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DEVELOPMENT OF MOLTEN CARBONATE FUEL CELL TECHNOLOGY
Technical Progress Report for the Quarter of April-June 1982

Work Performed Under Contract No. AC02-76ET11304

Energy Research Corporation
Danbury, Connecticut

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April - June 1982

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EXECUTIVE SUMMARY

Work during the reporting period focused on the investigation of appropriate microstructural characteristics (pore size, porosity) required for a ceramic filled ribbed anode and an open porosity cathode. This included screening of alternative starting nickel powders and processing methods used during plaque fabrication as well as continued development and testing of the low cost LiAlO_2 stabilizer. A 5000 hour bench scale test with improved anode hardware has shown a significant improvement in endurance/performance indicating that a reliable test vehicle is available for long-term testing.

Highlights of the work performed during this quarter are presented below.

Component Development

- Nickel plaques fabricated from a variety of commercially available starting powders were evaluated. The best results were obtained using Inco powder Types 123, 255 and 287. Precise control over electrode pore characteristics was attained by blending Inco powders (Types 123 and 287).
- Densification of plaques by cold pressing and additional sintering were also investigated as a means to control pore size distribution, and creep. Mercury porosimetry, results show that large pores in the anode can be eliminated by the densification treatment.
- Accelerated creep testing of stabilized vs. non-stabilized anodes indicate a significant improvement in creep resistance due to LiAlO_2 impregnation.
- A laboratory scale cell test of an anode with a higher LiAlO_2 content has shown improved stability and the test is continuing.

Bench Scale Testing

- Improved endurance performance has been demonstrate in a 5000 hour bench scale cell due to a nickel anode current collector and nickel coated cell housing. This provides an improved and more reliable test vehicle for long-term component evaluation.

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TASK 1. COMPONENT DEVELOPMENT

Microstructural characteristics related to the optimum performance of both anode and cathode have been further studied. A summary of recent electrode fabrication methods, materials and properties is also presented. Accelerated anode creep testing was initiated and promising results have been obtained with LiAlO_2 stabilized anode structures. A summary of three laboratory scale cell tests is discussed.

1.1 ELECTRODE MICROSTRUCTURE

The Molten Carbonate Fuel Cell utilizes the same starting materials and approximate structures for both electrodes; namely, a sintered porous Ni-matrix, which in the case of the cathode becomes oxidized in the cell. The microstructural requirements for the electrodes (anodes as opposed to cathodes), however, are very different. A self supporting, ribbed anode will require a different structure for the ribs than for the continuous web or base of the electrode. This is because the ribs may be required not only for support and channeling of fuel gases but may also be used to store electrolyte. For this reason the nickel rib matrix will have to be quite porous to accommodate heavy impregnation with fine ceramic material which will then provide good electrolyte retention for as large an amount of carbonate as possible. In contrast to this, the continuous electrode web, or base, of the shaped anode must provide good bubble barrier characteristics while still being easily wetted with carbonates. Hence a much finer pore structure with less void volume is necessary here. Finally, the cathode, according to recent agglomerate model proposals, should be highly porous with a preponderance of very large pores for good gas percolation but it should also be able to resist flooding while still providing enough fine porosity inside the agglomerated oxide particles to retain a continuous

carbonate film for good ionic bridging to the electrolyte matrix.

An updated version of development requirements for MCFC electrodes is shown in Table 1.1 illustrating specifications consistent with recent experience.

TABLE 1.1 ELECTRODE DEVELOPMENT REQUIREMENTS

Material		Thick- ness, mils	Pore Spectrum			
			Metallic		Impregnated	
			MPS, μm	%P	MPS, μm	%P
ANODE $\left\{ \begin{array}{l} \text{Ribs} \\ \text{Base} \end{array} \right.$	Ni + LiAlO ₂	50	10	60	3	55
		20	5	60	<3	55
					<u>Oxidized</u>	
CATHODE	Ni + NiO	20	15 (wide)	75	2-20	60

These development requirements will be used as a guide for our on-going component development effort.

1.2 NICKEL PLAQUE EVALUATIONS

In order to obtain suitable initial (nickel) plaques for LiAlO₂ filling that will lead to the desirable creep and sinter resistant structures for anode web and ribs, several alternative starting materials as well as different processing methods have been investigated to obtain the designated microstructural requirements. Areas examined include: 1) screening of commercially available nickel powders, 2) the effects of mixing two powders, 3) the effects of sintering temperature, and 4) the effects of cold pressing a sintered plaque.

