HIGH TEMPERATURE
MOLTEN CARBONATE FUEL CELLS

TECHNICAL PROGRESS REPORT FOR THE
PERIOD SEPTEMBER - DECEMBER 1977

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EXECUTIVE SUMMARY

Component Development

A hydrogen sintering furnace capable of producing 0.5 sq. meter electrodes was installed and operating procedures are being established.

To develop stabilized anode structures, a fine particle nickel-cobalt alloy powder was prepared from their hydroxide mixture through the steps of co-precipitation, spray-drying and reduction. Electrodes have been produced for small cell tests using this high surface area alloy powder.

The in situ method of electrolyte preparation was studied in detail to establish the effect of various thermal treatments and to optimize the reagent processing and mixing techniques. DTA & TGA analysis were performed for the reaction mixture. β -lithium aluminate appears to recrystallize from the α -lithium aluminate during the third thermal treatment at 675°C, causing a large reduction in the surface area. The method was found to be very sensitive to various processing and mixing techniques as small changes in latter resulted in mixtures with different proportions and shapes of α - β - γ -lithium aluminates.

In parallel to the above work, procedures were developed for the separate controlled syntheses of α - β - γ -lithium aluminates. While high surface area α -lithium aluminate was easily realized, further efforts are required to prepare high surface area γ -lithium aluminate.

Metal fiber reinforced tiles were fabricated with fibers of different diameters, lengths and loadings. Some problems were encountered in obtaining uniform distribution of random reinforcement, while Kanthal fiber screen reinforced tiles were found easier to manufacture.

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Equipment has been assembled to conduct potentiostatic corrosion tests on candidate materials for the cell frame and current collector.

Cell Testing

Efforts were directed towards improving anode and cathode structures, corrosion protection, wet seal efficiency, cell hardware design and thermal cycling capabilities. Performance was improved by decreasing the anode pore size with the cathode pore size unchanged. The teflon rolled cathode was found to be structurally intact at the end of a 400-hour test, and it developed a good bond with the tile, indicating a good potential for less expensive cathode structures. The diffusion bonded aluminum coating provided good protection of wet seal areas against corrosion. The wet seal efficiencies were increased by increasing the sealing pressure and for some cells it also resulted in a large decrease in cross-leakage as indicated by chromatographic measurements. A limited success in thermal cycling was achieved with Kanthal fiber random reinforced tiles. Tests have begun with tiles reinforced with Kanthal screen.

Lithium aluminate prepared by the synthesis method gave a cell performance similar to that obtained from the lithium aluminate prepared by the in situ method. Structural integrity of the lithium aluminate matrix was measured periodically over a 1400-hour period by noting OCV changes in a 7" x 7" size cell at a back pressure of 1/2 psi.

A steady performance has been achieved for 1300 hours, with the test continuing.

Stack Design & Development

Lightweight hardware has been designed to replace the heavy machined flanges and current collectors. This hardware will be tested in single cells next quarter.

Modeling & System Analysis

Several definitions for Nernst losses were evaluated. A method of computing an integrated average value with respect to the cell length was found satisfactory. This definition explains the bending of the constant conversion curve at higher terminal potentials.

The mathematical model was modified to incorporate the water-gas equilibrium.

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TASK 1. COMPONENT DEVELOPMENT: C. Herscovici, D. Kinnibrugh,
L. Paetsch, D. Dharja

1.1 Electrode Structures

1.1.1 Hydrogen Sintering Furnace Operation

The auxiliary systems for electrical power, water cooling and gas flows for the new sintering furnace were installed. A molecular sieve drier was received and will be integrated in the system to reduce the dew point of the protective gases below -100°F .

Several construction deficiencies became apparent during the initial tests. They were corrected to ensure the proper functioning of such devices as flame curtains, burn-off stack torches and furnace doors. Some design modifications were required to increase operational flexibility. The gas feed lines were changed to permit the use of Hydrogen, Nitrogen or any blend of the two gases. Auxilliary equipment, tools and materials were purchased. Special tools needed for loading and unloading the furnace were designed and produced. Operational and Safety Procedures have been formulated and operator training is proceeding.

To begin with, relatively thick electrodes were sintered. The purpose was to develop the art of packing and sintering nickel powder. Type 287 nickel powder supplied by The International Nickel Company, Inc., was sintered at 1650°F . Electrodes of size $13.5" \times 9" \times 0.042"$ with 82% porosity were prepared. During the next quarter, various sintering parameters such as packing techniques, temperatures, sintering time and compacting procedures will be studied. The goal is the establishment of procedures to obtain the desired thickness, porosity and pore size.

1.1.2 Anode Structures

In order to overcome the slow sintering of the fine pore anode structure during cell operation at 650°C , it is necessary to increase the effective hardness of the anode material. This may be achieved either by using an alloy, or by incorporating inert ceramic particles of refractory metal oxides in the structure.

Starting in October, a small hydrogen furnace was designed and constructed. It is presently being used for reduction and sintering of new types of anode materials for evaluation in small cells.

As a first step, it was decided to investigate the possibility of using a nickel-cobalt alloy for the anode, since this would be likely to possess a greater hardness than pure nickel at the operating temperature of the cell. Due to the higher cost of cobalt, an alloy containing only 10% by weight of this material was used.

The powdered metal alloy was prepared by co-precipitation of nickel and cobalt hydroxides from their respective salts, followed by washing and spray-drying to maintain a fine particle size. This material was readily reduced in a stream of hydrogen at 400°C or above. Following a careful reduction below 500°C in order to avoid excessive sintering due to the exothermic reaction, the temperature was raised into the range 750° - 850°C, where controlled pre-sintering of the alloy powder was carried out. The product was then compacted and sintered at 900°C to form electrodes incorporating a nickel reinforcing screen. Standard porous electrode sintering techniques were used. These electrodes will be evaluated in small cell tests.

1.2 Electrolyte Powder

Electrolyte powder preparation was continued in two parallel approaches. One approach is to improve the in situ method which involves multistep thermal treatment and grinding. A second approach is to develop the procedures for the synthesis of separate allotropes.

Lithium aluminate prepared by various procedures was characterized by X-ray diffraction analysis and Scanning Electron Microscopy. Several standard mixtures were prepared for calibration. Calibration curves of weight percent versus intensity were constructed for each phase and were used for the analysis of unknown samples.

1.2.1 Electrolyte Powder Preparation - "In situ" Method

The in situ method of electrolyte preparation refers to a three stage thermal treatment of an intimate blend of Li_2CO_3 + K_2CO_3 + Al_2O_3 powders: this synthetic approach to electrolyte powder preparation has been previously discussed in detail in the Eighth Monthly Progress Report. In our work, we have made use of reagent grade alkali carbonates and $\gamma\text{-Al}_2\text{O}_3$ obtained from Degussa, Inc. and identified as their product Degussa-C. It is generally observed that the LiAlO_2 product of this procedure is a mixture of the three known allotropic forms, exhibiting a variety of particle shapes and sizes: the particular LiAlO_2 distribution obtained by this method seems to be very sensitive to several process parameters. During the past quarter, efforts were initiated to identify some of the critical variables so that the process may be ultimately tailored to yield a consistent product with the desired LiAlO_2 distribution. In particular, development efforts were focused on studying the effects of the various thermal treatments and optimizing the reagent processing and mixing techniques. Determination of the LiAlO_2 characteristics is being performed by means of S.E.M. analysis of particle morphology, X-ray and gravimetric analyses of phase compositions and B.E.T. surface area measurements. Evaluation of some of the more promising LiAlO_2 matrix structures will also be achieved by means of in-cell testing with diagnostic back-up.

Composition of Reaction Mixtures

This in situ procedure is being revised and optimized with respect to a standard final electrolyte composition: 55 w/o LiKCO_3 + 45 w/o LiAlO_2 . A standard reaction mixture composition has been correspondingly selected and contains the following molar ratio of reagents: 1.00 $\gamma\text{-Al}_2\text{O}_3$ + 1.33 Li_2CO_3 + 0.76 K_2CO_3 . The selection of this reagent composition was influenced by the following considerations:

- (1) A Li_2CO_3 -lean, or conversely a K_2CO_3 -rich, reaction

environment is believed to favor the formation of rod-like β - LiAlO_2 particles.

- (2) The Li_2CO_3 content in the initial reaction mixture should be sufficient to ensure that the binary carbonate mixture remains in the liquid state throughout the various thermal treatments.
- (3) Maximum melt content of the desired composition (hence maximum K_2CO_3 content) to facilitate high rates of reaction and LiAlO_2 recrystallization.

As the reaction between Li_2CO_3 and Al_2O_3 proceeds, the binary carbonate mixture becomes progressively rich in K_2CO_3 with a concomitant increase in melting point. It is known from gravimetric monitoring of various reaction mixtures that the reaction generally achieves 50% completion during the first 525°C thermal treatment and nearly 100% completion during the second thermal treatment - 650°C for 30 hrs. Figure (1.2.1) depicts the binary Li_2CO_3 - K_2CO_3 phase diagram. The points superimposed on the liquidus curve of Figure (1.2.1), from right to left, correspond to the carbonate compositions of the reaction mixture at start (64 m/o Li_2CO_3), after 50% reaction (52 m/o Li_2CO_3) and after reaction completion (30 m/o Li_2CO_3). It can be seen from the figure that the melting points of the carbonate compositions are always lower than the temperatures of the corresponding thermal treatments as indicated by the dashed lines.

Electrolyte Preparations

A continuing series of in situ electrolyte preparations, each designed to illustrate the effect of a particular process variable, has been initiated during the past interim. Table (1.2.1) summarizes the general details of the various electrolyte preparations completed during this period and the available results on the characteristics of the LiAlO_2 products. Further discussion of the various preparations is given below.

