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IN-SITU ELECTROLYTE REPLENISHMENT FOR LONG FUEL CELL LIFE

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PREPARED FOR:

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PREPARED BY:

FUELCELL ENERGY INC. (FORMERLY ENERGY RESEARCH CORP.)
3 GREAT PASTURE ROAD
DANBURY, CT 06813

PRINCIPAL INVESTIGATOR: Richard Johnsen

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Daniel D. Park
(630) 252-2308
E-mail: daniel.park@ch.doe.gov
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1. INTRODUCTION

The carbonate fuel cell has many advantages over conventional methods of producing electricity. It converts hydrocarbon fuels directly into electricity with a high efficiency (>70% in a co-generation plant configuration) and consequently releases less carbon dioxide greenhouse gases (>30% less compared to a combined cycle gas turbine plant). Its adaptability to meet the customers' specific power requirements is ideally suited for distributed power generation. The advantages of distributed power generation include site flexibility, fuel source flexibility, less capital investment risk and elimination of transmission and distribution investments.

The fuel cell becomes economically competitive if its life exceeds 40,000h. The current predicted lifetime of the central cells of a stack is 44,000h, based on electrolyte inventory considerations. Methods of extending fuel cell life even further are being sought to enhance its commercial competitiveness.

Several electrolyte-related issues in the present design impose limitations on fuel cell life. For instance, the available space for electrolyte storage inside the cell is confined to the pore volumes of the electrodes and matrix. Moreover, the long-term loss of electrolyte from the electrodes and matrix during operation eventually renders the cell inoperable. Electrolyte depletion occurs primarily in three ways: lithiation of cell components, corrosion of the metallic cathode current collector and electrolyte vaporization. A fourth mode of electrolyte loss, electrolyte migration, adversely affects the end cells of a stack.

This research effort has focused on four major strategies to reduce electrolyte loss and increase electrolyte inventory:

- In-situ electrolyte replenishment within the cell by storing an electrolyte in the cathode gas chamber. The electrolyte is a solid at the operating temperatures but slowly absorbs into the cell over time. An added benefit of this design is it alters the electrolyte composition making it lithium-rich, which reduces electrolyte vaporization loss.
- Development of a novel cathode design having ribs to replace the baseline metallic cathode current collector. The current collector is responsible for significant electrolyte loss because when it corrodes it consumes lithium carbonate electrolyte. An added benefit of this design is it provides significant additional electrolyte storage space.
- Identification of a more corrosion-resistant material or coating for the cathode current collector to reduce electrolyte losses.
- Development of methods to reduce electrolyte migration, which depletes electrolyte from the positive end-cells of a stack.

2. RESULTS

2.1 DELAYED ELECTROLYTE ADDITION

A significant amount of lithium carbonate is consumed from the baseline electrolyte (62 mole% lithium carbonate/38 mole% potassium carbonate) relatively early in life due to the initial

lithiation of the fuel cell materials. The corrosion reaction on the cathode current collector forms solid lithium ferrite, which consumes lithium carbonate from the electrolyte. Subsequently, the lithium concentration decreases and the evaporation rate increases because the electrolyte becomes more potassium-rich (the vapor pressure of potassium carbonate is one order of magnitude greater than lithium carbonate).

Approximately 10% of the beginning-of-life (BOL) electrolyte inventory is consumed within the first 2,000h of operation. This creates an opportunity to replenish a significant amount of the electrolyte relatively early in life. If 10% of the BOL inventory were to be replenished after 2,000h of operation, a 30% increase in fuel cell life would be gained based on a FCE electrolyte fuel cell model.

A method of in-situ delayed electrolyte addition was developed and verified in single cell bench-scale testing. The extra electrolyte is stored in the cathode current collector, which is adjacent to the cathode (see Figure 1). The electrolyte isn't in direct contact with the cathode or it would be absorbed quickly. Rather, it is separated by the thickness (0.012") of the collector material. It is composed of lithium carbonate (melting point 720°C), which is a solid at the fuel cell operating temperatures (<650°C). Absorption into the cathode occurs as the melted electrolyte in the cathode wets the collector with a thin film and slowly dissolves away the solid lithium carbonate. This concept is a self-contained, unassisted process and doesn't require servicing downtime.

