced cathode structure used in a laboratory-size cell (1000 hours of endurance) and an intermediate-size cell (2000 hours of endurance). Moreover, due to better surface uniformity than with the nickel screen, the SS screen reinforced cathode offers lower contact resistance. The SS screen provides better current collection

* SAN/1196-11, Task 4.

** SAN/1196-9, Section 2.2.1.

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TABLE 2.1.3 MECHANICAL INTEGRITY OF CATHODE STRUCTURES

Criteria	Post-Test Observations For	
	Nickel-Screen Reinforced Cathode	SS Screen Reinforced Cathode
No. of Cell Tests Considered for the Evaluation	10	7
Cell Endurance, hours	1000-2000	1000-2000
Variation in Thickness, mils	3-6	0-2
Mechanical Strength	Poor, Very Difficult to Handle	Good Handleability
Condition of Reinforcement	Completely Oxidized and Considerable Loss of Integrity	Preserved its Integrity and Original Shape
Disintegration During Cell Operation	Extrusion into Current Collector Hole. Some Nickel-Oxide Observed in Gas Passages*	Not Yet Observed
Contact with Tile and Current Collector	Less Uniform	Uniform

* For cells having a configuration with cathode at bottom

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FIGURE 2.1.4

MECHANICAL INTEGRITY OF THE
POST-TEST CATHODE STRUCTURES REINFORCED WITH SS SCREEN

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than the nickel screen, and thus further reduces cell resistance.

Cell tests are now being conducted with thin cathode structures having SS screen reinforcement. Results of their mechanical integrity and performance will be presented next quarter.

2.1.3 Electrolyte Tile Structures

Last quarter, cell testing results and evaluation of different structures for the lithium aluminate matrix were presented. Testing and evaluation of other aspects of tile structures continued through the present quarter. The main areas investigated were evaluation of different electrolyte batches made by the aqueous slurry method and testing of different electrolyte compositions. The results are discussed below.

Evaluation of Electrolyte Made by Aqueous Slurry Method

As discussed in the previous quarterly Technical Progress Report, we began evaluation of electrolytes made by the aqueous slurry (modified in situ) method with Batch KI-3 (Cell 126). This quarter, testing was extended to the evaluation of the effect of different thicknesses of electrolyte tile made from the same batch (Cells 128 and 131).

Also, two more electrolyte batches made by the aqueous slurry (modified in situ) method were tested (Batches KI-1 and KI-6, Cells 132 and 127, respectively). These batches were basically made by the same process except for different heat treatments as described in an earlier report.* The details of cell components and a comparison of performance of these batches are reported in Tables 2.1.1 and 2.1.2. A brief discussion is presented in the following paragraphs.

* SAN/1196-9, Section 1.

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Cells 126, 131, and 128 were assembled with electrolyte tiles made from the same batch but with different thicknesses, 81, 63, and 36 mil, respectively. The electrode pairs in these cells were similar. As expected, a reduction in tile thickness lowered ohmic polarization. The representative cell resistances in these cells were 50, 26, and 18 m Ω , respectively. The large reduction in cell resistance from 50 to 26 m Ω is also partly due to a reduction in the contact resistance. As discussed in Section 2.1.1 for Cells 126 and 131, a reduction in ohmic polarization was reflected in improved cell performance. However, Cell 128 with the lowest ohmic resistance (18 m Ω) did not show corresponding improvement and displayed a lower performance than Cells 126 and 131.

The wet-seal efficiencies for both fuel and oxidant gases were 100%. Unlike Cells 126 and 131, Cell 128 displayed high anode and cathode polarizations. This could be due to improper electrolyte storage.

The observed performance stability of these cells was lower than those assembled with electrolyte made by the conventional in situ method (B-108). During the first 1600 hours of endurance for Cell 126, performance at 117 mA/cm² dropped from 830 mV to 700 mV. This was accompanied by an increase of about 35 mV in anode polarization* and 82 mV in ohmic polarization. However, the wet-seal efficiency, OCV and the cathode polarization (O₂-CO₂ gain) were constant. A similar behavior in endurance was also displayed by Cell 128. During 1055 hours of cell life, the ohmic resistance increased from an initial value of 18 m Ω to 90 m Ω , reflecting a similar drop in cell performance. A possible explanation for this behavior could be large structural changes in the electrolyte matrix leading to higher contact resistance. The cell components are now being

* Characterized qualitatively by a loss in performance while operating with lean fuel (~ 15% H₂) as compared with standard fuel.

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analyzed for stability. Post-test observation of these cells indicated no change in the thickness of Ni-Co anodes.

Cell 132 was assembled with a pair of electrodes similar to that of Cell 131 and electrolyte made by another modified in situ method KI-1 (55 wt% liquid carbonates). Surface area of the lithium aluminate matrix in this cell was $22 \text{ m}^2/\text{g}$ compared with $8 \text{ m}^2/\text{g}$ for Cell 131. Cell 132, with lower electrolyte content tile than Cell 131, displayed higher resistance ($60 \text{ m}\Omega$) and lower performance. Two possible reasons are: 1) a 7 mil variation in tile thickness and 2) pores too fine in the higher surface area matrix to yield an appreciable amount of electrolyte from the tile. The latter was confirmed by high anode polarization (loss in performance at $100 \text{ mA}/\text{cm}^2$ with a lean hydrogen fuel was 260 mV compared with the 30 to 40 mV usually observed), indicating a low electrolyte content in the anode. Liquid electrolyte content greater than 55% will probably be required for the high surface area LiAlO_2 matrix. The liquid content in this matrix (with respect to its thermomechanical characteristics) will be optimized. The cell test will then be repeated with the increased electrolyte content.

Cell 127, assembled last quarter with a thin tile made from electrolyte Batch KI-6 (60% liquid, 62-38/Li/K), displayed a stable performance up to 650 hours. The wet seals were good (96%, fuel side and 92%, oxidant side) and the OCV was low (1.30 V) but stable. Peak performance was 750 mV at $117 \text{ mA}/\text{cm}^2$. Like other cells with KI-batches, this cell also showed an increase in cell resistance from $20 \text{ m}\Omega$ to $64 \text{ m}\Omega$. The test was therefore terminated for post-test analysis.

In general, the initial performance of electrolyte made by the aqueous slurry method was good. Electrolyte content will be optimized for high surface area matrix use. The influence of phase stability on cell resistance will be analyzed for these batches.

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Evaluation of Electrolyte Compositions

The majority of MCFC developmental work performed at ERC to date has utilized a standard electrolyte composition of 50 mol% Li_2CO_3 + 50 mol% K_2CO_3 . Five different electrolyte compositions were chosen to optimize the electrolyte composition and tiles were fabricated accordingly.* Initial results on 68 mol% Li_2CO_3 + 32 mol% K_2CO_3 are discussed below.

Cells 129 and 130 were assembled to begin evaluation of these new electrolyte compositions. Cell 129 had lithium-rich electrolyte (68% Li_2CO_3 + 32% K_2CO_3) whereas Cell 130 had the standard composition to provide a basis for comparison and evaluation. Performance of Cell 129 (having higher melting, non-eutectic electrolyte) was 735 mV at 117 mA/cm². However the test for standard composition (Cell 130) was not conclusive due to its high ohmic resistance (130 mΩ).

The effect of operating temperature on cell performance for Cell 129 is illustrated below.

TABLE 2.1.4

CELL POTENTIAL AT 117 mA/cm²
WITH DIFFERENT CATHODE
GAS MIXTURES

Operating Temperature, °C	With Air/CO ₂ , mV	With O ₂ /CO ₂ , mV	Ohmic Resistance, mΩ
615	480	560	95
650	600	660	86
680	670	745	75

The OCV in Cell 129 was low, due to a steadily growing crossover which ultimately caused the cell's termination. However very little electrolyte creepage was observed, indicating

* SAN/1196-10, pp 13-15.

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no problem with retention characteristics. A possible explanation for crossover is an insufficient electrolyte content (dry tile) providing passages for crossover. This observation was also confirmed by high anode polarization and cell resistance during its early life. A similar behavior was also displayed by Cell 130. Electrolyte inventory in the cell components is now being analyzed. If needed, the electrolyte content will be optimized before further evaluation.