Figure 1.2.1

Li_2CO_3 - K_2CO_3 BINARY PHASE DIAGRAM INDICATING
CARBONATE COMPOSITION IN STANDARD REACTION
MIXTURE AFTER THERMAL TREATMENTS

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TABLE 1.2.1

CHARACTERISTICS OF VARIOUS IN SITU PREPARATIONS WHICH EMPLOYED DIFFERENT
REAGENT MIXING AND PROCESSING TECHNIQUES

Batch Code No.	Heat Treatment	Al ₂ O ₃ + LiAlO ₂ Conversion (%)	LiAlO ₂ Surface Area (m ² /g)	* LiAlO ₂ Phase Composition (%)		
				α	β	γ
IS-1	5hr. at 525°C in air	40	—	100	0	0
	30hr. at 650°C under CO ₂	95	—	80	20	0
	40hr. at 675°C under CO ₂	100	—	45	55	0
	Li ₂ CO ₃ addition; 15 hr. at 650°C under CO ₂	100	6.5	45	55	0
IS-2	13hr. at 525°C in air	55	—	100	0	0
	30hr. at 650°C under CO ₂	97	68.4	—	—	—
	40hr. at 675°C under CO ₂	100	13.8	72	—	—
IS-3 (a) + (b)	10hr. at 525°C in air	56	—	100	0	0
	30hr. at 650°C under CO ₂	98	63.2	—	—	—
IS-3 (a)	40hr. at 675°C under CO ₂	100	15.9	—	—	—
	Li ₂ CO ₃ addition; 15 hr. at 650°C under CO ₂	100	9.33	60	36	4
IS-3 (b)	40hr. at 650°C under CO ₂	100	44.6	—	—	—
	Li ₂ CO ₃ addition; 15 hr. at 650°C under CO ₂	100	—	76	23	1
IS-4	10hr. at 525°C in air	47	—	100	0	0
	30hr. at 650°C under CO ₂	100	—	81	1	18
	40hr. at 675°C under CO ₂	100	—	34	2	64
	Li ₂ CO ₃ addition; 15 hr. at 650°C under CO ₂	100	Not Yet Available	30	4	66
IS-5	10hr. at 525°C in air	57	—	100	0	0
	30hr. at 650°C under CO ₂	99	—	—	—	—
	40hr. at 675°C under CO ₂	100	—	—	—	—
	Li ₂ CO ₃ addition; 15 hr. at 650°C under CO ₂	100	Not Yet Available	23	—	—

*α-LiAlO₂ content determined by chemical analysis at E.R.C.

Approx. phase composition of (IS-1) determined by X-ray analysis using Debye Scherrer Patterns (+ 5% accuracy)

Phase compositions of (IS-3) and (IS-4) determined by X-ray analysis using intensity - scanning angle curves (+ 2.5% accuracy)

Preparation #IS-1

Electrolyte preparation (IS-1) was the first reaction batch to employ the aforementioned standard reagent composition ($1.00 \text{ Al}_2\text{O}_3 + 1.33 \text{ Li}_2\text{CO}_3 + 0.76 \text{ K}_2\text{CO}_3$): All subsequent preparations were also of this composition. A decrease in the temperature of the first thermal treatment, from 575°C to 525°C , was also introduced in this preparation and shall henceforth be adhered to. Carbonate powder preparation for this batch involved pre-fusion and manual pulverization of the resulting cast melt by means of mortar and pestil. Pulverization was continued until the carbonate powders were capable of passing a U. S. standard sieve size 100 (149μ). Carbonate powders $\leq 149\mu$ was somewhat arbitrarily established as a criterion for adequate reduction to facilitate intimate mixing with the alumina reagent. Finally, the reaction mixture was formed by thoroughly mixing the carbonate powders with the $\gamma\text{-Al}_2\text{O}_3$ reagent in a stainless steel twin-shell type blender manufactured by the Patterson-Kelley Co.

It is seen from the data in Table 1.2.1 for preparation (IS-1) that the first thermal treatment - 525°C for 5 hrs. - converted 40% of the Al_2O_3 to pure $\alpha\text{-LiAlO}_2$. The very broad diffuse X-ray diffraction lines obtained for this initial product implies an extremely small particle size. During the second heat treatment, at 650°C , additional $\alpha\text{-LiAlO}_2$ is formed simultaneous to the initial formation of $\beta\text{-LiAlO}_2$; a sharpening of the diffraction lines suggests an increase in particle size. The effect of the third heat treatment, at 675°C , was to decrease the $\alpha\text{-LiAlO}_2$ content and increase the $\beta\text{-LiAlO}_2$ content to yield an approximately equal mixture of these two allotropes. It may thus be concluded that $\alpha\text{-LiAlO}_2$ is recrystallizing to the β -crystalline form. The final heat treatment, which is performed after electrolyte adjustment by Li_2CO_3 addition, did not appear to alter the LiAlO_2 phase composition: The X-ray patterns

obtained for the products of the third and fourth heat treatments were virtually identical.

Regarding the characteristics of the final product obtained from preparation (IS-1), both the surface area and the yield of β -LiAlO₂ are undesirably low. There was, however, visual evidence of product contamination (yellow discoloration) and this may have had an influence on the final product.

S.E.M. micrographs of the washed LiAlO₂ products obtained after each thermal treatment of preparation (IS-1) are chronologically listed in Figures (1.2.2) through (1.2.5). It is seen from the micrographs that only after the third heat treatment - 675°C for 40 hrs. - are the desired rod-shaped particles of β -LiAlO₂ clearly present (Fig. [1.2.4]). The final product (Fig. [1.2.5]) is seen to be relatively rich in rod-shaped particles of approximately 2 μ in length by 0.5 μ in diameter, giving an aspect ratio of 4.

A sample of the initial reaction mixture from preparation (IS-1) was also sent out for D.T.A. and T.G.A. studies, the results of which are summarized below.

TGA + DTA RESULTS ON REACTION MIXTURE (IS-1)

Sample	Reaction mixture consisting of the following molar proportions 1.0 Al ₂ O ₃ + 1.33 Li ₂ CO ₃ + .76 K ₂ CO ₃
Results	Melts at 460°C complete at 485°C Yield = 81% at 800°C (final weight ÷ original weight) Weight loss begins at 335°C Maximum weight loss at 535°C Negligible weight loss by 800°C

The observed range of melting point is lower than the reported* range of 488 - 505°C for the same electrolyte composition. Similar

*Janz, G.J. and Lorenz, M.R., "Solid-Liquid Phase Equilibria for Mixtures of Lithium, Sodium and Potassium Carbonates", J. Chem. Eng. Data 6(3), 321-323 (1961).

5 μ

Figure 1.2.2: Electron Micrograph of a 40% α -LiAlO₂ + 60% Al₂O₃ mixture resulting from the initial 5hr. - 525°C firing of electrolyte preparation (IS-1).

5 μ

Figure 1.2.3: Electron Micrograph of an approx. 80% α -LiAlO₂ + 20% β -LiAlO₂ mixture resulting from the second firing - 650°C for 30hrs. - of electrolyte preparation (IS-1).

5μ

Figure 1.2.4: Electron Micrograph of an approx. 45% α -LiAlO₂ + 55% β -LiAlO₂ mixture resulting from the third firing - 675°C for 40hrs. - of electrolyte preparation (IS-1).

2μ

Figure 1.2.5: Electron Micrograph of an approx. 45% α -LiAlO₂ + 55% β -LiAlO₂ mixture obtained as final product of Preparation (IS-1).

lower melting temperatures have also been reported elsewhere.*

Initial weight losses at 335°C were probably due to loss of tightly bound water of adsorption. The presence of some moisture in the reaction mixture would also explain the observed higher than theoretical weight loss (theoretical yield = 86%). Partial carbonate decomposition could also have contributed to the observed weight loss.

Preparation #IS-2

The acquisition of a high purity alumina jar-mill provided an improved means of carbonate powder production for preparation (IS-2). Carbonate powder preparation for this batch involved pre-fusion followed by pulverization of the resulting cast melt by dry jar milling: In this way the possibility of SiO_2 contamination from the mortar and pestle was eliminated. Finally, the reaction mixture was formed by thoroughly mixing the carbonate powders with the Al_2O_3 in the aforementioned twin-shell type blender.

The criterion that the duration of the first thermal treatment is sufficient only when at least 45% of the $\text{Al}_2\text{O}_3 \rightarrow \alpha\text{-LiAlO}_2$ conversion occurs was also established for this preparation and shall be henceforth adhered to. The basis of this condition is the belief that the desired $\beta\text{-LiAlO}_2$ allotrope is a recrystallization product of fine particled $\alpha\text{-LiAlO}_2$: hence a final high yield of rod-like $\beta\text{-LiAlO}_2$ should depend upon an initial good yield of fine particled $\alpha\text{-LiAlO}_2$.

After exposure to the third heat treatment, it became apparent that reaction mixture (IS-2) was also contaminated. The material assumed so severe a yellow discoloration that the synthesis was terminated prior to the final firing. The high percentage of $\alpha\text{-LiAlO}_2$ (72%) still present in this mixture suggests a correlation between product contamination and poor yield of recrystallization products, however, lack of sufficient and controlled data precludes any conclusion regarding this phenomenon.

*"Fuel Cell Research on Second-Generation Molten-Carbonate Systems", Project 8984 Quarterly Status Report, prepared by the Institute of Gas Technology, Chicago, IL, for the Argonne National Laboratory, July-September, 1976.

Preparation #IS-3

Prior to preparation (IS-3), carbonate reagent processing had always involved fusion of the carbonate mixture followed by pulverization of the resulting cast melt. For this preparation, carbonate powder production was achieved by dry jar milling the unfused alkali carbonate mixture: mixing of the salts and comminution of the granular K_2CO_3 were accomplished in the mill simultaneously. The milled carbonate powders were then mixed with the Al_2O_3 in the twin-shell blender.