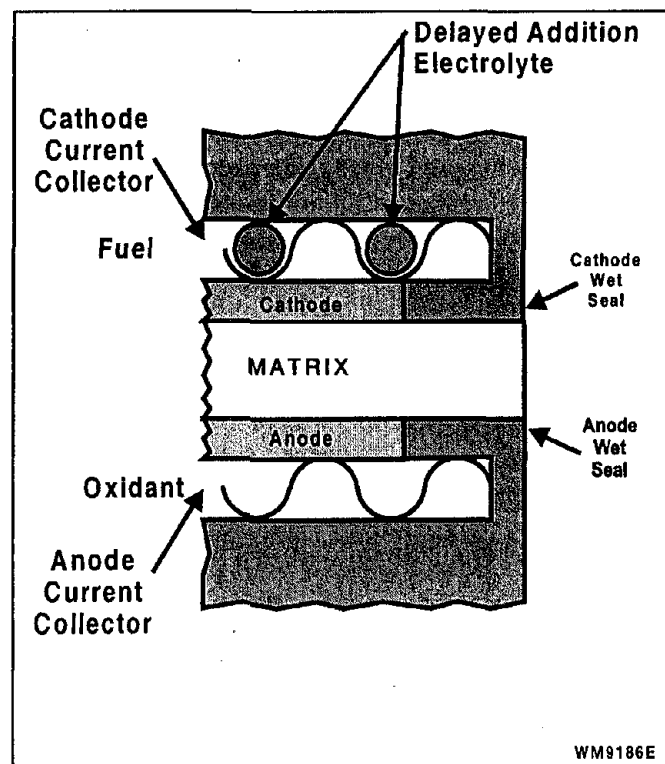


Figure 1. IN-SITU DELAYED ELECTROLYTE ADDITION:
A High-Melting Point Electrolyte is Stored in the Cathode Current Collector and Slowly Absorbs into the Cell

The rate of absorption of the extra electrolyte depends on time and temperature. Several bench-scale, single cell tests were performed to understand these relationships. The cells were operated at various temperatures to simulate the hot and cold regions of a full-area cell (2' x 4', ~8,000 cm²). In the hotter areas (650°C test temperature) absorption occurs relatively quickly. All of the lithium carbonate went into the cathode in <500h. In the cooler areas (620°C test temperature), the absorption is significantly slower. After 2,000h of operation, 75% of the lithium carbonate was absorbed. Thus, delayed electrolyte addition of lithium carbonate is feasible in the cooler regions of the cell. The performance of the cell wasn't impacted by the extra electrolyte in the corrugation.

This concept is also beneficial for use in the hotter regions of the cell because the lithium concentration of the electrolyte could be quickly increased, which would reduce electrolyte evaporation loss and cathode dissolution. The rate of electrolyte evaporation was measured in these cells. The anode and cathode gas streams were scrubbed after leaving the cell to measure any electrolyte vapor present. The results suggest that increasing the lithium concentration from 62% to 70 mole% by delayed electrolyte addition would suppress evaporation losses by ~40%.

Sodium carbonate was also evaluated for in-situ electrolyte replenishment. A bench-scale cell test was operated with a small amount of sodium carbonate in the collector for testing purposes. The electrolyte in the rest of the cell was 62Li/28K. Sodium carbonate was found to replenish the cell more slowly than lithium carbonate. After 2,300h of operation at 650°C, 69% of the sodium was absorbed into the cathode. Therefore, delayed addition of sodium carbonate is feasible in the hotter regions of the cell. It could be used in tandem with lithium carbonate in the cooler regions of the cell to achieve delayed addition through-out the cell.

The delayed addition concept was first tested in full-area stack, FA-20-2. Lithium carbonate was placed in the wet seal area of a cell. There is enough room in the wet seal area to increase the electrolyte inventory of the cell by ~3%. Post-test analysis verified that the electrolyte successfully replenished the cell. The corrosion rate of the collector wasn't adversely affected by the stored lithium carbonate. This concept is presently being tested in the active area (not only in the wet seal area) of a full-area stack, FA-5-7. The stack has logged 3,000h of operation to date. A small amount of lithium carbonate was added to the collector in different temperature regions of a cell (a large amount couldn't be added to one cell or it would've created back pressure and reduced the flow to that cell). The absorption rates in different areas will be determined during post-test examination.