2.2 Intermediate-Size Cell Testing

Cell testing at the intermediate-size level encompassed endurance testing of lightweight hardware (Cell S7-5), testing of SS screen reinforced cathode structures, and scaled-up electrolyte batches (Cells 7-30 and 7-31). Table 2.2.1 shows details of cell components for these tests and their performance is presented in Table 2.2.2. Evaluation of their performance is discussed below.

2.2.1 Lightweight Hardware Testing

During two previous quarters*, stability and performance of staggered-pattern, lightweight hardware were evaluated in intermediate-size cells (S7-2, S7-3, S7-4). During the 1000 to 2000 hours of endurance tests, stability and performance were found satisfactory. As described in the last quarterly Technical Progress Report, Cell S7-5 was assembled to test the straight pattern corrugated current collector and an improved design for the cathode frame derived from Cell S7-4.** As expected, the cell displayed better performance and a lower ohmic resistance than Cell S7-4. At 74 mA/cm^2 , Cell S7-5 performance improved by 256 mV from a cell potential of 454 mV for Cell S7-4.

* SAN/1196-9 & 10.

** SAN/1196-9, Section 2.2.

TABLE 2.2.1
INTERMEDIATE-SIZE CELL TESTING - DETAILS OF COMPONENTS

CELL NO.	ELECTRODES				ELECTROLYTE					PURPOSE OF TEST
	ANODE		CATHODE		COMPOSITION	BATCH NO.	TILE DENSITY (g/cm ³)	% OF THEOR. DENSITY	THICKNESS OF TILE (mil)	
	THICKNESS (mil)	POROSITY (%)	THICKNESS (mil)	POROSITY (%)						
S7-5	25	69	18	72	Std.	LB-1 (B-117)	2.412	98.2	69-70	To evaluate lightweight hardware-pattern #1 (straight type)
7-30	24	70	14	70	Std.	LB-1 (B-117)	2.390	97.2	65-66	Thin SS screen reinforced cathode & crossflow pattern
7-31	23	66	20	75	61% Liq. 50/50 Li/K	LB-2a	2.414	100.0	79-80	To test electrolyte tile with 61% liq. made in a scale-up batch

Std: Standard Composition is 55 wt% liq. carbonates, 45%, LiAlO₂
Li₂CO₃-K₂CO₃/ 50-50 mole%

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TABLE 2.2.2

INTERMEDIATE-SIZE CELL TESTING - SUMMARY OF CELL PERFORMANCE

CELL NO.	ENDURANCE (hr.)	IR CORRECTED VOLTAGE AT 111 mA/cm ² (@ 30 A) (V)	R (mΩ)	WET SEAL EFFICIENCY (Exit as % of inlet)		COMMENTS
				ANODE	CATHODE	
S7-5	92	0.682	6.4	100	95	The performance of the cell having straight pattern hardware was stable but low. The cell resistance and wet seal efficiencies were improved as compared with Cell S7-4.
	780	0.589	3.3	99	90	
	1140	0.531	3.7	86	100	
	1356	0.564	3.3	95	100	
	1544	0.762	7.4	100	98	
7-30	156	0.680	6.0	95	100	The cell assembled with thin SS screen reinforced cathode displayed lower performance than expected. The anode and cathode polarizations were high indicating a wetting problem.
	324	0.524	3.3	84	100	
	492	0.491	3.7	86	99	
7-31	30	0.920	5.0	86	100	The performance of the increased electrolyte content tile is good. However, the cell resistance is higher than expected. The test is continuing.
	434	0.890	5.5	85	89	
	624	0.848	4.4	89	100	

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Cell S7-5 accumulated 1750 hours of stable endurance after which it was terminated to examine stability of the lightweight hardware. Throughout the life of the cell, it displayed good and stable wet seals, OCV, and ohmic resistance. The cell performance was also stable. The anode and cathode polarizations were high, indicating a wetting problem at either electrode.

Bubble pressure measurements for Cell 7-17 and 7-19 were reported in earlier quarterly reports.* Similar measurements were made for Cell S7-5 during its early life and at 1700 hours of endurance before its termination. For the measurements during early life, a drop of 1 mV in OCV was observed at a back pressure of 1/2 psi. This is almost equal to the change in the Nernst term. However, bubble pressure measurements at 1700 hours showed a drop of 3 mV under similar conditions. These measurements are comparable to those in Cell 7-17 where the electrolyte tile contained 60% liquid as compared with 55% liquid for Cell S7-5.

During post-test observations, both staggered pattern and straight pattern current collectors were found intact. In general, their visual appearance was satisfactory. However, there was a thin corrosion layer on both current collectors. Some carbon deposition was also found in the fuel chambers.

2.2.2 SS Screen Reinforced Cathode Structures

Improving the integrity of cathode structures in intermediate-size cells continued during this quarter. Results on good stability and performance for a normal thickness cathode were presented earlier (Cell S7-3). Efforts were then directed toward testing stability of thin cathodes. Two cells were assembled with thin cathodes, one having 18 mil thickness (Cell S7-5) and the other having 14 mil thickness (Cell 7-30). During

* SAN/1196-7 & 8.

ENERGY RESEARCH CORPORATION

post-test analyses of Cells S7-5 and 7-30, the thin cathode structures were found intact and mechanically strong, confirming the observations presented in Table 2.1.3 of Section 2.1. As can be seen from Figure 2.1.4, the cathode from Cell S7-5 was uniform indicating that it had good contacts with both current collector and the electrolyte tile. A more comprehensive evaluation of the stability of thin cathodes will be presented next quarter.

2.2.3 Evaluation of Scaled-up Electrolyte Batches

Three scaled-up electrolyte batches (LB-1, LB-2, and LB-2a) were tested during the present quarter. The lithium aluminate structures in these batches were comparable, with a predominant amount of rod-shaped β -LiAlO₂. The performance of these cell tests is compared in Table 2.2.2. Cells S7-5 and 7-30 were assembled with electrolyte tiles from electrolyte batch LB-1, whereas Cell #1 in Stack 7-2 (Section 3.1) was assembled with an electrolyte tile made from the batch LB-2. Performance of these cells having 55% liquid in the tiles are low. However, Cell 7-31 having a higher liquid content electrolyte tile (61% liquid) and similar electrodes displayed an improved performance. Its initial performance was 770 mV at 111 mA/cm². Compared with the lower liquid content cell, this performance was higher by 200 mV (120 mV of which was due to a reduction in ohmic polarization). The balance could be attributed to improved electrode wetting characteristics. More tests are planned on scaled-up batches to study the influence of electrolyte content on performance.

2.3 Pilot-Size Cell Testing

After a satisfactory scale up from intermediate-size (300 cm²) to the pilot-size (1500 cm²) reported during the last quarter, efforts were concentrated on scale up of lightweight hardware. This quarter a second pilot-size cell was designed for testing lightweight hardware (S15-1). The cell

ENERGY RESEARCH CORPORATION

was assembled with components (electrode and electrolyte tile) with less thickness variation than the previous pilot-size cell. As expected, cell performance improved. It also established validity of the scaled-up components by displaying a performance level comparable to the intermediate-size cells. At 750 mV cell potential, the cell displayed 120 mA/cm² yielding a total power output of 120 watts.

Endurance testing on the first pilot-size cell (15-1) started last quarter was discontinued after 1400 hours. The cell, assembled with machined hardware, was thermally cycled two times. A description of the cell components for these two tests is presented in Table 2.3.1, and a detailed evaluation is given in Sections 2.3.1 and 2.3.2 below.

2.3.1 Lightweight Hardware Testing

The second pilot-size cell (S15-1) is designed to test the staggered pattern lightweight hardware for both the fuel and oxidant distribution as well as current collection. No separate current collector plates were used. Improvements in the cell design were based on the operating experience acquired from the first pilot-size cell. Heavier duty current leads were designed for this cell to permit electric current in excess of 300 amperes. The conventional bubbler-type humidifier was replaced by a larger capacity, diffuser-type humidifier. This would ensure proper humidification of large gas flows and prevent the cell from operating in the carbon deposition region. The rest of the auxiliary components remained the same as Cell 15-1.