The effect of pre-fusion of the alkali carbonate mixture was evaluated by comparing the initial reactivity of preparation (IS-3) with former batches which differed only in that the carbonate mixture had been pre-fused (e.g. IS-2). The initial reactivity of a reaction mixture is conveniently determined by gravimetrically monitoring reaction progress during a first low temperature firing - $525^\circ C$ for 5hrs. The results supported the conclusion that pre-fusion of the alkali carbonate mixture does not enhance reagent reactivity. Thus, this superfluous step of carbonate pre-fusion shall be omitted from subsequent preparations.

After the second heat treatment, preparation (IS-3) was divided into roughly two equal portions, identified as (a) and (b) in Table (1.2.1). Portion IS-3 (a) was subjected to the usual third heat treatment - $675^\circ C$ for 40hrs. Portion IS-3 (b) was again fired at $650^\circ C$ for an additional 40hrs. Comparison of the final products from these two portions shed some light on the effect of the elevated $675^\circ C$ heat treatment on the final $LiAlO_2$ product. It should be mentioned that both portions of (IS-3) did assume a buff-discoloration which became most obvious during the final firing after Li_2CO_3 addition. In this case, however, the discoloration was considerably less severe than in (IS-2).

Comparison of the data in Table (1.2.1) for preparations IS-3 (a) and IS-3 (b) indicates that the effect of the high temperature (675°C) thermal treatment is to increase the $\alpha \rightarrow \beta$ phase transformation with a concomitant decrease in the surface area of the product. Although a high surface area product is generally desirable, a high surface area α -LiAlO₂ matrix is unlikely to be stable in a working fuel cell. Thus, the high temperature heat treatment shall be used for future preparations of this type.

The large surface area decrease (41%) shown in Table (1.2.1) for the product of preparation IS-3 (a) as a result of the relatively mild heat treatment after Li₂CO₃ addition (15hrs. at 650°C) is surprising. It seems that this must be related to the increased melt content and, or the change in melt composition resulting from the Li₂CO₃ addition. This also suggests that LiAlO₂ recrystallization is occurring via the liquid phase.

S.E.M. micrographs of the final LiAlO₂ products of preparations IS-3 (a) and IS-3 (b) are shown in Figures (1.2.6) and (1.2.7), respectively. The micrographs show that preparation IS-3 (a), which was subjected to the more energetic 675°C heat treatment, yielded a product with a relatively high content of well defined rod-shaped particles. On the other hand, preparation IS-3 (b), which experienced a maximum firing temperature of 650°C, yielded a product which contains only a small content of ill-defined rods which are evidently in a rudimentary state of development. Hence, it seems that the higher temperature heat treatment is necessary to induce both a greater degree of α -LiAlO₂ phase transformation and rod-like particle growth.

1883-1

2μ

7500X

Figure 1.2.6: Electron Micrograph of an approx. 60% α - + 36% β - + 4% γ -LiAlO₂ mixture obtained as final Product of Preparation IS-3 (a).

1882-9

2μ

7500X

Figure 1.2.7: Electron Micrograph of an approx. 76% α - + 23% β - + 1% γ -LiAlO₂ mixture obtained as final Product of Preparation IS-3 (b).

Preparation #IS-4

Previous attempts at dry milling of the carbonate reagents invariably led to the problem of the material packing to the jar wall. Materials packing, in turn, can result in inadequate and irreproducible particle reduction. To prevent this packing of the fines, carbonate powder production for preparation (IS-4) was achieved by wet jar-milling of the unfused carbonate mixture using absolute isopropanol as inert liquid. A preliminary test of alkali carbonate insolubility in isopropanol verified the suitability of this liquid. This wet milling technique gave satisfactory results: materials packing was prevented and particle reduction was adequate.

All the previously mentioned preparations (IS-1 - 3) were contaminated to varying degrees, as manifested by the buff to yellow discoloration of the final products. One of the possible sources of contamination is iron from the twin-shell type blender used for reagent mixing. To investigate this possibility, preparation (IS-4) was performed. In this case the carbonate powders and Al_2O_3 reagents were thoroughly mixed by means of dry jar milling. The jar milled powders were then subjected to the usual 3-stage thermal treatment. The final product obtained from this preparation, although it did contain a mere tinge of buff-discoloration, was much whiter in appearance than any of the former preparations. Hence, jar mill reagent mixing does apparently alleviate contamination problems. Furthermore, the initial reactivity of mixtures blended in this way was similar to that of those blended in the twin-shell device, indicating that jar mill blending produces a suitably intimate reaction mixture.

Table (1.2.1) indicates the phase compositions of the LiAlO_2 products of each thermal treatment for preparation (IS-4). It is seen that in this case the predominant α - LiAlO_2 recrystallization product is γ - LiAlO_2 . Even after the second

heat treatment an appreciable quantity of the γ -allotrope was present. The reason why the γ -allotrope was the preferred recrystallization product in preparation (IS-4) is not presently understood. An accidental over-temperature of the reaction furnace is one plausible explanation, however there is no evidence that this occurred.

S.E.M. micrographs of the LiAlO_2 products of the second, third, and final heat treatments of preparation (IS-4) are listed chronologically in Figures (1.2.8) through (1.2.10). The particles of $\gamma\text{-LiAlO}_2$ contained in the final product (Fig. 1.2.10) are seen to be quite small, generally submicronic in size, and hence, the surface area of this product should be relatively high. The results of B.E.T. measurements on this final product of (IS-4), however, are as yet unavailable.

Preparation #IS-5

While the use of a jar mill for initial reagent blending seems desirable to avoid product contamination (e.g., IS-4), a problem of the reaction mixture packing to the jar wall was encountered. Materials packing could result in inhomogeneous mixing of the powdered reagents with consequential loss in reactivity of the mixture. To overcome this problem, electrolyte preparation (IS-5) was initiated by mixing the powdered reagents ($\gamma\text{-Al}_2\text{O}_3$ + wet milled, unfused carbonate mixture) by wet jar milling with isopropanol as inert liquid. Although materials packing were in this way prevented, the relatively large volume of liquid required to keep the slurry sufficiently fluid would render this mixing technique expensive for larger scale production. Furthermore, the initial reactivity of preparation (IS-5) was similar to that of dry blended reaction mixtures, indicating that wet blending does not improve reagent intimacy. Hence, dry milling seems the preferred mode of reaction mixture preparation and other means of minimizing materials

1883-11 2μ

7500X

Figure 1.2.8: Electron Micrograph of an approx. 81% α - + 1% β - + 18% γ -LiAlO₂ mixture resulting from the second firing - 650°C for 30hrs. - of preparation (IS-4).

1883-13 2μ 7500X

Figure 1.2.9: Electron Micrograph of an approx. 34% α - + 2% β - + 64% γ -LiAlO₂ mixture resulting from the third firing - 675 C for 40hrs. - of preparation (IS-4).

1883-16 1μ 15000X

Figure 1.2.10: Electron Micrograph of an approx. 30% α - + 4% β - + 66% γ -LiAlO₂ mixture obtained as final product of preparation (IS-4).

packing shall be considered. For example, optimum milling time needs yet to be established. Humidity control might also have beneficial effects.

The α -LiAlO₂ content in the final product of preparation IS-5 (23%) was determined by a chemical analysis which is being developed at ERC. X-ray determination of the β/γ -ratio, however, has not been performed for this product, nor has surface area data yet become available.

1.2.2 Electrolyte Powder Preparation - Synthesis Method

Although efforts to tailor the in situ method of electrolyte preparation to yield a mixture of lithium aluminates with a good particle distribution for use as fuel cell matrix are in progress, the method suffers from the disadvantages of long preparation time and high sensitivity to changes in process parameters. A scheme involving separate syntheses of the various allotropic forms of lithium aluminate was introduced in the last Quarterly Progress Report. A method being developed at Argonne for producing pure rod-like β -LiAlO₂ was utilized. Also, attempts were made to synthesize a LiAlO₂ powder that may be mixed with the β -rods to give a retentive matrix structure. The requirements are a high specific surface area and a proper particle geometry for close packing in the interstices between the rods. From a thermal stability point of view, we selected γ -LiAlO₂, as mentioned in the last quarterly report. However, preparation of high surface area γ -LiAlO₂ is a difficult task which has not as yet been realized.

Stability of Rod-Like β -LiAlO₂

A synthesis for producing pure rod-like β -LiAlO₂, presently under development at Argonne, employs LiOH, KOH and γ -Al₂O₃ as reagents. This synthesis has been performed at E.R.C. to produce 55 w/o LiKCO₃ + 45 w/o β -LiAlO₂ composites. It has been confirmed by means of X-ray analysis and S.E.M. that the procedure does yield pure rod-like β -LiAlO₂. The dimensions of the particles obtained are typically 1.0 to 1.5 in length and 0.5 in diameter. During

this quarter, analytical results have been obtained on such β -rods that served as electrolyte matrix for a working fuel cell. The fuel cell was operated for approx. 1000 hrs. at 650°C with a 55 w/o LiKCO_3 + 45 w/o $\beta\text{-LiAlO}_2$ electrolyte tile composition (Cell Test #82). X-ray analysis of the used LiAlO_2 indicated a phase composition of approx. 90-95% $\beta\text{-LiAlO}_2$ + 5-10% $\alpha\text{-LiAlO}_2$: apparently some $\beta \rightarrow \alpha$ phase transformation occurred in the operating fuel cell. S.E.M. micrographs of the unused and used LiAlO_2 are shown in Figures (1.2.11) and (1.2.12). Comparison of the micrographs of the used and unused specimens reveals no obvious change in the rod-like morphology. Apparently, the rod-like geometry of $\beta\text{-LiAlO}_2$ particles is stable in the operating fuel cell environment.