2.2 THE RIBBED CATHODE DESIGN

2.2.1 Introduction

The main purpose of the ribbed cathode design (referred to as the corrugated cathode design in Interim Report 2) is to extend fuel cell life by minimizing electrolyte loss, which occurs by the corrosion and formation of LiFeO₂ on the stainless steel cathode current collector. When the collector corrodes it forms LiFeO₂, which consumes Li₂CO₃ from the electrolyte. The metal current collector of the baseline design is replaced by a ribbed cathode in the advanced design. A comparison of the different designs is illustrated in Figure 2.

Two ribbed cathode designs have been developed. The first design is simpler (one piece) and therefore would be less expensive to make. The second design has a two piece cathode (a planar one next to the matrix and an adjacent inverted ribbed cathode). This design promises even further life enhancement because it provides increased electrolyte storage space. Also, the cell performance may be superior because the thickness of the planar cathode next to the matrix was reduced, which improves through-plane gas diffusion. Both designs promise to extend fuel cell life significantly compared to the baseline design.

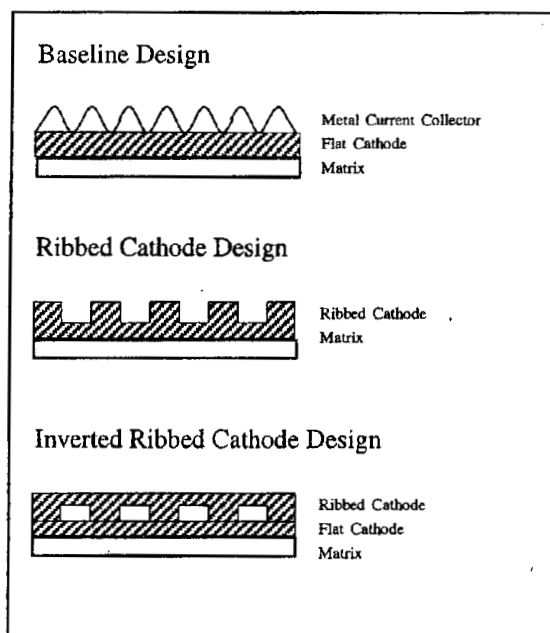


Figure 2. A COMPARISON OF THE BASELINE AND RIBBED CATHODE DESIGNS:
Elimination of the Metal Current Collector will Reduce Electrolyte Loss Significantly.

The corrosion of the cathode current collector is projected to consume ~70% of the total cell electrolyte inventory after five years of operation. Therefore, replacing the current collector with a ribbed cathode would prevent this loss from occurring. In addition, the ribbed cathode design provides additional electrolyte storage space inside the porous ribs. The electrolyte loss model developed at FCE predicts that the ribbed cathode has the potential to more than double fuel cell life, based on electrolyte inventory and loss rate considerations (see Figure 3).

During the course of the Phase II research, the ribbed cathode has been developed from the design to prototype stages. It has been successfully operated in bench-scale, single cell tests. A potential method of mass producing the ribbed cathode has been developed.

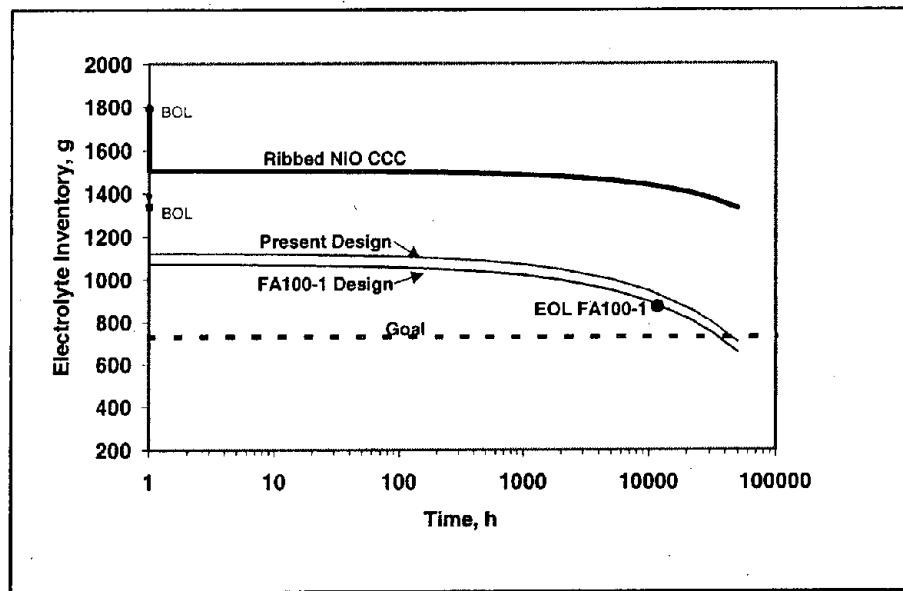


Figure 3. LIFE PROJECTION OF RIBBED CATHODE DESIGN:
Ribbed Cathode Promises Significantly Longer Life.