Several different types of nickel powder which are commercially available at reasonable cost have been examined as possible alternatives to INCO 287. These powders are shown in Table 1.2 as well as some of the results that were obtained after sintering them into plaques. To form porous plaques, each powder was dry-packed and sintered for 15 minutes in the hot zone of our continuous feed H₂-furnace at a temperature of 900°C. All the coarse grained powders resulted in plaques of low porosity (<60% void volume) and poor green strength. The Cerac nickel powder resulted in a high porosity and relatively large MPS plaque after sintering. However, it had

TABLE 1.2 PLAQUES FROM ALTERNATIVE Ni POWDER SOURCES AND TYPES

Powder Type	Particle* Size, μm	Calculated Porosity, %	Mean Pore Size, μm	Comments
Sherritt Gordon SF-300	-30+20	56**	11	All SF Ni-powders from Sherritt Gordon and the Chem Alloy powder are spheroidal in shape with a pebbly surface. They did not sinter at 800°C. After sintering at 900°C, plaques were brittle and quite fragile.
Sherritt Gordon SF 80 x 250	-150+75	56	-	
Sherritt Gordon SF 150 x 200	-106+75	50	-	
Sherritt Gordon SF 100 x 150	-150+106	59	-	
Chem-Alloy UB-200	+75-45	57	-	
Cerac	~1	82**	9	Ni particles spherical in shape. Did not sinter well at 800°C. Plaques were also brittle and fragile after 900°C sintering.
Inco 287	2.6+3.3†	86**	14	Ni particles are chain-like structures of relatively fine irregular segments. No difficulties in forming durable sintered plaques.
Inco 255	2.2+3.0†	90**	14	
Inco 123	3+7†	60**	6	Ni particles have a regular spherical shape with a "spiky" surface. No problems encountered during sintering process.

* Tyler Sieve Analysis except where indicate.

† Fisher Sub-Sieve analysis.

** Hg porosimetry on Std. Sintered Plaques.

poor strength and handling characteristics. The best results were obtained with the three INCO Ni powders, Types 123, 255 and the standard 287, as the starting powders. These three powders with different Ni-particle structures are commercially produced by variation of the carbonyl pyrolysis process used to manufacture the materials.*

Experiments were also performed to evaluate the effect of mixing the two types of INCO nickel powders that are farthest apart in their properties. Mixing of Types 123 and 287 in various proportions and the resultant effects on plaque porosity and bubble pressure capability are illustrated in Figure 1.1. It will be noted that with an increasing Type

FIGURE 1.1 EFFECT OF MIXING DIFFERENT NICKEL POWDERS

*Tracey, V.A., "The Properties and Some Applications of Carbonyl-Nickel Powders", Powder Metallurgy, 9, (17) 1966.

123 content there is a linear decrease in porosity and MPS down to ~60% void volume with pores of approximately 4 μm . A corresponding increase in room temperature bubble pressure from 0.7 to 1.7 psi is shown to occur simultaneously which suggests that any precisely tailored pore spectrum can be obtained by this blending procedure. It will thus be possible to enhance the bubble barrier capabilities of the anode base while maintaining adequate porosity in the rib structure by the appropriate use of the various nickel particle sizes in different layers when fabricating the electrode.

Furnace temperature is an easily controlled process variable in electrode fabrication. During this period the effect of a higher sintering temperature on plaque pore structure was also examined. A higher sintering temperature (1000°C) is desirable since it may reduce additional in-cell sintering and creep during fuel cell operation. However, it was feared that the higher temperature could result in an undesirable decrease in porosity and an increase in MPS due to excessive particle growth. Table 1.3 summarizes our findings.

TABLE 1.3 EFFECTS OF TEMPERATURE ON SINTERING
DURING ANODE PLAQUE FABRICATION

TEST PLAQUE #	POROSITY, % (heat treatment)			MEAN PORE SIZE, μm		
	(780 °C)	(1000 °C)	Δ	(780 °C)	(1000 °C)	Δ
1	88	85	-3	12	12	0
2	86	82	-4	9.5	12.5	+3
3	88	86	-2	13	13	0

All plaques utilized the same nickel powder (Ni-287; average particle size $\sim 3 \mu\text{m}$; surface area $\sim 0.6 \text{ m}^2/\text{g}$) and all were sintered for 15 minutes at peak temperature in the hot zone of the H_2 -furnace. The 1000°C plaques, however, received a presinter treatment of 15 minutes at 780°C , because the experiment was run consecutively on parts of the same plaque. Nevertheless, the present runs suggest that, as a result of the higher sintering temperature during anode plaque fabrication, there is only a slight reduction in porosity (between 2 and 4 percent) with possibly a slight increase in mean pore size. Further testing will be done to determine whether these plaques are more resistant to sintering and creep during fuel cell operation.