Preparation of $\gamma\text{-LiAlO}_2$

As discussed in the Sixth Quarter Technical Progress Report E-3-6 (Section 2.4.3), a synthesis of $\gamma\text{-LiAlO}_2$ was fashioned after the work of F. Klein* and attempted. Analytical results have been obtained this quarter for the LiAlO_2 product of this preparation. X-ray diffraction analysis indicated the phase to be approx. 95% $\gamma\text{-LiAlO}_2$ with a balance of $\alpha\text{-LiAlO}_2$. An S.E.M. micrograph of the $\gamma\text{-LiAlO}_2$ product is shown in Figure (1.2.13). The micrograph (Fig. ([1.2.13])) depicts particle sizes ranging from approx. 0.3 to 2.0 μ . Several of the particles are clearly bipyramidal in shape.

A second attempt at synthesis of $\gamma\text{-LiAlO}_2$, the method of which was described in a 1974 Hungarian Patent**, was also discussed in the Sixth Quarter Technical Progress Report E-3-6 (Section 2.4.3). Briefly, the LiAlO_2 forming reaction was between LiOH and Al(OH)_3 in the presence of Li_2CO_3 + K_2CO_3 at 700°C. Although the authors

*Klein, F., "Les piles a gaz de haute temperature: electrolyte de carbonates alcalins fondus," Part 1, Ph.D. Thesis, University of Nancy, France, 1971.

**Sooki-Toth, G. et al, "Method for the One-Step Production of the γ -Lithium-Metaaluminate Support and Cast Electrolyte of High-Temperature Fuel Elements", Hungarian Utility Patent Application 167 545, March 21, 1974.

2μ

Figure (1.2.11) Electron Micrograph of unused β -LiAlO₂ prepared by reaction of LiOH + KOH + Al₂O₃.

1μ

Figure (1.2.12) Electron Micrograph of β -LiAlO₂ after use as matrix in fuel cell (1000 hrs. at 650°C).

1μ

Figure (1.2.13): Electron Micrograph of γ -LiAlO₂
prepared by heat treating Li₂CO₃ + γ -Al₂O₃ at
700°C and 920°C.

of the patented process reported an exclusive yield of γ -LiAlO₂, X-ray analysis of the product obtained by this procedure indicated the phase to be predominantly β -LiAlO₂ ($\approx$ 95%), with traces of the α - and γ -allotropes present. An S.E.M. micrograph depicting particle morphology of this β -LiAlO₂ is shown in Figure (1.2.14). The particle shape of this β -LiAlO₂ product (Fig. 1.2.14) might be described as very squat rods. The particle size is quite large, approximately 6 μ in length by 3.5 μ in diameter. Some clump-like particles are also evident in the micrograph, probably corresponding to the α -allotrope which often assumes this morphology. A B.E.T. surface area determination on this LiAlO₂ indicated a low surface area of 3.5 m²/g.

Preparation of α -LiAlO₂: (Prep. #G₄-1)

Investigation of new methods of preparing LiAlO₂ with desirable characteristics for use as fuel cell matrix components has continued during this period. In particular, a solid-state reaction between γ -Al₂O₃ (Degussa-C) and excess Li₂CO₃ (reagent grade powder) was performed under a partial pressure of CO₂ at 600°C. The formulation of the reaction mixture, 1.0m Al₂O₃ + 1.76m Li₂CO₃, was chosen to provide enough excess Li₂CO₃ for the electrolyte of an eventual 55 w/o LiKCO₃ composite. The progress of the Al₂O₃ $\rightarrow$ LiAlO₂ conversion was monitored gravimetrically. The reaction reached 90% completion during the first 5 hrs., but a total of 60 hrs. at 600°C were required before 100% theoretical weight loss was observed. With the powdery product obtained was blended the desired K₂CO₃ content, and the final mixture was thermally homogenized by heating under CO₂ at 600°C for 16 hrs.

X-ray analysis of the LiAlO₂ product of this procedure indicated pure α -LiAlO₂. An S.E.M. micrograph showing particle morphology of this α -LiAlO₂ is presented in Fig. (1.2.15). The particles appear as rather large clump-like aggregates. The high B.E.T. surface area observed for this product, 58.2 m²/g, suggests that the aggregates are composed of very small primary particles

5 μ

Figure (1.2.14): Electron Micrograph of β -LiAlO₂ (95%) prepared from LiOH + Al(OH)₃ in the presence of LiKCO₃ at 700°C.

| 2 μ |

Figure (1.2.15) Electron Micrograph of α -LiAlO₂
prepared from γ -Al₂O₃ + Li₂CO₃ at 600°C.

of α -LiAlO₂. Although the criterion of a high surface area is met, this product might undergo recrystallization in the operating fuel cell.

1.3 Electrolyte Tiles

1.3.1 Small Tile Manufacturing Procedures

During this period, we have incorporated a process improvement for the 1.5" dia. electrolyte tiles. We started to use specially constructed insulating mold panels and changed the heating and cooling procedures. These changes eliminated failures due to cracks and extrusion of the electrolyte. At the same time, we have introduced a mold spacer that makes it possible to control the tile thickness within $\pm 1\%$.

1.3.2 7" x 7" Kanthal Fiber Reinforced Tiles

Our main objective in the area of large tiles was the development of manufacturing methods for Kanthal reinforced electrolyte tiles. Some problems were encountered in obtaining uniform distribution of random reinforcement with low wire content, especially for larger diameter wires. This difficulty lead to cracks and/or large thickness variations. A summary of the tiles manufactured with different diameters, lengths and loadings of reinforcement is given in Table 1.3.1. Recently a tile was obtained (No. H-52) using 0.005" diameter Kanthal wires with a low loading of 2.5%. However, as seen from Table 1.3.1 it still needs improvement to achieve uniform thickness. A few tiles were also made using a woven screen of the Kanthal fibers as shown in Table 1.3.1. We found that a tile reinforced with woven screen is easier to manufacture compared to that with random reinforcement.

1.3.3 Hydrogen Permeability of the Electrolyte Tiles

We are developing a method to measure the tile permeability at ambient temperatures. The permeability was calculated as the flow rate of hydrogen through a unit area of a tile of unit thickness

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1.3.1. Kanthal Reinforced Electrolyte Tiles

Experiment No	Kanthal Alloy	Reinforcement		Weight %	Tile Density g/cm ³	Remarks
		Diameter inches	Length inches			
G-64	D	.00175	.125/.250	2.50	2.39	OK
G-77	D	.00175	.125/.250	2.90	2.30	Remanent Tension Cracks
G-78	D	.00175	.125/.250	4.00	2.34	Tested in Cell 7-10
H-14	D	.00175	5/6	6.90	2.23	OK
H-23	D	.00175	.125/.250	2.50	2.30	OK
H-24	D	.00175	.125/.250	2.50	2.29	Tested in Cell 7-15
H-25	D	.0089	.125/.250	2.50	2.32	Blisters; Cracks
H-27	D	.0089	.125/.250	5.00	2.37	Broken Corner
H-30	D	.0089	.125/.250	10.00	2.50	Tested in Cell 7-16
H-32	A-1	.0063	.125/.250	15.00	2.57	Bend Tile
H-33	A-1	.0063	.125/.250	20.00	2.66	Bend Tile
H-36	A-1	.0063	.125/.250	7.50	2.58	OK
H-37	A-1	.0063	.125/.250	5.00	2.50	Non Uniform Reinforcement Distribution
H-38	A-1	.0063	.125/.250	5.00	2.65	Broken Corner
H-39	A-1	.0063	.250/.750	5.00	2.36	Unsintered Corners & Edges
H-40	A-1	.0063	.250/.750	5.00	2.44	Large Thickness Variations
H-42	A-1	.0063	.250/.750	7.50	2.47	OK
H-43	A	.005	Screen (20 x 20)	2.3	2.46	Tested in Cell 7-18
H-47	A-1	.005	.250/.500	2.5	2.23	Broken Corner
H-48	A-1	.005	.250/.500	2.5	—	Thermocouple Malfunction Electrolyte Extruded
H-49	A-1	.005	.250/.500	2.5	2.20	Cracks
H-50	A-1	.005	Screen (20 x 20)	2.8	2.33	Cracks
H-51	A-1	.005	Screen (20 x 20)	2.60	2.33	OK
H-52	A-1	.005	.250/.500	2.5	2.32	OK - Thickness variations

for a unit pressure drop.

$$P = \frac{V \cdot \delta}{AT(\Delta P)}, \text{ where,}$$

P - Permeability, $\frac{\text{cm}^4}{\text{kg} \cdot \text{sec.}}$

δ - Tile Thickness, cm

A - Area, cm^2

T - Time, sec.

V - Gas Volume, cm^3

(ΔP) - Pressure Drop, $\frac{\text{kg}}{\text{cm}^2}$

In Table 1.3.2 some representative results obtained to date are presented. To interpret the results, more data will be accumulated and will be correlated with the tile density. The method is being developed as a quality control technique in tile manufacture.

1.3.4 Higher Rate Tile Production

With the aim of developing methods suitable for a high rate production of electrolyte tiles, we have designed an experimental mold that will substantially reduce the press time. The new mold was tested in experiments H-44 and H-45. A few constructive details different from our first mold were verified. We have ordered parts and materials for the heating and insulating attachments. The complete assembly will be finished and tested in the following months.

1.3.5 15" x 15" Tile Manufacturing

A mold for 15" x 15" electrolyte tile has been designed. It is basically a scale-up of the 7" x 7" electrolyte tile mold with minor changes. Material for the mold has been received and will be machined and tested in the next quarter. For the same task, a 750 ton press has been acquired and will also be installed in the next quarter.