2.2.2 Fabrication Method

The baseline cathode (35 mil thick, planar) is fabricated by dry-doctoring INCO Ni 255 powder onto a graphite plate and sintering the powder bed in a tunnel furnace. The ribbed cathode has been fabricated in a similar manner. A prototype ribbed cathode was made by machining grooves into a thick planar cathode of 75% porosity to make the ribs. It was then pressed between two flat plates to increase the rib density (72% porosity) for the purpose of reducing shrinkage during operation. This method is useful for prototype fabrication but is not easily transferable to mass production. A different fabrication method suitable for mass production was developed. In this case, the ribbed structure is dry-doctored onto a mold with flow channels and sintered through a tunnel furnace.

The ribbed cathode concept is not expected to significantly impact fabrication costs because its fabrication process is similar to the baseline process. The impact on material costs is also negligible, as shown in Table 1.

Table 1. MATERIALS COST ANALYSIS OF RIBBED CATHODE:
No Impact on Material Costs is Expected.

	<u>Baseline Cell</u> % of Cell Cost	<u>Ribbed Cell</u> % of Cell Cost
Cathode	10.88	21.76
CCC	8.94	0.0
Electrolyte	3.2	4.16
	23.02	25.92
		(23.02)
Cost Increase		~3.0

2.2.3 Creep Strength

Providing adequate creep strength in the ribbed cathode presented a technological challenge early on. The creep rate of the planar 35 mil thick baseline cathode projects to a 15% thickness reduction (or 5 mil per cell) in four years of operation. However, a ribbed cathode having the same porosity as the baseline cathode would creep more than the baseline because it is three times thicker.

Creep tests were performed to optimize the creep strength of the ribbed cathode. The creep test sample configuration is illustrated in Figure 4. The creep test conditions were 670°C and 35 psi compressive load for 1,000h in the cathode gas environment. The cathode electrolyte was 62 mole % Li_2CO_3 /38 mole % K_2CO_3 with a 0.5 mole % MgCO_3 additive.

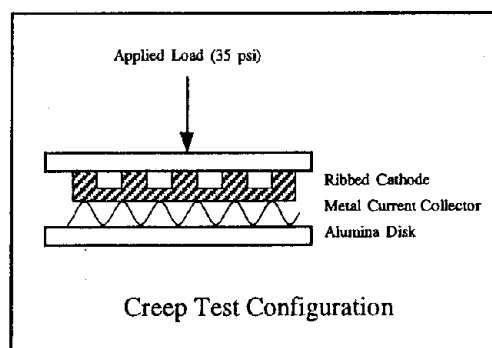


Figure 4. SAMPLE CONFIGURATION OF CATHODE CREEP TESTS:
A Collector Adjacent to the Cathode Simulates the Anode Current Collector in the Cell.

The creep test results are summarized in Table 2. Five different ribbed cathode configurations were evaluated. The variables tested were rib type, powder type, porosity, and rib to groove width ratio. The results indicate that the Ni powder type has the greatest effect on creep. Inco Ni 287 powder (Ribbed #2) crept only half as much as Inco Ni 255 powder (Ribbed #3). Ni 255 has been preferred over Ni 287 in the past because of its superior fuel cell performance. However, it may not be important in the ribbed cathode design because there's less in-plane gas shielding diffusional loss without a cathode current collector present.

The creep amount of the Ni 287 ribbed cathode (Ribbed #1 and #2) and the baseline planar Ni 255 cathode are approximately the same. This was achieved by densifying the ribs and by optimizing the nickel powder type for the ribbed design. Next, the cell performance and endurance of the ribbed cathode were evaluated.

Table 2. SUMMARY OF RIBBED CATHODE CREEP TESTS:
The Powder Type and Rib Density have the Largest Affect on Creep.