Nickel electrodes and the electrolyte tile for this cell were fabricated by improved techniques. The dimensional tolerances and pore structure of these components have been improved as described in Task 1 of this report. The cell frame and the manifold designs were based on a sub-scale lightweight hardware cell (S7-3). A provision was made to permit uniform

TABLE 2.3.1 PILOT-SIZE CELL TESTING - DETAILS OF COMPONENTS

CELL NO.	ELECTRODES				ELECTROLYTE					PURPOSE OF TEST
	ANODE		CATHODE		COMPOSITION	α -LiAlO ₂ (%)	BATCH NO.	DENSITY (g/cm ³)	THICKNESS OF TILE (mil)	
	THICKNESS (mil)	POROSITY (%)	THICKNESS (mil)	POROSITY (%)						
15-1	23	70	23	72	45/55 S/L 50/50 Li/K	8	LB-1	2.331	105	Scale-up of heavy machined hardware to the pilot size
S15-1	19	71	19	77	39/61 S/L 50/50 Li/K	6	LB-2a	2.386	75	Scale-up of lightweight hardware to the pilot size (staggered pattern)

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electrolyte makeup during cell operation. Figure 2.3.1 illustrates the cell components including cell frames with lightweight hardware.

The start-up procedure followed was the same as that described in our earlier report*. Figure 2.3.2 shows the test facility and assembly of the cell. The cell displayed a good OCV (1.08 V). The torque application range established in the first cell to apply a uniform holding pressure was followed from the beginning of the cell life. This resulted in higher wet-seal efficiencies (93% for the fuel side and 99% for the oxidant side) and a lower ohmic resistance (1.3 m Ω) than those of Cell 15-1. As expected, the second pilot-size cell displayed a better performance than the first one. At 100 amperes (75 mA/cm²), the performance of Cell S15-1 with standard oxidant (air/CO₂) was 870 mV as compared with 600 mV for Cell 15-1.

For the standard oxidant, at 750 mV the cell displayed a current density of 120 mA/cm² (see Figure 2.3.3). This is equivalent to a current of 160 A and a power output of 120 watts. Performance of the cell with the noble oxidant (O₂/CO₂) has been compared with the standard oxidant in Figure 2.3.4. The O₂-CO₂ gain at 150 A (112 mA/cm²) was 90 mV, about 20 mV higher than that observed for our state-of-the-art laboratory-size cells.

The performance of the scaled-up lightweight hardware has been compared with a similar intermediate-size cell (S7-3) in Figure 2.3.5. Performance of the pilot-size cell is practically the same as that of the intermediate-size cell. This establishes the scale-up of lightweight components.

* SAN/1196-11, pp. 38.

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FIGURE 2.3.1 COMPONENTS OF A PILOT-SIZE LIGHTWEIGHT
HARDWARE CELL (S15-1)

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FIGURE 2.3.2 ASSEMBLY AND TEST FACILITY - PILOT-SIZE CELL

FIGURE 2.3.3 POWER OUTPUT OF A LIGHTWEIGHT HARDWARE PILOT-SIZE CELL AS A FUNCTION OF OPERATING CELL POTENTIAL (CELL S15-1)

FIGURE 2.3.4 PERFORMANCE OF A PILOT-SIZE LIGHTWEIGHT HARDWARE CELL
WITH THE STANDARD AND NOBLE OXIDANT (CELL S15-1)

Cell Temperature: 650°C

Anode Gas: 74.2% H₂, 18.5% CO₂, 7.3% H₂O

Cathode Gas: 15% O₂, 30% CO₂, 55% N₂

Cell #	S7-3	S15-1
Performance at-hrs.	453	57
Electrode Area, cm ²	271	1340
Cell Resistance, mΩ	3.7	1.2
Gas Flows, amp.	100	400

FIGURE 2.3.5 SCALE-UP OF A STAGGERED PATTERN LIGHTWEIGHT HARDWARE TO THE PILOT-SIZE

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2.3.2 Endurance Testing and Thermal Cycling

Testing of the first pilot-size cell (15-1) assembled last quarter was discontinued after 1400 hours of life. Performance of the cell for 850 hours of endurance, including a thermal cycle, was discussed in the previous quarterly report. The cell did not show any decay in its performance after the first thermal cycle. As planned, the cell was thermally cycled a second time before its termination for post-test examination. Cell performance then dropped from 885 mV to 805 mV at 30 A, and cell resistance increased from 1.7 m Ω to 2.6 m Ω . A drop was also observed in wet seal efficiencies and in OCV.

Post-Test Analysis

All the scaled-up auxiliary components such as pre-heaters, heaters, manifolds and insulation blocks were found to be satisfactory with no corrosion or cracks. No misalignment, contact or short circuit problems were noticed. A large electrolyte creepage was observed on the anode frame with a thick layer of corrosion products. The diffused aluminum-coated wet seal area of the anode had some corrosion and blurred edges at the entry. The anode frame showed carbon deposition, which indicated a need for improvement in humidifier design.

The nickel anode on an average sintered by 4 mils from 23 mils original thickness. No corrosion was observed in the kanthal screen used as tile-reinforcement. However one half of the electrolyte tile, the current collectors and the electrodes were found mechanically weak and corroded. This could be due to an accidental failure in carbon-dioxide supply during the early cell life, leading to a crossover between fuel and oxidant chambers. The lower performance observed also reflects this problem.

ENERGY RESEARCH CORPORATION

2.4 Diagnostics

During this quarter, two cells (118 and S7-3) were analyzed for post-test electrolyte distribution in all the porous components. Structural stability of the electrodes and LiAlO_2 matrices were analyzed for both cells, however the porosimetry results for the matrix of Cell S7-3 are not yet available.

Cell 118 was a laboratory size cell which operated for 1700 hours*. Cell No. S7-3 (a 300 cm^2 cell) was constructed with lightweight current collectors and Ni electrodes. This cell was operated for 1900 hours with stable performance during the first 900 hours*.

The X-ray and electron diffraction analyses and electron microprobe analyses results for the used and unused Ni-Co anode are described in Section 2.4.5.

2.4.1 Electrolyte Inventory

Electrolyte inventory and distribution in post-test cell components are calculated from the measurements of weight loss resulting from washing of carbonates. The results obtained for Cells 118 and S7-3 are summarized in Table 2.4.1. Using these results and porosimetry curves, the largest pore size filled with electrolyte is calculated.

The tile and the Ni-Co anode of Cell 118 are similar to those of Cells 110 and 112**. Comparable results are obtained for the anode wetting in all these cells. A 3.8% pore volume in Cells 110 and 112 and a 3.2% pore volume in Cell 118 were filled with electrolyte. The anode of Cell 118 seems in dry condition as the electrolyte filling is only up to 0.05 μm pores. As seen in Table 2.4.1, the cathode of Cell 118 seems considerably flooded as 62% of the cathode pore volume is filled. The LiAlO_2 matrix pore volume is seen to be only 63% filled.

* SAN/1196-10.

** SAN/1196-10 & 11.

TABLE 2.4.1

ELECTROLYTE INVENTORY AND DISTRIBUTION IN THE POROUS COMPONENTS
OF CELLS 118 AND S7-3

Cell No.	Endurance (hrs)	Amount of Electrolyte in Unused Tile (g)			Amount of Electrolyte in Cell Components After Termination (g)			% Pore Volume Occupied, (largest pore size μm filled) by Electrolyte		
		Initial	Addition + Storage	Total	Anode	Cathode	Tile	Anode	Cathode	Tile
118	1700	3.71	0.81	4.52	0.01	0.32	1.76	3.2 (.05)	61.9 (1.6)	63.4 (0.9)
S7-3	1900	82.6	9.95	92.55	0.28	1.89	53.1	2.7 (2.2)	15.4 (2.5)	72.8* -

* Calculation made on basis of estimated thickness.

TABLE 2.4.2

STRUCTURAL STABILITY OF ELECTRODES

Cell No.	Anode								Cathode							
	Porosity (%)		Mean Pore Size (μm)		Thickness (mil)		Surface Area (m^2/g)		Porosity (%)		Mean Pore Size (μm)		Thickness (mil)		Surface Area (m^2/g)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
118	71	47	3.0	4.7	22	21	0.3	0.2	69	52	3.1	0.7	25	—	0.3	1.2
S7-3	66	47	7.0	10.7	27	21	0.2	0.1	73	50	10.2	10.3	20	22	0.1	0.4

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All the pores over $0.9\text{ }\mu\text{m}$ are empty. Similarly high unfilled post-test matrix porosities have been previously observed (Cells 104, 110 and 111)* for this particular powder batch which is characterized by a broad pore size distribution. (See Figure 2.4.7 of this report).