TABLE 1.3.2

HYDROGEN PERMEABILITY OF THE ELECTROLYTE TILES

TILE	ELECTROLYTE	DENSITY	PERMEABILITY
NO.	BATCH NO.	g/cm ³	$\frac{\text{cm}^4}{\text{kg. sec.} \times 10^4}$
H-03	B-103	2.268	2.02
H-15	B-104	2.301	0.95
H-19	B-104	2.334	0.90
H-22	B-105	2.417	0.64
H-20	B-105	2.386	4.14
H-28	B-106	2.290	0.78
H-29	B-107	2.366	1.35
H-31	B-107	2.368	3.81

1.4 Cell Frame and Current Collector

During this period, equipment has been assembled to conduct potentiostatic corrosion tests on small samples of test materials for the current collector and gas seal areas. The apparatus is described elsewhere* and involves the use of a gold/ CO_2 - O_2 (2:1) reference electrode and a potentiostat to measure corrosion currents, and to observe corrosion rates at fixed potentials under controlled gas atmospheres. Past experience with this type of equipment indicates that good predictions of corrosion rates in the fuel cell environment can be obtained.

For gas seal applications the most desirable composition is probably a stainless steel of the 300 or 400 series containing 5 to 10% aluminum in the surface layer. The Kanthal alloys have a similar composition, but the high bulk aluminum content gives rise to undesirable mechanical properties and hardware fabrication difficulties. Kanthal is nevertheless well suited for other applications such as tile reinforcement.

It was observed that diffusion of aluminum into type 316 stainless steel caused it to become ferromagnetic at room temperature. This is a strong indication that a fundamental structural change has occurred, and that surface diffusion is more than superficial.

Several other types of stainless steel have been coated with a 0.002 inch thick layer of aluminum by means of the wire metallizing technique and heat-treated at 1000°C in a reducing atmosphere to diffuse the aluminum into the surface. A subsequent heat treatment in air is carried out to burn off any excess aluminum. This is followed by a clean up with fine abrasive to remove loose particles.

Of special interest are types 446 and E-Brite 26-1 stainless steels because of their high chromium content. After treatment their surface compositions would be similar to that of the Kanthal alloys. These materials are being evaluated.

A search for a more suitable cathode current collector will be

*H. J. Davis and D. R. Kinnibrugh, J. Electrochem. Soc., 117, 394, (1970).

initiated. In this case, the surface protection must be based on an electrically conducting oxide, preferably nickel oxide, and aluminum should be absent. A number of materials will be evaluated with the new potentiostatic corrosion equipment.

TASK 2.   CELL TESTING: J. Yasi, P. Patel and D. Dharja

In the last quarter, different forms of lithium aluminate were compared with respect to their electrolyte retention characteristics. During the present quarter, the study was continued to further evaluate the effect of the lithium aluminate structure on the cell performance. Other work in small cell testing was aimed at improving the anode and cathode structures, the wet seal including good corrosion protection, and cell hardware design.

Large cell tests were focused on thermal cycling of Kanthal fiber reinforced tiles. The characterization of various factors affecting the cell performance such as cross-leakage, electrode flooding in terms of O_2 - CO_2 gain* at the cathode, and wet seal efficiency was continued. Periodic measurements of the $LiAlO_2$ matrix integrity in terms of bubble pressure were also initiated.

2.1 Small Cell Testing

Various components tested include a teflon rolled cathode reinforced with nickel screen, two anodes with mean pore size lower than that of standard anode, and electrolyte tiles with different $LiAlO_2$ structures and electrolyte compositions. A summary of these tests is presented in Tables 2.1.1 and 2.1.2. A detailed discussion and evaluation of the test results is given below.

2.1.1 Comparison of Anode Structures

The influence of the anode structure on cell performance was explored by testing two anodes with average pore sizes of 7.3 and 6.0 microns manufactured by the Union Carbide Corporation and the Gould Inc., respectively. Both the tests were carried out with tiles cut from the same large tile, the cathode having a 12 micron

* O_2 - CO_2 gain (or oxygen-gain) is defined as a gain in cell potential due to a change in oxidant composition from standard air- CO_2 to a noble O_2 - CO_2 mixture, keeping fuel composition and flow unchanged.

TABLE 2.1.1
DETAILS OF SMALL CELL TESTING

CELL NO.	ELECTRODES						ELECTROLYTE			Purpose of Cell Test ^a
	Thickness In.	Anode Mean Pore Size μ m	% Porosity	Thickness In.	Cathode Mean Pore Size μ m	% Porosity	Composition	Tile Density ¹ gm/cc	Tile Thickness (mils)	
91	0.026	7.3	73	0.022	12	80	60 wt. % Liq. (62/38 mol. % $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) 40 wt. % Solid LiAlO_2	2.31	64	75% of LiAlO_2 mfg. by Method III 25% of LiAlO_2 mfg. by Method I
92	0.022	12	80	0.022	12	80	55 wt. % Liq. (50/50 mol. % $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) 45 wt. % Solid LiAlO_2	2.34	105	75% of LiAlO_2 mfg. by Method III 25% of LiAlO_2 mfg. by Method IVA
93	0.022	12	80	0.013	—	54	"	2.40	107	Teflon rolled cathode pressed on a 80 x 80 mesh nickel screen
95	0.022	12	80	0.022	12	80	"	2.36	101	75% of LiAlO_2 mfg. by Method III 25% of LiAlO_2 mfg. by Method IVB
98	0.0026	7.3	73	0.022	12	80	"	2.41	98	LiAlO_2 prepared by in situ method, (Batch No. 1S-1) Different anode pore structure ²
99	0.019	6	72	0.022	12	80	"	2.39	79	Smaller protrusion
100	0.026	7.3	73	0.022	12	80	"	2.39	80	Anode flange coated with aluminum
101	0.026	7.3	73	0.022	12	80	"	2.30	101	LiAlO_2 mixture: 75% by Method III, 25% by Method IVD, (Batch G ₄ -1)
102	0.020	4.8	71	0.022	12	80	"	2.30	106	Anode flange having diffusion bonded aluminum coating
103	0.027	7.3	73	0.022	12	80	60 wt. % Liq. (50/50 mol. % $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) 40 wt. % Solid LiAlO_2	2.28	98	LiAlO_2 structure same as Cell 101 but with increased carbonate content from 55 wt. % to 60 wt. %
104	0.020	4.8	71	0.026	7.3	75	55 wt. % Liq. (50/50 mol. % $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) 45 wt. % Solid LiAlO_2	2.42	75	Different ratio of anode to cathode mean pore sizes

*NOTE: Method I is the standard method (in situ method)
Method III involves use of alkali hydroxides as the reagents for synthesis of β - LiAlO_2
Method IVA involves a high temperature synthesis of γ - LiAlO_2 (1000-920°C) from Li_2CO_3 & Al_2O_3
Method IVB involves LiAlO_2 synthesis from LiOH & $\text{Al}(\text{OH})_3$ + (Li_2CO_3 & K_2CO_3) at 700°C (page 21).
The method yielded β - LiAlO_2 instead of γ - LiAlO_2
Method IVD is a synthesis of α - LiAlO_2

1. Experimentally measured density
2. Anode mfg. by Gould, Inc.

TABLE 2.1.2
SUMMARY OF PERFORMANCE OF SMALL CELLS

Cell No.	Endurance Hours	IR-Corrected Voltage at 94 mA/cm ² (0.8A), Volts	Cell Resistance mohms	Wet Seal Efficiency Exit Gas Flows as % of Inlet		Comments
				Anode	Cathode	
91	170	0.71	47	92	98	Cathode appeared to be flooded as expected from low α -LiAlO ₂ content.
	400	0.86	128	90	97	
	570	0.77	85	87	96	
	735	0.52	179	87	98	
92	140	0.63	62	87	102	Mixture of β and γ LiAlO ₂ gave poor electrolyte retention characteristics due to low surface area of both the allotropes. Hence high O ₂ -CO ₂ gains, electrolyte creepage and anode frame corrosion were observed.
	400	0.76	46	90	96	
	675	0.52	149	95	100	
93	160	0.78	85	83	91	The teflon rolled cathode was found structurally intact at the end of the test, indicating a good future for such a structure.
	330	0.76	107	75	90	
	450	0.59*	158	68	91	
95	145	0.801	76	98	100	Like Cell 92, this cell displayed poor electrolyte retention characteristics.
	220	0.756	83	69	98	
	360	0.80	105	67	98	
	460	0.61*	234	69	101	
98	113	0.58	135	98	94	High O ₂ -CO ₂ gains were observed which explains the lower performance of the cell.
	258	0.54	158	94	98	
	412	0.73	150	91	93	
	502	0.66	204	88	91	
99	38	0.96	141	84	99	Performance dropped initially and then stabilized.
	137	0.81	149	87	95	
	303	0.81	132	91	97	
	482	0.83	172	88	90	
	561	0.78	153	80	93	
	611	0.74	193	75	70	
100	72	0.75	148	86	98	Aluminum coated anode flange was found to be well protected on terminating the test.
	191	0.74	146	94	95	
	338	0.68	131	97	98	
	403	0.68	201	96	90	
101	34	0.88	82	71	96	As expected, mixture of β and α LiAlO ₂ gave better performance due to improved electrolyte retention characteristics, imparted by high surface area α -LiAlO ₂ .
	111	0.91	115	70	90	
	185	0.96	113	92	95	
	303	0.95	144	86	97	
	414	0.89	152	83	96	
102	46	0.90	115	82	98	Low density tile (89% of theoretical) cross leaked very early.
	50	0.85	173	82	98	
	131	0.69	155	83	97	
103	34	0.89	68	90	95	Increase in electrolyte content from 55 to 60 wt. % improved the wet seal efficiencies compared to Cell 101.
	161	0.84	60	92	96	
	209	0.85	56	92	97	
	358	0.89	75	-	-	
	405	0.91	69	100	93	
	538	0.87	60	80	95	
104	121	0.69	76	85	90	Cell performance improved with the cell life and stabilized. This may be due to periodic addition of electrolyte. Test is continuing.
	226	0.74	52	97	100	
	461	0.77	48	87	97	
	704	0.77	44	94	99	

*IR corrected voltage at 58 mA/cm²

mean pore size (Cell 99 and 100).