Ribbed Cathode Design #	Rib Type	Nickel Powder Type	Cathode Porosity in Loading-Bearing Area (%)	Ratio of Rib to Groove Width	Cathode Thickness Pre-test (mil)	Creep (mil)	Creep (%)
Baseline Planar	None	Ni 255	78	None	35	4	11
#1	Machined	Ni 287	72	1.2:1	97	2	2
#2	Machined	Ni 287	72	0.9:1	95	4	4
#3	Machined	Ni 255	72	0.9:1	104	9	9
#4	Molded	Ni 255		0.8:1	96	12	13
#5	Machined Inverted	Ni 287 (ribbed) Ni 255 (planar)	72 (ribbed) 77 (planar)	1.2:1	112 (95, ribbed, 17 planar)	6	5

Standard Test Conditions = 1000h @ 670%, 35 psi load, simulated cathode gas = 17% CO₂, 11% O₂, 12% H₂O, 60% N₂

2.2.4 Ribbed Cathode Cell Performance and Endurance

The ribbed cathode design variations #1, 3, 4 and 5 (as described in Table 2) were tested in bench-scale (7" x 7") single cells. A comparison of the beginning-of-life (BOL) cell voltages of the various designs is illustrated in Figure 5. The Ni 287 ribbed cathode designs (Ribbed #1 and #5) had the best performance, even superior to the baseline planar cathode. The improvement in BOL cell voltages arises from having no collector, which causes gas shielding diffusional loss. The performance benefits become even greater at higher currents, as shown in Figure 6.

The performance of the Ni 255 ribbed cathode (Ribbed #3, Ribbed #4) was inferior to the Ni 287 ribbed cathode, as expected, because of its higher creep rate. An improvement in performance stability by the Ni 287 ribbed design is evident in Figure 7. The stability improvement is attributed to having less electrolyte loss and a larger BOL electrolyte inventory. The single cell tests on the Ni 287 ribbed cathodes (designs #1 and #5) have demonstrated improvements in longevity and performance. Plans are now underway to test the ribbed cathode design in an 18" x 18" area stack.

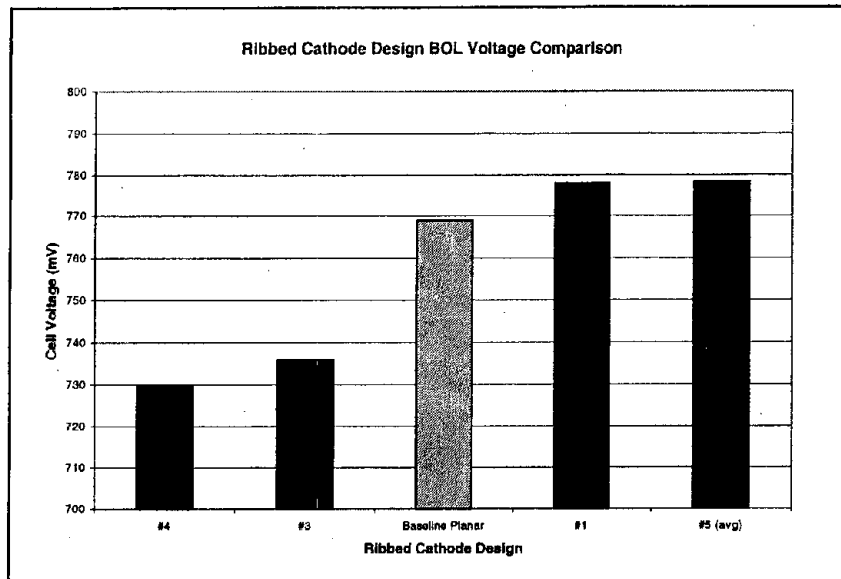


Figure 5. CELL VOLTAGE COMPARISON OF BASELINE AND RIBBED DESIGNS:
The Ni 287 Ribbed Cathode has Superior Performance Compared to the Baseline.