Cell S7-3 had components similar to Cell 113** and comparable electrolyte contents were measured in the electrodes of these two cells. The percent pore volume occupied by electrolyte in anode and cathode of Cell 113 was 0.5% and 16.5% respectively, as compared with 2.7% and 15.4% in anode and cathode of Cell S7-3. The electrolyte loss was also similar in both cells, but considering the smaller wet-seal to active area ratio in 300 cm^2 cells, the loss in Cell S7-3 is high. This high loss, which resulted in an unfilled matrix porosity of 27%, matches with the post-test observation of excessive creepage on both the anode and cathode frames. The largest pore size filled for the two electrodes of Cell S7-3† is similar, while the anode for Cell 118 seems to be drier than the cathode and the LiAlO_2 matrix. (See Table 2.4.1). Similarly, drier anodes were observed on post-test analyses of Cells 110 and 7-18, as described in our previous Technical Progress Report (Section 4). More data will be accumulated to explain this behavior.

2.4.2 Stability of Electrodes

Structural changes in the electrodes of Cells 118 and S7-3 were measured by Hg-porosimetry and BET surface area analyses on pre- and post-test electrode samples.

Both electrodes used in Cell 118 were higher surface area ($0.3\text{ m}^2/\text{g}$) Ni-Co electrodes whereas nickel electrodes were used in Cell S7-3. The results obtained from porosimetry and surface area analyses (presented in Table 2.4.2) show a large de-

* SAN/1196-10 & 11.

** SAN/1196-10.

† Pore structure data for LiAlO_2 is not yet available.

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crease in porosity for the Ni-Co anode of Cell 118. This result does not match previous results of a similar Ni/Co anode used in Cell 110*. Nor does this porosity change agree with the thickness measurements because the final anode thickness was only 1 mil less than the initial thickness of 22 mils. Furthermore, improper washing of the fine Ni-Co anode pore structure could lead to erroneous results such as low porosity or low electrolyte content as was determined in Section 2.4.1. As the size of the electrode was small, this analysis could not be repeated, but another cell, 7-26 (300-cm² size) which also had a Ni-Co anode, is presently being analyzed. Large structural changes have been noticed for the post-test cathode of Cell 118. Similar results were obtained for Cells 110 and 111 as reported in the previous quarterly report.

The pore size distribution curves for the electrodes of Cell S7-3 are shown in Figures 2.4.1 and 2.4.2.

The Ni anode of Cell S7-3 also shows a large decrease in porosity. The measured decrease in this anode thickness (6 mil) agrees with the porosity decrease determined by Hg-porosimetry. The concomitant increase in the mean pore size of the anode is evident in the scanning electron micrographs (SEMs) of pre- and post-test samples (Figures 2.4.3 and 2.4.4, respectively). As expected, these figures indicate that growth in both particle and pore size occurred during in-cell anode sintering. The SEMs of pre- and post-test cathodes are not yet available and will be presented in the next report. The cathode of Cell S7-3 shows a decrease in porosity but no change in the mean pore size. The volume of the different pores was reduced in a similar proportion (See Figure 2.4.2). It is interesting to note that this cathode was a SS screen reinforced structure.

2.4.3 Phase and Particle Stability of LiAlO₂ Matrix

Phase changes in the LiAlO₂ matrix of Cell S7-3 were determined by X-ray and wet chemical analyses of pre- and

* SAN/1196-11.

Fig. 2.4.1 Pore Volume Distribution Curves for Pre and Post-test Anode of cell S7-3

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Figure 2.4.2 Pore Volume distribution curves for pre and post-test cathode of cell S7-3.

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1945-7

450X

PO141

FIGURE 2.4.3 ELECTRON MICROGRAPH OF
Ni-ANODE BEFORE TEST (CELL S7-3)

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PO142

FIGURE 2.4.4 ELECTRON MICROGRAPH
OF Ni-ANODE AFTER 1900 HR. OF
OPERATION (CELL S7-3)

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post-test material. The results obtained are presented in Table 2.4.3.

As seen in the table, transformation of beta to both alpha and gamma occurred : $\beta \rightarrow \alpha$ (21%) and $\beta \rightarrow \gamma$ (18%). These results are comparable to the results obtained for Cell 113* which contained the same matrix material (Batch 112 LiAlO_2) and was operated for 1600 hours. The final lithium aluminate composition for Cell 113 was 35% α + 40% β + 25% γ as compared with 40% α + 35% β + 25% γ for Cell S7-3. This initially low surface area matrix ($2.8 \text{ m}^2/\text{g}$) appeared stable with respect to further surface area loss (see Table 2.4.3). Actually a small increase in surface area was observed for both Cells S7-3 and 113.

Cell testing (S7-3) induced changes in lithium aluminate particle morphology have also been evaluated by scanning electron microscopy of pre- and post-test matrix samples. These micrographs (presented in Figures 2.4.5 and 2.4.6) show a decrease in rod-shaped particles which is consistent with the decrease in the beta-phase content. In general, however, no essential change in particle size is apparent after 1900 hours of cell testing. This observation agrees with the stable surface area results obtained for this matrix material.

2.4.4 Pore Structure Stability of LiAlO_2

The operational stability of the LiAlO_2 matrix pore structure of Cell 118 was measured by Hg-porosimetry on pre- and post-test matrix powder. The porosimetry curves are obtained on loose powder samples of LiAlO_2 and are subsequently corrected for tile compaction by adjusting the porosities of those of the pre- and post-test electrolyte matrix. BET surface area measurements were also obtained on the pre- and post-test matrix powder.

The stability data for the Cell 118 matrix is presented in Table 2.4.4 and the pore volume distribution curves of the pre- and post-test matrix are presented in Figure 2.4.7.

* SAN/1196-11.

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TABLE 2.4.3
 PHASE STABILITY OF LiAlO_2 MATRIX
 IN CELL S7-3

Description of Sample	Phase Composition (w/o)			Surface Area m^2/g
	% α	% β	% γ	
Initial LiAlO_2	27	61	12	2.8
Post-test LiAlO_2	40	37	23	3.2
% Change	+33	-39	+92	+14%

TABLE 2.4.4
 STRUCTURAL STABILITY OF LiAlO_2 MATRIX

Cell No.	Mean Pore Size (μm)		80% Pore Volume Range (μm)		Porosity (%)		Surface Area (m^2/g)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
118	1.8	0.64	0.18-6.4	0.22-9.4	64.0	64.0	5.1	3.4

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1907-6

3000X

PO143

Figure 2.4.5 Electron Micrograph of LiAlO_2 (Batch B-112) Prior to Use in Cell S7-3. (25% α + 60% β + 15% γ)

PO144

3000X

Figure 2.4.6 Electron Micrograph of LiAlO_2 After 1900 hr Testing in Cell S7-3. (40% α + 35% β + 25% γ)

SAN/11304-12

Figure 2.4.7 Pore Volume Distribution Curves for Pre- and Post-test Matrix of Cell 118

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The porosity and pore size distribution of the LiAlO_2 did not change significantly. This observation is consistent with previous analyses of the same matrix material (Cells 110 and 111)*. A 33% decrease in the initial $5.1 \text{ m}^2/\text{g}$ surface area of this matrix powder was observed. As seen in Figure 2.4.7, the pore size distribution in the unused tile was divided into two steps (0.1 to 0.3 μm , and 1 to 10 μm); however, the used sample had a smooth distribution.

In summary, the following observations can be made to rationalize the performance trends of Cells 118 and S7-3.

Cell 118

This cell, assembled with high surface area Ni-Co anode and cathode electrodes operated for 1700 hours, with an accidental thermal cycle at 1000 hours. The anode structure did show some coarsening (unlike Cell 110), but still maintained a mean pore size (MPS) of 4.7 μm at the end of 1700 hours. This sintering could be due to the crossleak in the cell, as observed after 1000 hours. Cathode MPS decreased from 3.1 μm to 0.7 μm . This cathode was obviously too fine and thus resulted in cathode flooding as suggested by the high (62 Vol%) electrolyte inventory.