The cell with the 7.3 micron anode displayed 125 mV of O_2 - CO_2 gain at a current density of 117 mA/cm². O_2 - CO_2 gain reduced to 75 mV when the anode was changed to 6.0 micron pore size indicating that lowering of anode pore size improved electrolyte distribution between the two electrodes.

2.1.2 Testing of a Teflon Rolled Cathode

Test results from Cell 69 indicated that the teflon rolled structure is mechanically weak. A new teflon rolled electrode was made by pressing it on a 80 x 80 mesh nickel screen and was endurance tested in Cell 93. The cathode structure at the end of the test was rigid and it developed a strong bond with the tile indicating a good potential for teflon rolled cathode structures. The O_2 - CO_2 gain at peak performance and 117 mA/cm² was 70 mV. However, the cell displayed lower performance, which may be due to loss in OCV resulted from cross-leak. The testing of Cell 93 was discontinued after 400 hours because accidental misalignment of anode and cathode frames resulted in poor wet seal efficiencies.

2.1.3 Lithium Aluminate Structure

Some effects of the particle size and the composition of various allotropes, α , β and γ of lithium aluminate on electrolyte retention characteristics and cell performance were discussed in the Sixth Quarter Technical Progress Report. A scheme employed for the qualitative evaluation of various structures consisted of the performance parameters such as polarization characteristics, O_2 - CO_2 gain, cell life, performance stability, wet seal efficiency, electrolyte creepage, corrosion, gas cross-leak and the structural parameters of the electrodes and the electrolyte.

Results of various tests carried out to study $LiAlO_2$ structure are summarized in Table 2.1.3.

TABLE 2.1.3
COMPARISON OF VARIOUS LITHIUM ALUMINATE STRUCTURES

Cell No.	ELECTROLYTE TILE					PEAK PERFORMANCE ³		Cell Life* Hours
	LITHIUM ALUMINATE				Electrolyte Composition	IR-Corrected Voltage Volts	O ₂ /CO ₂ Gain mV	
	%α-LiAlO ₂	%β-LiAlO ₂	%γ-LiAlO ₂	Method Of Manufacture ²				
67	minor	major	traces	Method I	Std. ¹	0.93	70	676
81	minor	>90	traces	75% by Method III 25% by Method I	Std.	0.91	95	383
82	traces	100	traces	Method III	Std.	0.85	100	530
91	minor	>90	traces	75% by Method III 25% by Method I	60 wt.% Liq. (62/38 mole % Li ₂ CO ₃ /K ₂ CO ₃) 40 wt.% Solid LiAlO ₂	0.77	120	572
92	traces	75	25	75% by Method III 25% by Method IVA	Std.	0.75	115	555
95	traces	100	traces	75% by Method III 25% by Method IVB	Std.	0.81	105	358
101	25	75	traces	75% by Method III 25% by Method IVD	Std.	0.91	65	421
103	25	75	traces	75% by Method III 25% by Method IVD	60 wt.% Liq. (50/50 mole % Li ₂ CO ₃ /K ₂ CO ₃) 40 wt.% Solid LiAlO ₂	0.85	95	700
104	45	**	**	Method I	Std.	0.77	105	750
test continuing								

test continuing

*Time until performance was greater than 0.55 V at 117 mA/cm²

**Balance components are β and γ -LiAlO₂

1. Std. electrolyte composition is 55 wt.% Liq. (50/50 mol % Li₂CO₃/K₂CO₃)
45 wt.% Solid LiAlO₂

2. See footnote of Table 2.1.1

3. At 94 mA/cm²

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The LiAlO_2 structures studied may be broadly classified into the following groups.

Group - I:	Major Component:	$\beta\text{-LiAlO}_2$
	Minor Component:	$\gamma\text{-LiAlO}_2$
	Traces:	$\alpha\text{-LiAlO}_2$
Group - II:	Major Component:	$\beta\text{-LiAlO}_2$
	Traces:	α & $\gamma\text{-LiAlO}_2$
Group - III:	Major Component:	$\beta\text{-LiAlO}_2$
	Minor Component:	$\alpha\text{-LiAlO}_2$
	Traces:	$\gamma\text{-LiAlO}_2$

Cells from Group - I and II (Cells 82, 92 & 95) exhibited lower performance, shorter life, relatively higher creepage of electrolyte and $\text{O}_2\text{-CO}_2$ gain. Both β & $\gamma\text{-LiAlO}_2$ forms have a low surface area and hence contributed to the lowering of the electrolyte retention. Cells in Group - III exhibited better performance. This may be due to increase in surface area of the lithium aluminate matrix.

Cell 101 (Group - III) displayed an average and steady performance. However, the anode wet seal efficiency was low, which may be explained by improved electrolyte retention characteristics (25% high surface area $\alpha\text{-LiAlO}_2$) leading to less electrolyte availability for sealing. Based on this reasoning, a cell with similar lithium aluminates and with increased carbonate content (Cell 103) was tested. Cell 103 exhibited an improved anode wet seal efficiency and a steady performance confirming the above concept. However, increased carbonate content also resulted in a small drop in performance for which an explanation has yet to be found. Both Cells 101 and 103 exhibited an average performance supporting an important concept, suggested by ERC in the last report, namely that instead of using the in situ method, separate synthesis of the desirable forms of lithium aluminate should be evaluated. To achieve a thermally stable lithium aluminate matrix, efforts are necessary to develop a high surface area $\gamma\text{-LiAlO}_2$ synthesis

procedure as discussed in Section 1.2.

2.1.4 Corrosion Study

A systematic study has been initiated to evaluate the corrosion of the wet seal areas. The performance of various forms of sealing material is presented in Table 2.1.4. The degree of protection was qualitatively determined by cell endurance and visual observations of fuel and oxidant seal corrosion during post-test analyses. Aluminum gaskets, aluminum spray coatings and a diffusion bonded aluminum spray coating were tested. Preliminary results show that the diffusion bonded aluminum coating appears to be satisfactory in protection of wet seal against corrosion.

2.1.5 Cross Leak Measurement

The entrance and exit gas compositions of the cells were analyzed with a gas chromatograph to measure cross leak between the fuel and oxidant chambers. The scheme used to characterize cross-leak, analyzes for nitrogen at the anode exit stream to detect a cross-leak from cathode to anode. To detect a cross-leak from anode to cathode, an O_2 - CO_2 gas mixture is supplied at the cathode and a nitrogen diluted gas mixture is supplied at the anode. The amount of nitrogen at the cathode exit is the measure of cross-leak from anode to cathode.

Chromatographic measurements revealed a relationship between tile density and cross-leak. Cell 102 used a low density electrolyte tile (@ 89% of theoretical density). The cell was found to be severely cross-leaking. In general, the cells with more dense tiles had relatively smaller or no cross-leak. Efforts are now being made to arrive at an optimum tile density.

The effect of sealing pressure on cross-leaking and on the wet seal efficiency was studied. The results are shown in Table 2.1.5. The presence of nitrogen in the anode exit gas stream

TABLE 2.1.4

CORROSION STUDY

CELL NO.	WT. & LIQ. IN TILE	TYPE OF SEAL AND ITS THICKNESS MILS		ENDURANCE TIME @ 650°C (HRS)	MAX. SEALING PRESSURE USED PSIG	PROTECTION OFFERED TO THE WET SEAL AGAINST CORROSION*	
		ANODE	CATHODE			ANODE	CATHODE
98	55	Al gasket 2 mils	Al gasket 1 mil	1300	67.6	Good	Good
99	55	Al gasket 2 mils	Al gasket 1 mil	680	51.6	Poor	Good
100	55	Aluminum Spray Coating 2 mils	Al Gasket 1 mil	410	53.3	Fair	Good
101	55	Al gasket 1 mil	Al gasket 1 mil	560	53.8	Poor	Fair
102	55	Diffusion bonded aluminum coating 2 mils	Al gasket 1 mil	500	69.4	Good	Good
7-16	55	Al gasket 2 mils	Al gasket 1 mil	660	15.4	Fair	Good

* Criteria Used

Good: Both edges of sealing-lips of the frame unaffected, good wet seal efficiencies

Fair: One of the edges suffered corrosion, moderate wet seal efficiencies

Poor: Severe corrosion of the edges & bad wet seal efficiencies

TABLE 2.1.5

EFFECT OF SEALING PRESSURE
ON CROSS LEAK AND WET SEAL EFFICIENCIES

CELL NO.	CELL LIFE, HOURS	SEALING PRESSURE, Psig	CROSS LEAK, (from Cathode to Anode) % N ₂ in anode, (Dry Basis)	WET SEAL EFFICIENCY %	
				ANODE	CATHODE
99	208	20	2.40	66.6	95.2
	212	32	0.90	86.0	92.3
	398	45	0.29	92.0	83.0
100	50	12	4.40	82.1	97.7
	55	14	2.70	86.2	97.6
	248	36	0.53	88.0	96.4
101	16	9	3.20	84.5	94.6
	20	12	0.40	76.9	96.3
	214	29	0.19	80	94.5

reported in the table, indicates a leak from cathode to anode. It is seen from the table that the increase in pressure resulted in a large decrease in cross-leak and also improved wet seal efficiencies.

2.1.6 Electrolyte Addition

Cells 98, 99 and 100 were used for electrolyte addition. No corrosion was observed on the current collectors or the frames due to added electrolyte. However, no significant improvement was found. This may be due to relatively low density of the electrolyte tile or because the electrolyte was added too late. The concept was confirmed by earlier electrolyte addition in Cell 104. Electrolyte was added at 300 and 600 hours. We think that electrolyte additions helped to maintain a steady performance for the 750 hours observed so far (Figure 2.1.1).

2.1.7 Test Stand Improvements

Modifications were made to the test stand design to improve the alignment and centering of the small cells.

Cell 104 has an improved CO₂ distributor to give better protection to cell components. Results on corrosion and wet seal efficiency will be reported after post-test analysis.