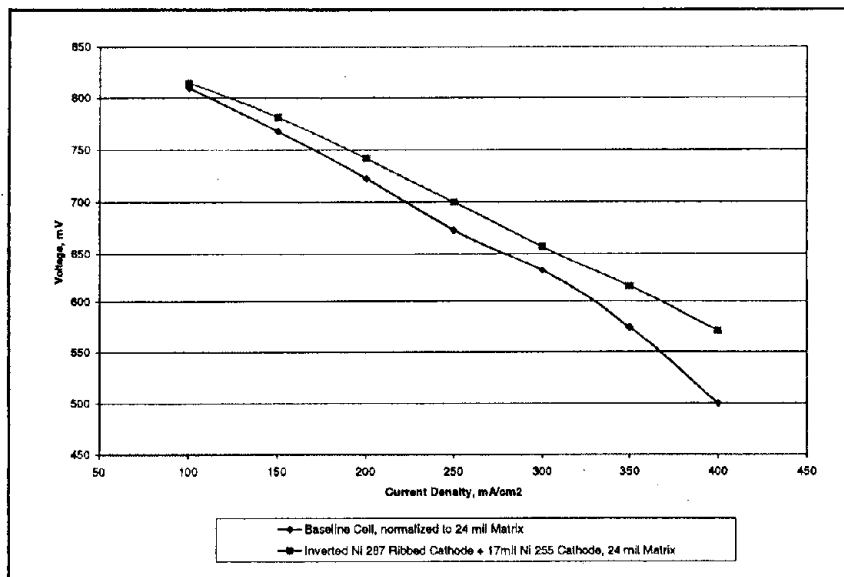


Figure 6. HIGH CURRENT DENSITY TEST OF BASELINE AND RIBBED DESIGNS:
The Ribbed Design Benefits from Reduced Gas Shielding.

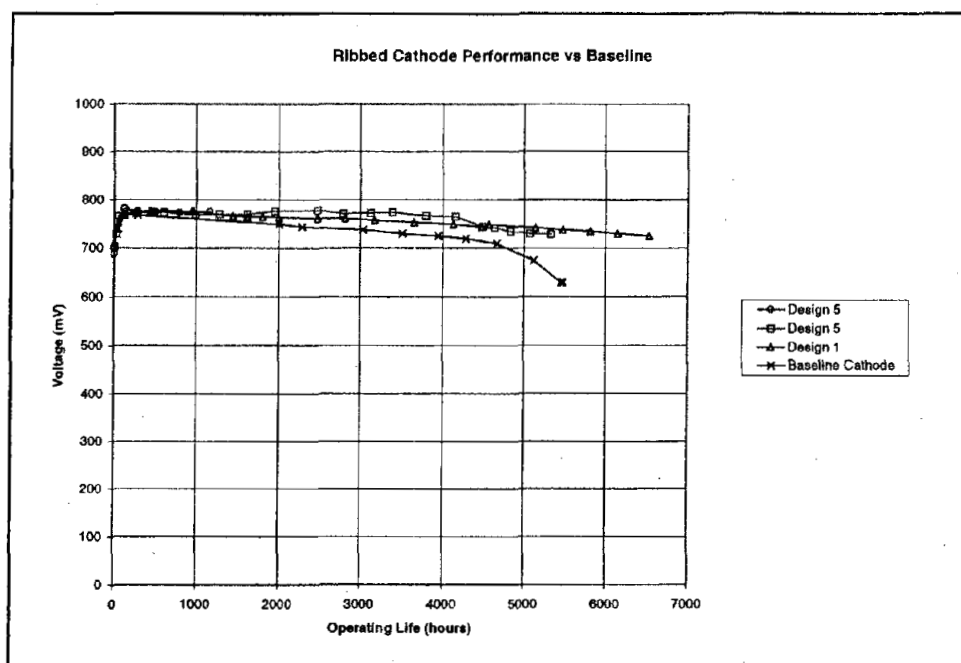


Figure 7. ENDURANCE OF BASELINE AND RIBBED CATHODE CELLS:
The Ribbed Cathode Cells have Superior Performance and Endurance.

2.3 CATHODE CURRENT COLLECTOR OPTIMIZATION

The cathode current collector forms a corrosion layer of lithium ferrite, which consumes lithium carbonate electrolyte during operation. Approximately 25% of the lithium carbonate in the electrolyte is depleted after 40,000h of operation. A possible method of reducing electrolyte loss is to aluminize the current collector surface. Aluminum applied to the surface diffuses into the metal at operating temperatures and forms a protective aluminide layer. The side of the collector facing the cathode can't be aluminized or the resistance of the cell would be too high. However, the side facing the gas channel can be aluminized. Corrosion tests and post-test analysis have shown that electrolyte consumption due to collector corrosion is reduced in half by aluminizing the collector (see Figure 8).

Another possible method of reducing electrolyte loss to the collector is to identify an alternate collector material having a lower corrosion rate than the baseline material, 316L. However, adequate electronic conductivity must be maintained to avoid increasing the cell resistance. Several candidate materials were corrosion tested. The ohmic resistance of the corrosion layers was measured during testing (the results are presented in Figure 9). The materials that were tested were all high-alloy austenitic stainless steels, such as Nitronic 30, Nitronic 50, 20Cb-3, 309, 253MA, 310, 316Ti, 304, 347 and also Co-plated 316L. The following results were obtained:

- Nitronic 30 has nearly equivalent electrical resistance to 316L (as shown in Figure 9) but a somewhat lower corrosion rate (as determined by metallographic examination).