Cell S7-3

This lightweight hardware cell (endurance, 1900 hours) was assembled with a tile from electrolyte Batch 112, which was later found to have a typically low ($3 \text{ m}^2/\text{g}$) surface area. This resulted in high cell resistance, lower wet seal efficiency, lower cell performance, and a high (40%) electrolyte loss. A lower electrolyte loss may be expected in intermediate-size cells with higher surface area LiAlO_2 .

* SAN/1196-11.

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2.4.5 Pre- and Post-Test Diagnosis of Ni-Co Anodes

Nickel-cobalt anodes fabricated at ERC have shown good performance stability (e.g., Cell 110)*. This cell (8.5 cm²) was voluntarily terminated and structural parameters (thickness, porosity, pore size distribution and BET surface area) were measured to explain the stable cell performance. Our measurements showed that all the structural parameters were unchanged after 3000 hours. Further analyses by X-ray, SEM, etc. could not be performed on this anode because of the sample size restrictions. To gain understanding of the mechanisms, identically prepared batches** of Ni, Ni-Co and Ni-Co-Cr have been prepared and studied. In addition, we are also performing detailed analysis of anode samples from a large 300-cm² cell (7-26) which operated for 2100 hours (the first 1300 hours at a stable performance level). The reason for decay in the later period may have been the electrolyte batch used in this cell (Batch 112), which was subsequently found to be unstable[†]. The results of post-test diagnosis on Cell 7-26 anode should therefore be interpreted with caution because of the performance decay in the cell. Additional tests with voluntarily terminated cells are planned. The following is a summary of initial results obtained from Cell 7-26.

Two samples, one scraped from a pre-test plaque and one from a post-test electrode of Cell 7-26, have been tested. The specimen in the case of the "used" anode was scraped from the side of the electrode/tile interface. These powdered samples as well as the electrodes from which they came were submitted to exhaustive analysis by a) X-ray powder analysis, b) reflection and selected area electron diffraction, c) electron microprobe analysis, and d) scanning electron microscopy.

* SAN/1196-10

** Refer to Section 1.1 of this report.

† Refer to Section 2.4.3 of this report.

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In this work, our main interest was to learn whether the metal particles that make up the sintered electrode structure consist of a homogeneous alloy of the metallic components (i.e., a single solid-solution phase) or if microsegregation had somehow taken place even though the material was coprecipitated from the homogeneous salt solution. It was expected that high resolution X-ray powder analysis would yield the key patterns showing either two superimposed sets of rings - one pertaining to (FCC) nickel and one to (HCP) cobalt - or one single (FCC) pattern, slightly distorted, showing that a small change in nickel unit cell dimension had taken place as a result of the inclusion of Co atoms in the lattice. However X-ray analysis yielded only the undistorted pattern for nickel. This could mean that insufficient cobalt was present to be detected, although this is doubtful in view of the fact that a high resolution goniometer with geiger counter detector was used to obtain the information. Thus it is more reasonable to assume (in view of the similarity of nickel and cobalt atomic dimensions and the fact that these elements have great mutual solubility) that there is a high likelihood for the formation of a homogeneous alloy without a great deal of distortion of the basic atomic lattice of nickel.

No significant patterns were obtained from the reflection and selected area electron diffraction patterns of the pre-test sample, but a surprising and important piece of information was obtained from the electron diffraction patterns of the post-test powder scraped from the surface of the 2000 hour "used" anode. These patterns indicated the presence of CoO plus NiO in the form of a homogeneous solid solution, with NiO the predominant material. (Both

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have a FCC crystal lattice.) This is in good agreement with much of our recent thinking: that a nickel oxyhydroxide barrier layer grows at the electrode/tile interface which, as it thickens, becomes the major factor causing polarization increases as well as permanent long-term performance losses in the MCFC system.

Electron microprobe analyses of the undisturbed surface of the pre- and post-test electrodes have also been made. These have shown the presence of nickel and cobalt in the percentages of 90 to 10, respectively. A very small amount of copper, iron, and aluminum were also detected in one of the patterns, but since these elements did not shown uniformly in all of the runs, their presence is not very significant.

Scanning electron microscopy, porosimetry, and surface area results are not yet available and will be presented in the next report.

Based on the results and diagnostic data available so far, it appears that the better stability of Ni-Co structures under cell operating conditions may be attributed to a) greater hardness of the Ni-Co alloy as compared with pure Ni or Co, and b) surface oxidation of Ni and Co at cell operating potential to act as inhibitor of surface diffusion.

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TASK 3 STACK DESIGN AND DEVELOPMENT M. Vassalotti
P. Patel and
D. Dharia

Efforts under this task were focused on testing a second lightweight stack (STK 7-2) and developing a manifold seal, as described below.

3.1 Lightweight Stack Testing

Operating experience of the first lightweight stack (STK 7-1) was discussed in the previous quarterly report. A second lightweight 3-cell stack (STK 7-2) was designed, fabricated, and assembled. Details of components of these stack tests are presented in Table 3.1.1. The initial performance of Stack STK 7-2 and post-test observations for Stack STK 7-1 are described in Sections 3.1.1 and 3.1.2, respectively.

3.1.1 Design and Testing of Stack STK 7-2

The second lightweight stack was designed with 3 cells and staggered pattern, sheet metal hardware similar to that used in the first stack (STK 7-1). This stack incorporated two bipolar plates and two end frames, thus forming a true lightweight cell at the center of the stack. The design and fabrication procedure to make bipolar plates was similar to that described earlier.* Voltage leads were provided on each bipolar plate to monitor performance of each cell.

The operating experience gained from Stack STK 7-1 provided useful design improvements for the auxiliary components such as pneumatic compression system, preheaters, and humidifiers. The compression system was improved to apply a uniform sealing pressure on the gas manifolds (seals). As discussed in Section 3.2, an insulating coating of alumina was

* ERC Technical Progress Report No. SAN/1196-11, Oct.-Dec. 1978.

TABLE 3.1.1 LIGHTWEIGHT HARDWARE STACK TESTING
DETAILS OF COMPONENTS

Stack	Cell No.		ELECTRODES		ELECTROLYTE TILES			
			Thickness (mils)	Porosity (%)	Average Thickness (mils)	Density g/cm ³	Batch No.	Composition*
STK 7-1	1	anode	21	65	103	2.2	LB-2	55% LiKCO ₃ 45% LiAlO ₂
		cathode	20	76				
	2	anode	24	69	103	2.1	LB-2	55% LiKCO ₃ 45% LiAlO ₂
		cathode	21	78				
STK 7-2	1	anode	25	68	68	2.3	LE-2	55% LiKCO ₃ 45% LiAlO ₂
		cathode	20	79				
	2	anode	24	68	80	2.4	LB-2a	61% LiKCO ₃ 39% LiAlO ₂
		cathode	20	78				
	3	anode	25	68	82	2.3	LB-2a	61% LiKCO ₃ 39% LiAlO ₂
		cathode	21	76				

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applied on the manifolds by a plasma-spray technique. The alumina coated manifolds as received had a dielectric strength of 800 volts and a coating porosity of 3%. Aluminum foil gas-kets used in the wet seals of the first stack were replaced by diffusion-bonded aluminum coatings to provide better corrosion-protection and to simplify stack assembly procedure.

Performance

Stack assembly and start-up procedures were similar to Stack STK 7-1. The stack assembly along with its auxiliary equipment and control panel is shown in Figure 3.1.1.

As expected, the stack displayed an improved OCV of 1.04 V/cell as compared with 0.95 V/cell for Stack STK 7-1. This represents a reduction of approximately 65% in short-circuit current through the manifold seal. However, the total stack OCV of 3.12 V still is lower than the theoretical value of 3.27. Application of operating procedures established in the previous test yielded 97% of gas seal efficiency for both fuel and oxidant sides.