A ceramic ring was placed around the electrolyte disc in Cell 99 and 101 to shield the cell from direct heat radiation. At the end of the test, the ring was found to be stuck to the edge of the tile. Future tests will be made with a larger ring.

2.2 Large Cell Testing

Work in large cell testing during the present quarter included a study of the thermal cycling capability of Kanthal fiber reinforced tiles. A tile containing 62/38 Li/K mole ratio with 60% liquid content was also tested to compare its performance with the tile having 50/50 mole ratio of Li/K and 55 wt. % liquid, with which the majority of testing has been performed. Details of these tests are given in Table 2.2.1 and the performance is summarized in Table 2.2.2.

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

FIGURE 2.1.1 ENDURANCE TESTING - CELL 104

TABLE 2.2.1

DETAILS OF LARGE CELL TESTING

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CELL NO.	ELECTRODES						ELECTROLYTE			Purpose of Cell Test
	Anode			Cathode			Composition	Tile Density gm/cc	Tile Thickness (mils)	
	Thickness In.	Mean Pore Size μm	% Porosity	Thickness In.	Mean Pore Size μm	% Porosity				
7-15	0.026	7.3	73	0.022	12	80	60 wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 40 wt. % Solid LiAlO ₂	2.29	105	Electrolyte tile reinforced with Kanthal-D fibers 1.75 mil dia. 2.5 wt. % of tile, 1/8-1/4" length
7-16	0.026	7.3	73	0.022	12	80	55 wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.50	106	Electrolyte tile reinforced with Kanthal-D fibers 8.9 mil dia. 8.0 wt. % of tile, 1/8-1/4" length
7-17	0.027	7.3	73	0.023	12	80	60 wt. % Liq. (62/38 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 40 wt. % LiFAlO ₂	2.31	83	62/38 mol. ratio of Li/K
7-18	0.020	5	71	0.026	7.3	73	55 wt. % Liq. (50/50 mole % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.46	89	Electrolyte tile reinforced with a screen woven (20 x 20) from 0.005" dia. Kanthal wires

TABLE 2.2.2

PERFORMANCE OF LARGE CELLS

CELL NO.	ENDURANCE HOURS	IR-CORRECTED VOLTAGE AT 92 mA/cm ² volts	RESISTANCE mohms	WET SEAL EFFICIENCY EXIT GAS FLOWS AS % OF INLET		COMMENTS
				ANODE	CATHODE	
7-15	88	0.84	1.0	91	98	Before 1st recycle
	260	0.80	2.0	88	93	Before 2nd recycle
	330	0.79	3.0	87	93	After 2nd recycle
7-16	90	0.62	5.6	86	100	
	140	0.77	6.0	85	97	Before 1st recycle
	310	0.56	8.0	75	101	After 1st recycle
7-17	116	0.78	1.5	90	102	Cell exhibited high
	252	0.78	1.7	96	99	O ₂ -CO ₂ gain, however,
	544	0.80	1.9	92	101	performance was stable.
	722	0.79	1.6	90	100	Test continuing
	987	0.77	1.3	93	100	
	1302	0.81	1.5	84	99	
7-18	143	0.90	2.6	86	82	Test continuing
	167	0.91	2.6	86	82	
	285	0.91	2.8	84	82	
	306	0.85	2.9	84	82	Before 1st recycle
	386	0.90	3.0	78	81	After 1st recycle

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2.2.1 Thermal Recycling

Effect of thickness of Kanthal fiber reinforcement on thermal cycling was studied for two Cells, 7-15 and 7-16, having a random fiber orientation. At present, a cell with reinforced Kanthal screen (7-18) is under test. The performance details for the Cells 7-15 and 7-16 are given below.

The Cell 7-15 was thermally cycled twice as shown in Table 2.2.2. A small drop in wet seal efficiency and an increase in cell resistance were observed during this period. This cell, with 60% electrolyte in the tile exhibited a very low resistance as seen from Table 2.2.2. When it was recycled a 3rd time, it developed a cross-leak and the test was terminated. A life-graph is shown in Figure 2.2.1. On termination, Kanthal fibers were found corroded as observed in Cell 7-10 indicating that Kanthal D should be replaced with fibers having a higher aluminum content such as Kanthal A-1.

The Cell 7-16, with 55 wt. % liquid and an electrolyte tile reinforced with much larger diameter Kanthal fibers, dropped in performance after the first thermal cycle. The anode wet seal efficiency was low while the cathode wet seal efficiency was almost 100%. The cell developed a cross-leak after 500 hours and the test was terminated. Post-test studies showed a large amount of electrolyte creepage and corrosion in both anode and cathode compartments. This suggests that a large amount (9 wt. %) of Kanthal fiber reinforcement of large diameter (8.9 mil) decreases the electrolyte retention characteristics. For further testing we have selected 5 mil diameter Kanthal fibers. Also the random orientation of these fibers not only limits the uniform mixing of the fibers with the powder but also decreases wet seal efficiency. Therefore a test has been started with a woven screen of Kanthal fibers (Cell 7-18). A detailed comparison of these tests will be reported next quarter.

FIGURE 2.2.1 ENDURANCE TESTING - CELL 7-15

2.2.2 Effect of Electrolyte Composition

Cell 7-17 was put on test with a tile having 60 wt. % liquid (62-38 mole % Li_2CO_3 - K_2CO_3) and 40 wt. % solid lithium aluminate manufactured by the in situ method. The cell performance was stable as shown in Figure 2.2.2 up to 1300 hours. The effect of fuel and oxidant utilizations on the cell performance at a cell life of 815 hours is presented in Table 2.2.3. For the noble gas mixture at the cathode with 50% conversion, increase in fuel conversion from 50% to 75% results in a voltage decrease of 25 mV at 184 mA/cm². A constant utilization performance curve with air-CO₂ at cathode is presented in Section 4.1 of this report.

As mentioned in our earlier report, in order to evaluate the cell components, a breakdown of cell overpotentials is necessary. In the absence of a reference electrode, oxygen-gain at the cathode is used as an indicator of cathode polarization. Figure 2.2.3 shows cathode polarization in terms of O₂-CO₂ gain with increase in load for Cell 7-17. It can be concluded from Figure 2.2.3 that the cathode is under a diffusion-control regime even if the performance is stable. A reduction in tile thickness or a decrease in anode pore size, and/or reducing particle size of lithium aluminates will eliminate the cathode flooding and will result in an improved cell performance. Figure 2.2.3 also compares Cell 7-17 with Cell 7-14, which had a thin tile containing 55 w/o liquid carbonates (50:50 k/o - Li/K). As expected, lower values of O₂-CO₂ gain were observed for Cell 7-14 indicating an unflooded cathode, which explains its higher performance.

Comparison of Cell 7-17 with Cell 7-13 (6th Quarter Technical Progress Report), both having 60 wt. % liquid, suggests that the electrolyte with 62/38 Li/K ratio gave a more stable performance (so far 1300 hours of almost steady performance) compared to that obtained with the electrolyte containing 50/50 Li/K.

FIGURE 2.2.2
 Endurance Testing - CELL 7-17

TABLE 2.2.3

EFFECT OF FUEL AND OXIDANT UTILIZATION ON THE CELL PERFORMANCE(CELL: 7-17) *

UTILIZATIONS % FUEL/OXIDANT	CELL VOLTAGE (mV) AT CURRENT DENSITY, AMPERES (mA/CM ²)								HOURS
	15 (55)	20 (74)	25 (92)	30 (111)	35 (129)	40 (147)	45 (166)	50 (184)	
50/25	940	890	835	785	740	700	660	620	815
50/50	920	870	830	780	735	685	645	610	815
75/25	905	855	810	760	715	660	640	600	815
75/50	895	850	800	745	700	670	625	585	815

* Fuel Composition: 74.2% H₂, 18.5% CO₂, 7.3% H₂OOxidant Composition: 33.33% O₂, 66.67% CO₂

Temperature: 650°C
 Gas Flows: 100 amps.
 Electrode Area: 271 sq. cm.
 Anode: 74.2% H₂,
 18.5% CO₂,
 7.3% H₂O
 Cathode: 29.6% CO₂,
 14.8% O₂,
 55.6% N₂
or
 33.3% O₂,
 66.7% CO₂

FIGURE 2.2.3 O₂-CO₂ GAIN FOR CELL 7-17 and 7-14

2.2.3 Bubble Pressure Measurement

After about 1100 hours of stable performance, back pressure was applied to the anode exit gas of Cell 7-17. The back pressure was slowly increased to 10 inches of water (about 1/2 psi). OCV dropped by only 3 mV, of which 1 mV is due to drop in the Nernst term. The test was repeated at a cell life of 1440 hours and almost the same tile integrity was observed. The drop in OCV was 4 mV at 10 inches of backpressure. These results are encouraging because they indicate a good edge seal and tile integrity i.e., at least 10" of bubble pressure even after 1100 hours and 1400 hours of life test.

2.2.4 Comparison of Wetting of Electrodes

Electrode wetting could be qualitatively characterized by O_2 - CO_2 gain at the cathode. A preliminary attempt was made to correlate O_2 - CO_2 gain with the pore size of electrodes for various large cells. Table 2.2.4 compares various component details including anode and cathode pore sizes, electrolyte compositions, tile density and thickness with O_2/CO_2 gain at a current density of 111 mA/cm². A cell having the same pore structure for the anode and the cathode (both 12 μ) displayed lowest performance and very high O_2 - CO_2 gain (Cell 7-13). A reduction in anode pore size from 12 μ to 7.3 μ reduced O_2 - CO_2 gain to less than one-half with tile thickness being approximately the same (Cells 7-15 and 7-17). With the same pair of electrodes (7.3 μ anode, & 12 μ cathode), a reduction in the thickness of the electrolyte tile from 106 mils (Cell 7-16) to 52 mils (Cell 7-14) results in a further reduction of O_2 - CO_2 gain. However no difference in O_2 - CO_2 gain was observed by changing the liquid content of the tile from 60 to 55 wt. % (Cells 7-15 & 7-16). This may be attributed to difference in lithium aluminate characteristics. This was not considered in the present study, but will be considered in the future analysis.