As outlined in Table 1.1 the base of the shaped anode will require a uniform, small, mean pore size to achieve the required bubble-barrier characteristics. One simple way to reduce anode MPS is to cold press the porous Ni plaque after plaque fabrication to a given pore volume. Thus an anode plaque with an initial porosity of 66% was pressed 16 mils to a final porosity of 50%. Results of a plaque compression experiment are shown by comparison of Hg-porosimetry curves in Figure 1.2 and are summarized in Table 1.4.

TABLE 1.4 COMPARISON OF AN UNPRESSED
VS COLD-PRESSED ANODE PLAQUE

Structure	Thickness, mil	Hg-Porosity, %	MPS, μm
Original	31	66	8
Pressed	15	50	3
Δ	-16	-16	-5

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FIGURE 1.2 Hg-POROSIMETRY OF UNPRESSED VS
COLD PRESSED ANODE PLAQUE

This test suggests that it is possible to reduce MPS by simply cold pressing the sintered plaque to a given porosity. This technique has other inherent advantages such as good control over the thickness uniformity of a plaque. Hence, cold pressing of sintered anode plaques can be used to reduce the MPS for increased bubble barrier capabilities if the reduction in total pore volume is of minor concern.

1.3 ACCELERATED ANODE CREEP TESTING

During this quarter, work was performed on out-of-cell, anode creep tests. It is essential for continuous high cell performance and the feasibility of using a dual porosity ribbed electrode structure that porous plaques be physically stable throughout a cell's life. A new test apparatus was fabricated as shown in Figure 1.3, which enabled accelerated (approximately 700°C) out-of-cell creep testing of various anode structures.

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FIGURE 1.3 ELECTRODE CREEP STABILITY TEST APPARATUS

Creep behavior is measured as the difference between plaque shrinkage under load (under the weighted ceramic ring) vs. unloaded shrinkage (outside the ring) as illustrated in Figure 1.4. Also, as can be seen, the center unloaded area is subjected to lateral stretching and pulling forces which may inherently afford some insight into the three dimensional decomposition of forces applied to an actual structure such as it will occur in the proposed anode ribs.

M0334

FIGURE 1.4 SCHEMATIC OF FIRST CREEP EXPERIMENT RESULTS

Creep test experiments and results performed this quarter are summarized in Figure 1.5. All tests were subjected to a humidified H₂/CO₂ fuel atmosphere at 700°C and a static compressive load of 50 psi. Enough 50/50 LiKCO₃ was added to the test specimen such that when molten, would fill 100%

M0378

FIGURE 1.5 THICKNESS REDUCTION DUE TO ANODE CREEP

of the plaque void volume, plus an additional 10% for hardware wetting. As can be seen, a significant improvement in creep resistance is obtained with the LiAlO₂ impregnated plaques. It should also be noted that there was virtually no difference in the results when the time at 700°C was shortened from 265 hours to 65 hours suggesting that the majority of the sintering occurs in less than 65 hours.

1.4 LABORATORY-SCALE COMPONENT SCREENING

Cell No. 160:

The primary purpose of this test was to screen a 60 wt% carbonate-filled, hot-pressed tile comprised of low surface area γ -LiAlO₂ (3 m²/g) derived from low cost Kaiser® C-70 alumina. In addition, the cell was intended to establish the catalytic activity by itself of a fine mesh (20x20) gold screen reinforcement material. Thus the behavior of the cell was sought primarily with respect to H₂-crossover, wet seal tightness, current-potential performance. The performance of the cell with respect to a plain gold mesh electrode would provide the baseline comparison for new cathode compositions to be sintered on gold screen as the reinforcement material. This would eliminate any interference such as is being suspected in the case of nickel oxide interaction with the presently used stainless steel reinforcements.

The performance of this cell was disappointing in that the OCV was never greater than 0.96V. In addition gas cross leakage developed after ~200 hours of operation. For these reasons the cell was terminated at 500 life hours. On cell disassembly the slump character of the tile was seen to be the major cause of the problem. It had severely extruded in the seal areas and the gold screen on the cathode side had become embedded in the matrix and was completely covered with electrolyte.

The results of this test clearly indicate the need for reduced liquid content with this low surface area LiAlO₂ powder. More attention will therefore be paid to the out-of-cell slump test behavior with these new materials.