- Nitronic 50, 20cb-3, 309, 310, and 253MA have higher electrical resistance than 316L, but less corrosion.
- The electrolyte consumption rate is 30% higher for 304 and 347 compared to 316L.
- 316Ti and Co-plated 316L have similar electrical characteristics as 316L. The corrosion rates are similar to the baseline 316L material.

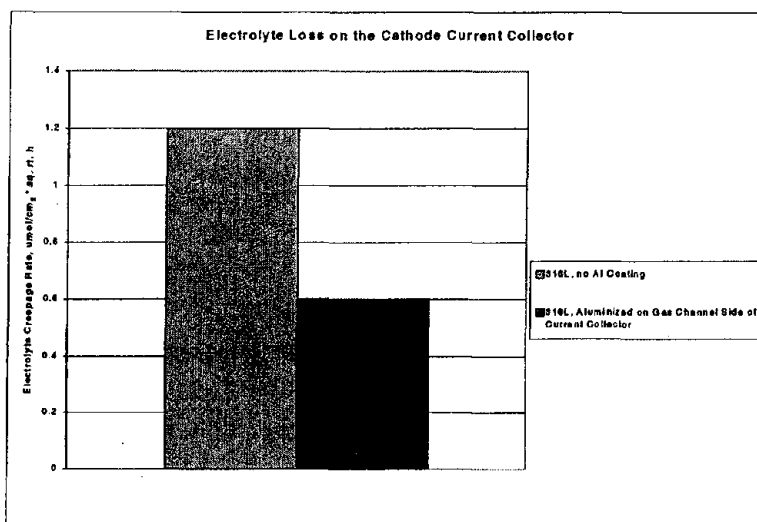


Figure 8. ELECTROLYTE LOSS REDUCTION BY ALUMINIZING THE COLLECTOR:
Aluminization Reduces the Electrolyte Loss Rate in Half.

This analysis indicates that, in general, a trade off exists between conductivity and corrosion resistance. Materials with lower corrosion rates (and lower electrolyte losses) usually have higher resistivities (because of a denser corrosion layer) compared to 316L.

2.4 ELECTROLYTE MIGRATION REDUCTION

The positive end-cells of a stack lose electrolyte faster than the central cells because of electrolyte migration. Migration is caused by the higher ionic mobilities of the positive ions in the electrolyte towards the negative-polarity end of the stack. The electrolyte migrates out of the positive end-cells, through the porous manifold gaskets located on the vertical edges of the stack, to the negative end-cells, as shown in Figure 10. The gaskets make contact with the electrolyte in the matrix and thus provide a continuous path for migration. A barrier placed in the gasket (U.S. Patent 5,110,692, Farooque et al) is presently being used to reduce electrolyte migration. Additional methods for reducing migration are under investigation. These methods have focused on the restriction of electrolyte movement out of the cell.