Performance of the stack with standard oxidant (air-CO₂) has been compared with noble oxidant in Figure 3.1.2. Performance of Cells #2 and #3 in the stack was quite comparable to a single cell (S7-3). However, as can be seen from Figure 3.1.3, Cell #1 displayed lower performance than Cells #2 and #3. Resistance and polarization measurements of individual cells and the stack explained this behavior. Stack ohmic resistance of 20 m Ω , 6.7 m Ω /cell, is higher than that of a single cell having similar components (4 m Ω). However oscilloscopic measurement of individual cell resistances indicated that almost 50% of the total stack resistance was contributed by Cell #1 only (9.4 m Ω). The electrolyte tile in this cell had lower electrolyte content (55 wt%) than the other tiles in the stack (61 wt%). Also, at 111 mA/cm², this cell (Cell #1) displayed higher cathode polarization (113 mV)*

* As characterized by O₂-CO₂ gain.

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FIGURE 3.1.1 ASSEMBLY AND TEST FACILITY FOR THE LIGHTWEIGHT
STACK TESTING

FIGURE 3.1.2 PERFORMANCE OF A LIGHTWEIGHT STACK WITH THE STANDARD OXIDANT AND NOBLE OXIDANT

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FIGURE 3.1.3 COMPARISON OF PERFORMANCE OF INDIVIDUAL CELLS
 IN A LIGHTWEIGHT STACK (STK7-2)

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than that observed for good cells (70 mV). The two observations, higher ohmic resistance and cathode polarization, indicate that the cathode of Cell #1 is running dry.

3.1.2 Post-Test Observations of Stack STK 7-1

Performance of STK 7-1 was described in the last quarterly progress report*. All the components including the lightweight bipolar plate performed successfully. However the ZrO_2 manifold seal was found to be electrically conductive and needed further improvement to minimize short-circuit currents. To determine the path of electrical leakage, a quick test was made. At the operating temperature, the electrical resistance between the stack end-plate and the manifold was measured. It showed low resistance, 20 m Ω , indicating a short-circuit. The zirconia gasket was then replaced by a composite gasket having an insulator (asbestos) layer sandwiched between two zirconia layers which were impregnated with about 1% carbonates. The resistance then increased 100X to 2 Ω , yielding much lower current leakage. This test indicated a need for better insulating gasket material. As discussed in Section 3.2, a systematic evaluation of insulating coatings was undertaken following this test to minimize parasitic currents across the manifold seal.

Post-test examination showed no significant corrosion on manifolds, end frames, and other supporting structures. The bipolar plates were intact and mechanically strong. The gas channels (corrugations) were practically undamaged. However a thin layer of corrosion products was observed. This could be due to a crossover between fuel and oxidant chambers either through the wet seals or through the electrolyte tile. Gas chromatography measurements before termination did confirm the gas crossover.

* SAN/1196-11.

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As a result of the crossover, the anode of Cell #2 was also found partially oxidized. All the components of Cell #1 were normal with no significant structural damage or corrosion. Some carbon deposition was observed in anode preheaters and in the entry manifold, indicating a need for an improved humidifier design.

3.2 Manifold Seal Development

As discussed in Section 3.1, testing of the first light-weight stack (STK 7-1) identified a need for further improvement of the manifold seal. Five seemingly incompatible characteristics are required of the manifold seal material: 1) low porosity, 2) high temperature stability, 3) chemical stability in molten alkali carbonates, 4) high electrical insulating capacity, and 5) conforming elasticity which should remain relatively unaltered by thermal cycling. A zirconia gasket, impregnated with carbonates, offered good gas sealing properties along with stability. However its electrical insulating capacity was found to be low. Initially, an added layer of insulating material between the manifold and zirconia gasket was selected. An alumina coating on the manifold sealing edges was applied by plasma-spraying. A test stand was designed and built to perform screening tests on the sealing materials (Figure 3.2.1). The temperature controlled furnace permits experiments at desired temperature. Sealing properties of new gasket materials were characterized by monitoring the inlet and outlet gas flows and the electrical resistance. Results of the tests conducted to optimize carbonate content and coating thickness are summarized in Table 3.2.1. As evidenced in this table, the configuration with less thickness of alumina coating and high carbonate content in the zirconia gasket was not stable, while the configurations with low carbonate content did not provide proper gas sealing. A configuration with 7 mil thick coating and 1% carbonate content provided good gas sealing efficiency, stability, and a reasonably high electrical resistance. Based on this, a 10 mil thick

FIGURE 3.2.1 SCHEMATIC OF TEST FACILITY FOR THE MANIFOLD SEAL DEVELOPMENT

TABLE 3.2.1 MANIFOLD SEAL DEVELOPMENT FOR LIGHTWEIGHT STACK

TYPE	MANIFOLD SEAL MATERIAL				Volume % of carbonates impregnated	Endurance at 650°C (hours)	Gas seal efficiency, (% of inlet flow)	Ohmic resistance across the manifold assembly (Ω)	COMMENTS
	ALUMINA COATING								
	PROCESS USED FOR APPLICATION	THICKNESS (mils)	DIELECTRIC STRENGTH* (volts)	POROSITY (%)					
Alumina-Zirconia	Plasma Spray	3	250	4	10.0	2 15	95 < 50	150 ~100	The coating and the sealing face were found corroded.
Alumina-Zirconia	Plasma Spray	7	550	3	0.5	3 20	80 70	180 160	The coating was intact. However, the gas-seal efficiency was low.
Alumina-Zirconia	Plasma Spray	7	550	3	1.0	2 18 67 89 113	97 100 99 100 100	80 110 160 70 80	The gas seal efficiency was good. However, the resistance was fluctuating. A part of the coating from the manifold was found chipped off.
Cotronics Ceramic Paper	As Received	62	6200	Highly Porous and Compressible Structure (Exact Value was not supplied.)	0.0	2 24 150	100 100 100	8 8 8	The material provided good gas seal and electrical insulation. However, it was found unstable in molten carbonates.

* Supplied by the manufacturer

ENERGY RESEARCH CORPORATION

alumina layer with 1% carbonate content in the gasket was selected for stack test STK 7-2.

A ceramic paper (manufactured by Cotronics) was also tested. While it had very high insulating property and gas seal efficiencies, it was found to be unstable in molten carbonate electrolyte.

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TASK 4 MODELING AND SYSTEM ANALYSES D. Burns, D. Patel
and D. Dharja

System analyses using the present MCFC system model are presented in Task 4.1. Further development of the system model is described in Task 4.2.

4.1 System Analyses

System study was continued with the configuration presented in the last quarterly report*. Evaluation of O₂-blown coal gasifier fuel was performed and fuel cell performance was estimated using both air and oxygen as an oxidant.

The effect of fuel and oxidant utilizations on fuel cell performance and other system parameters was studied. The air-blown coal gasifier fuel and the air (burner oxidant) were selected for this purpose. The impact on system performance of CO₂ product exchange device (PED), substituting the burner, was predicted. The results are discussed in the following subsections.

4.1.1 Evaluation of O₂-Blown Coal Gasifier Fuel

A Westinghouse O₂-blown coal gasifier was considered as a source of fuel. A steam requirement of 0.24 mol per mol of fuel gas (178.6 kg per 100 SCM of fuel gas) was estimated to prevent carbon deposition. Fuel gas compositions before and after the steam addition step are listed in Table 4.1.1.

Cell performance was projected with the non-carbon depositing composition and compared with the corresponding performance of air-blown gasifier fuel. Figure 4.1.1 shows the effect of feed stock composition on fuel cell performance. The OCV, terminal potential, and polarization losses are compared at 161 mA/cm² (150 ASF) in Table 4.1.2 for the air-blown

* Technical Progress Report, SAN/1196-11, Oct.-Dec. 1978.