Cell No. 161:

The purpose of this test was to evaluate a low cost anode which contained a larger level (20 wt%) of inexpensive ceramic stablizer (LiAlO₂). The post-impregnated plaque was 57%

porous with a 3.2 μm mean pore size. The cell was assembled with a relatively thick (36 mil) SS-reinforced cathode which before in-situ oxidation was 76% porous with a 9 μm mean pore size. The tile was non-reinforced, 71 mils thick, produced from medium surface area $\gamma\text{-LiAlO}_2$ with 60 wt% liquid content of 50/50 Li/K carbonate. The effect of the heavily impregnated anode on electrode stability and post test electrolyte retention will be evaluated as well as the behavior of the non-reinforced tile with respect to gas cross leakage and wet seal tightness.

This cell has accumulated 1500 hours of endurance during this reporting period. As shown (Figure 1.6) the cell was stable for the first 1200 hours of operation. During this

FIGURE 1.6 LIFE GRAPH OF CELL NO. 161

period the cell maintained an OCV of 1.065-1.070V with performance levels of $\sim 0.8V$ at 115 mA/cm^2 and a cell resistance of $\sim 0.5 \Omega \cdot \text{cm}^2$. Gas cross leakage declined from a maximum of 1.5% N_2 in the fuel exhaust of 350 life hours to 0.6% N_2 at 1100 hours due to periodic additions of electrolyte. At 1200 life hours a malfunction in the gas delivery system resulted in an overnight loss of CO_2 with the cell on endurance load. As shown (Figure 1.6) this loss resulted in a 20 mV drop in OCV due to increased gas leakage and a 70 mV drop in 115 mA/cm^2 performance due to increased cell resistance and gas cross leakage. Electrolyte additions have been initiated in the hope that the cell will recover some of its losses.

Cell No. 162:

This cell was assembled with a tape cast matrix to evaluate the effects of a thin matrix electrolyte structure. The tape cast matrix was 23 mils thick produced from $8 \text{ m}^2/\text{g}$ (B.E.T.) surface area γLiAlO_2 powder with 52 wt% liquid content of 50/50 Li/K carbonate. For the purpose of comparison this cell contained an electrode pair essentially identical (cut from the same original plaque) as those used in Cell No. 161 (described previously).

Cell 162 was terminated after only 160 hours of operation due to gas cross leakage which developed after several days and rapidly worsened. This cell attained an initial O.C.V. of 1.057V with 115 mA/cm^2 performance of 0.610V. Cell resistance which was slightly high ($0.88 \Omega \cdot \text{cm}^2$) during the first 72 hours of operation and increased rapidly ($1.7 \Omega \cdot \text{cm}^2$ at 150 life hours) with the worsening gas cross leakage. Electrolyte additions initiated after 100 hours of operation did not improve cell performance or O.C.V. and the test was terminated at 160 hours with an O.C.V. of 0.98V.

Post test inspection of the terminated cell revealed components with good mechanical integrity, no significant dimensional changes and no unusual coloration. A large amount of electrolyte creepage was noted on the outside of the anode frame and the components seemed dry (of electrolyte) as evidenced by poor bonding upon cell tear down. Several cracks were visible in the tape cast matrix however that did not appear to be the result of concentrated loading or uneven component thickness. Component samples have been submitted for quantitative analysis and results will be reported as they become available.

TASK 2. BENCH-SCALE CELL TESTING

Cell 7-40 has accumulated 5000 hours of stable operation during this period. This cell which contains a Nickel-200 anode current collector and a plasma sprayed coating of nickel within the fuel chamber has shown a significant improvement in endurance performance over previous bench-scale cells which contained SS-316 anode hardware. A comparison of this cell with the previous best bench-scale cell (7-38) is presented in the updated life graph (shown in Figure 2.1). The medium load performance level (with standard gas utilization) after 3500 hours was 808 mV at 115 mA/cm² which is within 50 mV of peak performance at 100 life hours. A further decay (45 mV) in the 115 mA/cm² performance occurred in the last 1000 hours of

FIGURE 2.1 ENDURANCE COMPARISON OF NICKEL VS SS-316 ANODE HARDWARE

operation. Almost half (18 mV) of this loss can be attributed to increased ohmic resistance due in part to tile dryness and the remaining losses are due primarily to Nernst effects (changes in gas composition as shown by a drop in OCV) resulting from a deteriorating anode fuel seal (87%). It can therefore be said that the total electrode polarization, $\eta_{act} + \eta_{diff}$, at this current density has not changed significantly over 5000 hours of operation. The lower rate of performance decay and slower increase in resistance of Cell 7-40 HS compared with Cell 7-38 can be attributed to the nickel current collector and nickel coated housing. This improved, more corrosion resistant, anode housing and current collector will provide a more reliable test vehicle for future endurance testing and points to the important (immune to corrosion) requirement for the bipolar plate material on the fuel side.