TABLE 2.2.4

ELECTRODE PORE SIZE ANALYSIS - LARGE CELL

CELL NO.	ELECTRODE PORE SIZES, miltons		ELECTROLYTE TILE			MINIMUM O ₂ -CO ₂ GAIN AT 30 AMP (111 mA/cm ²)	
	ANODE	CATHODE	COMPOSITION	DENSITY,* g/cc	THICKNESS, mils	AT mv	AT CELL LIFE, hours
7-13	12	12	60 wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 40 wt. % Solid LiAlO ₂	2.31	92	260	156
7-14	7.3	12	55 wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.29	52	60	120
7-15	7.3	12	60 wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.29	105	95	163
7-16	7.3	12	55 Wt. % Liq. (50/50 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.50	106	95	260
7-17	7.3	12	60 wt. % Liq. (62/38 mol. % Li ₂ CO ₃ /K ₂ CO ₃) 45 wt. % Solid LiAlO ₂	2.31	83	115	1274

*Experimentally measured density

TASK 3. STACK DESIGN & DEVELOPMENT: J. Yasi and D. Dharja

3.1 Development of Sheet Metal Hardware

So far all the cell tests have been performed with machined frames in order to study various electrode structures, electrolyte configurations and wet seals. Work has now begun to design and test the lightweight sheet metal hardware replacing heavy machined frames. Obviously, sheet metal hardware offers the advantages of reduced material cost and reduced machining cost. The thickness of the sheet metal will be optimized with respect to forming capabilities and corrosion resistance.

To begin with, lightweight hardware will be tested in a single cell and then in 2-4 cell stacks. Preliminary design for the single cell is shown in Figure 3.1.1. The first structure has been designed using formed sheet metal of 10 mils thickness. The design provides for current collection, gas flow routing and electrode support. Testing will begin in the next Quarter.

Figure 3.1.1

CELL DESIGN FOR TESTING LIGHTWEIGHT FRAME MATERIAL

NEXT ASSY	USED ON
APPLICATION	

TASK 4. MODELING & SYSTEM ANALYSIS: P. Patel and D. Dharja4.1 Nernst Losses

In the Sixth Quarter Technical Progress Report (No. E-3-6) a concept for definition of Nernst Losses was introduced by the equations (1), (2) and (3). The term E_{average} , ($= E^{\circ} + \text{Average Nernst Term}$), was defined by several methods. The two methods as defined below to compute integrated average value of Nernst Losses with respect to cell length were further evaluated.

Definition - I

$$E_{\text{average}} = \frac{1}{L} \int_0^L E(x) dx$$

Where, $E(x)$ is value of cell e.m.f. at distance x from the entrance.

Definition - II

$$E_{\text{average}} = \frac{\int_0^L E(x) \cdot I(x) dx}{\int_0^L I(x) dx} = \frac{1}{L} \int_0^L E(x) \frac{I(x)}{I_{\text{avg}}} dx$$

where, $I(x)$, the local current density, is used as a weighting factor.

Nernst losses corresponding to the above definitions were calculated for typical anode and cathode gas compositions used in cell testing and 50% conversion of both fuel and oxidant. Figure 4.1.1 represents the variation in the Nernst Losses as a function of cell potential, by both the definitions. The power density - based Nernst Losses (Definition - II) remain constant and hence can not explain bending of the constant conversion plot at higher terminal voltages. Also, the value of Nernst losses, 89 mV, obtained by this method is quite low as compared to 101 mV obtained from the constant conversion plot. It is interesting to note that this value of 89 mV is exactly the same as that obtained from the integrated average of E with respect to fuel conversion (Equation 4, Sixth

Temperature = 650°C

Anode: 74.16% H₂, 18.54% CO₂, 7.3% H₂O

Cathode: 29.58% CO₂, 14.79% O₂, 55.63% N₂

Conversions: Fuel: 50%

Oxidant: 50%

Resistance: 0.15 ohm

Electrode Area: 8.56 sq. cm

FIGURE: 4.1.1, NERNST LOSSES BASED ON DIFFERENT DEFINITIONS

Quarterly Report).

The Definition - I, as described in the previous report, shows an initial, linear, and relatively small increase in Nernst Losses with the terminal cell potential. Then, it follows an exponential increase as the terminal potential approaches the value of E corresponding to the exit gas composition. This qualitatively justifies the constant conversion polarization characteristic of the fuel cell.

Figure 4.1.1 shows that for Definition - I Nernst Losses increase from a value of 94 mV at 0.65 volt of terminal cell potential to about 107 mV at 0.9 V which yields an arithmetic average Nernst Losses of 100.5 mV. The value of 101 mV Nernst Losses obtained by the extrapolation of the constant conversion plot generated from Model MCFC1, matches well with this average. This implies that the constant conversion polarization at low cell potentials is not a straight line in a true sense. It appears so because the variation in Nernst Losses of 5-10 mV is not noticeable with the graphics made on a 200 mV per linear inch scale. Figure 4.1.2 shows experimental polarization behavior of Cell 7-17 at a constant utilization of fuel and oxidant (50% fuel and 50% oxidant). The extrapolation of constant conversion plot to zero current density has an intercept of 1.0 volt, which gives Nernst losses of 100 mV. It is interesting to note that this number is in good agreement with average theoretical Nernst Losses obtained by Definition - I. However, it should be noted that the model considers co-current flow whereas the Cell 7-17 has a mixed flow system obtained by keeping the two flanges (Figure 2.1, 3rd Quarter Technical Progress Report) in a cross configuration. Thus, Definition - I appears to explain the constant conversion polarization curve and it will therefore be used to explain the breakdown of cell overpotentials.

4.2 Water Gas Equilibrium

The computer program for the Model MCFC1 is modified to include a new subroutine which incorporates the water gas equilibrium. Figure 4.2.1 compares the performances predicted by the Model MCFC1

Cell 7-17

Fuel Conversion : 50%

Oxidant Conversion: 50%

Anode: 74.2% H₂, 7.3% H₂O,
18.5% CO₂Cathode: 29.6% CO₂, 14.8% O₂,
55.6% N₂

Temperature: 650°C

Electrode Area: 271 sq. cm.

Cell Life: 793 Hours

FIGURE 4.1.2 CONSTANT CONVERSION POLARIZATION CURVE & NERNST LOSSES

FIGURE 4.2.1 INCORPORATION OF WATER GAS EQUILIBRIUM IN THE MODEL MCFC1

with and without water gas equilibrium. The model curve without consideration of water gas equilibrium is slightly above and parallel to the experimental curve. The incorporation of a water gas equilibrium results in a model curve which explains the experimental data more accurately.

Using this modified version of MCFC1 (Model MCFC1WG), Nernst Losses were recomputed. As seen from Table 4.2.1 the Nernst Losses are higher by only 1-2 mV than those computed without water gas equilibrium for the straight line portion of the constant conversion curve. However, this difference is quite significant at higher cell potentials where the constant conversion plot is non linear.

TABLE 4.2.1

EFFECT OF WATER GAS EQUILIBRIUM ON NERNST LOSSES

Temperature 650°C
 Anode: 74.16% H , 18.54% CO , 7.30% H O
 Cathode: 29.58% CO , 14.79% CO , 55.63% N
 Conversions: Fuel: 50%
 Oxidant: 50%
 Cell Resistance: 0.15 ohm
 Electrode Area: 8.56 sq. cm.

CELL POTENTIAL, volts	NERNST LOSS,* mV	
	WITHOUT WATER GAS EQUILIBRIUM	AFTER INCORPORATION OF WATER GAS EQUILIBRIUM
0.65	93.6	94.1
0.75	95.6	96.4
0.85	100.3	102.0
0.90	106.7	111.0
0.92	112.8	124.0
0.93	120.6	138.1
0.935	125.7	151.5

*For cocurrent flow configuration

FUTURE WORK PLAN

In the next reporting period efforts will be concentrated on the following tasks.

Component Development

Sintering & compacting procedures will be developed to manufacture electrodes of desired thickness, porosity and pore size. Stabilized anode structures fabricated from Ni-Co powder will be sintered and evaluated.

Optimization of grinding and mixing procedures for the in situ method will be continued to obtain the desired lithium aluminate matrix. Manufacture of tiles reinforced with Kanthal screen will be continued. A press for fabricating 15" x 15" tiles will be installed, and pressing of 15" x 15" tiles will begin.

To develop corrosion resistant frame and current collector materials, various stainless steels including SS316 and SS446 will be evaluated with the new potentiostatic corrosion equipment. Results will be compared with the aluminum coated samples. The effect of reducing and oxidizing atmospheres on the corrosion currents will also be studied. In parallel with these efforts, lightweight hardware obtained by forming thin sheet metals will be developed. In this way lightweight corrosion resistant hardware will be developed during the program.

Cell Testing

Efforts will be continued to obtain compatible anode and cathode structures and electrolyte configurations. A variety of lithium aluminate matrices will be tested and evaluated. The structural stability of the lithium aluminate matrix will

be investigated.

Thermal cycling capabilities of tiles with Kanthal fiber screens will be determined and will be compared with random reinforcement.

The 7" x 7" cell will be scaled up to a 15" x 15" cell. Test stations will be constructed.

Modeling & System Analysis

The water-gas equilibrium will also be incorporated in the model MCFC2 (one which considers diffusion polarization of hydrogen at the anode) and its effect on modeling will be investigated (MCFC2WG). MCFC system analyses will be resumed in this quarter with the modified model MCFC1WG.

The mathematical model MCFC2WG will then be extended to incorporate oxygen diffusion polarization at cathode.

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