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TABLE 4.1.1

O₂-BLOWN COAL GASIFIER FUEL COMPOSITIONS

Component	Concentration, mol%	
	Carbon Depositing	Non-Carbon Depositing and Water Gas Equil- ibrated at 650°C
H ₂	23.1	29.5
CO	38.0	19.5
CH ₄	2.3	1.8
H ₂ O	15.4	21.1
CO ₂	20.5	27.4
H ₂ S	0.8	0.6

TABLE 4.1.2

PERFORMANCE COMPARISON OF AIR-BLOWN AND O₂-BLOWN
GASIFIER FUEL CASES

	Air Blown	O ₂ Blown
Cell Potential at 161 mA/cm ² , mV	791	797
Nernst and Electrode Polarizations, mV	182	164
Ohmic Polarization, mV	45	45
OCV, mV	1018	1006

FIGURE 4.1.1

EFFECT OF FEEDSTOCK COMPOSITION ON
FUEL CELL PERFORMANCE

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and the O₂-blown gasifier fuel cases. The gain in performance at 161 mA/cm² by using the O₂-blown gasifier fuel instead of the air-blown gasifier fuel was very little (only 6 mV). To a major extent, this might be attributed to the increase in product (CO₂ and H₂O) concentrations along with the reactant (H₂) concentration at the anode. The product concentration increase was caused by the absence of N₂ (diluent) and the larger steam requirement in the O₂ blown case. The reactant (O₂ and CO₂) concentrations at cathode increased by a smaller extent than on the anode side, since N₂ entering the system through burner air worked as diluent again.

Material and energy balance with operating conditions at 161 mA/cm² is presented in Table 4.1.3. Power output was 939.4 kW per 100 SCMH of fuel gas from the gasifier, yielding about the same fuel cell subsystem efficiency (CH₄-free, HHV basis) of 46% as in the case of air-blown gasifier fuel.

4.1.2 Effect of Oxidant Composition on Cell Performance

Oxidant for the fuel cell is introduced in the system through the burner. A comparison of air and O₂ as oxidant was made using O₂-blown gasifier fuel. The polarization curves for the two cases are compared in Figure 4.1.2. Use of pure O₂ eliminated the diluent (N₂) from the system, yielding high reactant (O₂ and CO₂) concentrations at the cathode. This resulted in improved cell performance. It was observed that the use of O₂ increased the performance at 161 mA/cm² from 797 mV (with air) to 865 mV. Still, the gain in performance should be weighed against the cost of O₂ production for the economic operation of the system. With O₂ as oxidant, OCV increased to 1057 mV. Assuming ohmic polarization of 45 mV, Nernst losses and electrode polarizations were estimated to be 147 mV.

TABLE 4.1.3

MATERIAL AND ENERGY BALANCE

(O₂-Blown Coal Gasifier Fuel - Air [CO₂] Oxidant)

Stream No.	Temp. °C	Heat Content BTU/hr	Flow Rates - lb mole/hr-----								
			H ₂	CO	CH ₄	CO ₂	H ₂ O	N ₂	O ₂	H ₂ S	Total
1	650	88708	2.73	1.80	0.17	1.95	2.54	0.00	----	0.06	9.24
2	677	155623	0.36	0.32	0.17	7.29	4.90	0.00	---	0.06	13.09
3	287	74235	----	----	----	---	0.19	17.38	4.62	----	22.19
4	731	377748	----	----	----	7.77	5.85	17.38	3.85	----	34.85
5	597	26218	----	----	----	21.61	32.28	95.81	10.62	----	160.33
6a	621	453525	----	----	----	7.82	10.15	30.13	3.85	----	51.95
6b	621	1250404	----	----	----	21.56	27.99	83.06	10.62	----	143.23
7a	677	431404	----	----	----	3.97	10.15	30.13	1.93	----	46.17
7b	677	1377603	----	----	----	21.56	27.99	83.06	10.62	----	143.23
8	677	277704	----	----	----	3.92	5.85	17.38	1.93	----	29.08
9	677	1531304	----	----	----	21.61	32.28	95.81	10.62	----	160.33
<p>Operating Conditions: Temperature = 650°C, Pressure = 150 psia, Current Density = 161 mA/cm²</p> <p>Utilizations: Fuel = 85%, Oxidant: O₂ = 50%, Cell Voltage = 0.797V</p> <p>Active Area = 100 cells in series each with 0.58 m² area = 58 m²</p> <p>Heat Content Basis: H₂ (g), CO₂ (g), H₂O (g), CO (g), CH₄ (g), N₂ (g), O₂ (g) at 25°C, Heat Content = Zero</p> <p>Total Heat of Reaction in the Fuel Cell = 427156 BTU/hr, Total Heat of Reaction in the Burner = 147890 BTU/hr</p> <p>Heat Equivalent of Electricity Generated = 255164 BTU/hr</p> <p>Load of Heat Exchanger (Q) = 205122 BTU/hr</p>

FIGURE 4.1.2

POLARIZATION CURVES WITH
O₂ BLOWN COAL GASIFIER FUEL

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Material and energy balances with operating conditions at 161 mA/cm² are presented in Table 4.1.4. Power output was 1.017 mW per 100 SCMH of fuel gas from the gasifier, yielding the fuel cell subsystem efficiency (CH₄-free, HHV basis) of 50%.

4.1.3 Effect of Fuel Utilization

Fuel utilization was varied from 50% to 85% at a constant O₂ utilization of 50%. The performance curves obtained are compared in Figure 4.1.3. As expected, cell performance increased with a decrease in fuel utilization because of the reduced Nernst loss. Cell voltage at 161 mA/cm² is listed along with system efficiency and reactant compositions in Table 4.1.5. The following observations were made from this table:

- Cell voltage increased by 21 mV at 70% utilization and by 42 mV at 50% utilization over that of 791 mV at 85% utilization.
- Fuel cell subsystem efficiency (fuel cell power output/HHV of CH₄-free fuel) increased with increase in utilization.
- H₂ concentration in the anode effluent was very low (1.7%) at 85% utilization. A further increase in utilization might result in a diffusion limited anode.
- With decrease in utilization, combustion of spent fuel in the burner increased, increasing the load of the heat exchanger.
- Change in the fuel utilization did have an impact on the cathode inlet gas composition because of the nature of the system configuration (combustion of the anode effluent). With the decrease in fuel utilization, O₂ concentration decreased, whereas CO₂ concentration increased to some extent. Increase in diluent (N₂) through burner air decreased O₂ concentration and increase in fuel flow increased CO₂ concentration. So at lower fuel utilizations, the possibility of higher O₂ diffusion polarization could arise.

TABLE 4.1.4

MATERIAL AND ENERGY BALANCE

(O₂-Blown Coal Gasifier Fuel - O₂ [CO₂] Oxidant)

Stream No.	Temp. °C	Heat Content BTU/hr	Flow Rates - lb mole/hr							
			H ₂	CO	CH ₄	CO ₂	H ₂ O	N ₂	O ₂	Total
1	650	88708	2.73	1.80	0.17	1.95	2.54	--	0.06	9.24
2	677	55623	0.36	0.32	0.17	7.29	4.90	--	0.06	13.09
3	287	15868	----	----	----	---	---	--	4.62	4.62
4	1031	319380	----	----	----	7.77	5.66	--	3.85	17.29
5	566	1132613	----	----	----	43.28	62.53	--	21.28	127.09
6a	621	222617	----	----	----	7.83	10.46	--	3.85	22.14
6b	621	1229382	----	----	----	43.23	57.74	--	21.28	122.24
7a	677	177588	----	----	----	3.97	10.46	--	1.93	16.36
7b	677	1357644	----	----	----	43.23	57.75	--	21.28	122.24
8	677	127460	----	----	----	3.92	5.66	--	1.93	11.51
9	677	1407773	----	----	----	43.28	62.53	--	21.28	127.09

Operating Conditions: Temperature = 650°C, Pressure = 150 psia, Current Density = 161 mA/cm²Utilizations: Fuel = 85%, Oxidant: O₂ = 50%, Cell Voltage = 0.865VFuel: O₂-Blown Coal Gasifier, Oxidant: O₂Active Area = 100 cells in series each with 0.58 m² area = 58 m²Heat Content Basis: H₂(g), CO₂(g), H₂O(g), CO(g), CH₄(g), N₂(g), O₂(g) at 25°C - Heat Content = Zero

Total Heat of Reaction in the Fuel Cell = 427156 BTU/hr

Heat Equivalent of Electricity Generated = 277010 BTU/hr

Load of Heat Exchanger (Q) = 275152 BTU/hr

Figure 4.1.3

Effect of Fuel Utilization on Cell Performance

TABLE 4.1.5

EFFECT OF FUEL UTILIZATION ON SYSTEM PARAMETERS

Fuel Utilization, %	Cell Voltage at 161 mA/cm ² , volts	Cathode Inlet Gas Composition, mol %		H ₂ Concentration in the Anode Effluent, mol %	Fuel Cell Subsystem Effic- iency*, %
		O ₂	CO ₂		
85	0.791	5.8	12.9	1.7	45.6
70	0.812	5.2	13.5	3.7	38.5
50	0.833	4.3	14.3	6.7	28.2

*Based on HHV of CH₄-free fuel

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4.1.4 Effect of Oxygen Utilization

Oxygen utilization was varied from 50% to 30% at a constant fuel utilization (85%). The polarization curves were similar and a decrease in utilization improved cell performance. The cell voltage at 161 mA/cm^2 and other system parameters are summarized in Table 4.1.6. The following observations were made:

- The increase in performance by decreasing O_2 utilization from 50% to 30% was only 9 mV.
- Process air flow rate increased with the decrease in O_2 utilization, which would result in an increased loss of electrolyte.
- Fuel cell subsystem efficiency did not change considerably.

4.1.5 Impact of CO_2 PED on System Performance

The recycle of CO_2 from anode effluent to cathode inlet gas can also be accomplished by CO_2 Product Exchange Device (PED). Substitution of CO_2 PED for gas burner reduced the diluents (N_2 , H_2O) from the cathode inlet gas, yielding higher cell performance.

The present computer program was modified to incorporate the system configuration with CO_2 PED which is shown in Figure 4.1.4. The system was evaluated assuming a CO_2 PED efficiency of 100%. The results are compared with the burner case in Table 4.1.7. The following observations/conclusions were made:

- A performance gain of 44 mV was achieved by substituting CO_2 PED for burner.
- The performance gain can be further increased by reducing the fuel utilization and by partial recycling of the anode effluent after separation of CO_2 and H_2O .

Material and energy balance with operating conditions at 161 mA/cm^2 for the CO_2 PED case is presented in Table 4.1.8. Power output was 279 kW per 100 SCMH of fuel gas from the gasifier, yielding 48% fuel cell subsystem efficiency (CH_4 -free, HHV basis).

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TABLE 4.1.6

EFFECT OF O₂ UTILIZATION ON SYSTEM PARAMETERS

O ₂ Utilization, %	Cell Potential at 161 mA/cm ² , volts	Process Air Flow, 10 ³ g mol/hr	Fuel Cell Subsystem Efficiency,* %
50	0.791	30.2	45.6
30	0.800	50.2	46.2

Fuel Utilization - 85%

*Based on HHV of CH₄-free fuel

FIGURE 4.1.4
SCHEMATIC OF MCFC SUBSYSTEM WITH CO₂ PED

TABLE 4.1.7
COMPARISON OF SYSTEM PERFORMANCE FOR CO₂ PED AND BURNER CASES

System Configuration	Reactant Concentrations at Cathode, mol%				Cell Potential @ 161 mA/cm ² , mV	E _{inlet} [*] mV	E _{exit} [*] mV	Reactant Concentrations in Stream 4, mol%	
	Inlet		Exit					O ₂	CO ₂
	O ₂	CO ₂	O ₂	CO ₂					
CO ₂ PED 100% Efficiency	10.3	19.6	6.1	10.9	834	1046	862	14.8	28.8
Burner	5.8	12.9	3.2	7.8	790	1018	836	8.6	18.4

*E = Nernst Potential

Fuel Utilization = 85%

Fresh Air Flow: Burner Case - 2 STOAIR
CO₂ PED Cases - 2 STOAIR for Fuel Cell

TABLE 4.1.8
MATERIAL AND ENERGY BALANCE
(CO₂ PED - 100% Efficiency)

Stream No.	Temp. °C	Heat Content BTU/hr	Flow Rates - lb mole/hr-----							
			H ₂	CO	CH ₄	CO ₂	H ₂ O	N ₂	O ₂	Total
1	650	154584	2.97	1.56	0.44	2.38	2.30	7.31	---	16.97
2	677	224067	0.36	0.32	0.44	7.38	4.91	7.31	---	20.82
3	287	61911	----	----	----	---	0.16	14.49	3.85	18.50
4	399	160703	----	----	----	7.48	0.16	14.49	3.85	25.98
5	659	1363879	----	----	----	27.04	1.20	108.00	14.36	150.59
6a	621	322565	----	----	----	7.30	0.29	25.92	3.85	25.98
6b	621	1202054	----	----	----	27.22	1.07	96.58	14.36	139.22
7a	677	287034	----	----	----	3.45	0.29	25.92	1.93	31.58
7b	677	1324003	----	----	----	27.22	1.07	96.58	14.36	139.22
8	677	190585	----	----	----	3.63	0.16	14.49	1.93	20.21
9	677	1420451	----	----	----	27.04	1.20	108.00	14.36	150.59
10	677	98792	----	----	----	7.48	----	----	---	7.48

Operating Conditions: Temperature = 650°C, Pressure = 150 psia, Current Density = 161 mA/cm²

Utilizations: Fuel = 85%, Oxidant: O₂ = 50%

Fuel: Air-Blown Coal Gasifier

Oxidant: Air

Active Area = 100 cells in series each with 0.58 m² area

Heat Content Basis: H₂(g), CO₂(g), H₂O(g), CO(g), CH₄(g), N₂(g), O₂(g) at 25°C - Heat Content = Zero

Total Heat of Reaction in the Fuel Cell = 422830 BTU/hr.

Heat Equivalent of Electricity Generated = 266930 BTU/hr

Load of Heat Exchanger (Q) = 56534 BTU/hr

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4.2 Fuel Cell Subsystem Model

The MCFC subsystem model reported earlier* has been extended to perform the following additional functions:

- It can now calculate the amount of steam required to prevent carbon deposition in the anode, both in the presence and absence of anode recycling. Earlier these calculations were done manually and fed to the system program as input data.
- It can consider carbon dioxide recovery from the fuel gas (during the gas clean-up) and recycling of this CO₂ to cathode.
- It can consider the effect of anode recycling on the fuel cell stack performance.
- It can consider both the co-current and the counter-current flows of the fuel and the oxidant gas streams in the anode and the cathode compartments, respectively.
- It calculates the total number of fuel cells required for a given power output from the MCFC stack. It also calculates the electrical efficiency of the MCFC stack and the concentration profiles in the fuel cell.
- In spite of the above mentioned additional capabilities, the system program now performs the entire calculations in just 4 minutes on an IBM 370/160 computer compared with the 20 minutes taken earlier. This has been achieved by using an improved algorithm for system calculations.
- Presently the model is being modified to consider temperature gradients in the cell and the crossflow of the fuel and the oxidant gas streams. Results will be presented in the next quarterly report.

* ERC Technical Progress Report SAN/1196-11, Oct.-Dec. 1978.

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FUTURE WORK PLAN

In the next reporting period, efforts will be directed at the following tasks:

Component Development

- Manufacturing procedures for the 1500 cm² electrodes and electrolyte tiles will be improved to further reduce the dimensional tolerances to ± 1 mil.
- Ni-Co-Cr mixed powder reduction and sintering procedures will be developed to obtain anodes of surface areas ≥ 0.3 m²/g.
- Separate synthesis procedures will be further developed to increase the mole fraction of the γ -LiAlO₂ to a higher level (close to 100%).
- Another test cell will be assembled to examine the effects of gas composition and coatings on potentiostatic corrosion current measurements.

Cell Testing

- Efforts will be continued to further improve cell performance by reducing tile and cathode thickness (compared to that of Cell 131).
- New electrode structures (Ni-Co-Cr) and new high surface area matrices, as developed in Task 1 will be tested. Electrolyte content will be optimized for different matrices to reduce anode and cathode overpotentials.
- Endurance testing of the second pilot size cell (S15-1) assembled with lightweight hardware will be continued. A goal of 1000 hours is set for the endurance. The cell will also be thermally cycled.
- Design of a pressurized cell, test facility will be completed and construction of the test stand will be initiated.

ENERGY RESEARCH CORPORATIONStack Design and Development

- Testing of Stack STK 7-2 will be continued up to 300 or more hours. Upon termination, the wet seal and manifold seal areas will be examined for corrosion. The next stack will then be designed based on the experience gained in the first two stacks.

Modeling and System Analyses

- The cell performance model will be extended to include cross-current and counter-current flow configurations.

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