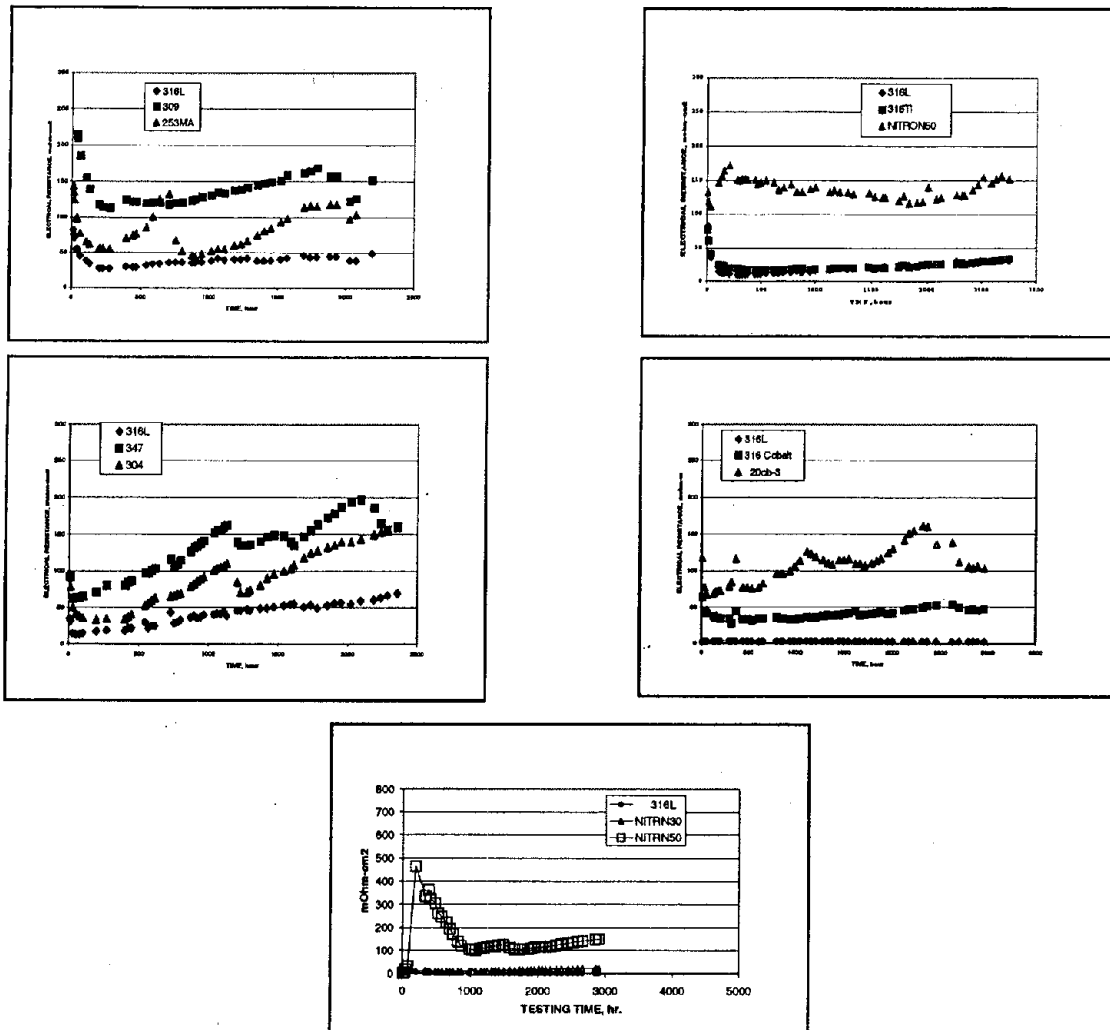


Figure 9. ALTERNATE CURRENT COLLECTOR MATERIAL CORROSION TESTING (650°C, SIMULATED CATHODE GAS ENVIRONMENT):
316L has Low Resistance, but a Relatively High Electrolyte Loss Rate

An out-of-cell test was performed to evaluate a plasma sprayed ceramic coating onto the manifold gasket flange area of the stack for restricting electrolyte movement out of the cell. A 75% ZrO_2 /24% MgO plasma-sprayed coating was successfully applied to a stack simulator test. The coating adhered well through multiple thermal cycles but did not significantly reduce migration compared to the uncoated baseline design. Since the coating density was only 85%, it is possible that the electrolyte still moved through the pores of the coating.

Two other migration tests were conducted to test a "mosaic" design concept, which consists of placing 4mil thick, solid stabilized zirconia strips against the stack face to block electrolyte movement out of the matrix and into the gasket. A 25% reduction in electrolyte migration was achieved in an out-of-cell migration test by the mosaic design. This concept is currently being tested in several full-area stacks.

Another migration test was performed to evaluate a new bipolar plate coating that is needed for corrosion protection. The baseline coating is 2mil thick aluminum applied by thermal spraying.

It is porous and absorbs significant electrolyte; therefore, it may increase migration. The new coating is thinner Al-clad. It promises to reduce costs, enhance corrosion protection and reduce migration. The Al-clad layer is dense and well bonded to the bipolar stainless steel plate. It converts to a diffused intermetallic compound layer during fuel cell operation, providing corrosion protection. Previously, sprayed aluminum coatings required 2mils of aluminum to achieve a uniform diffusion layer. Out-of-cell electrolyte migration tests indicate that the aluminum clad material is sufficient to produce a uniform diffusion layer because it is denser than the sprayed coating. The electrolyte migration due to the coating was reduced by 45% by Al-cladding, as demonstrated in the migration test.

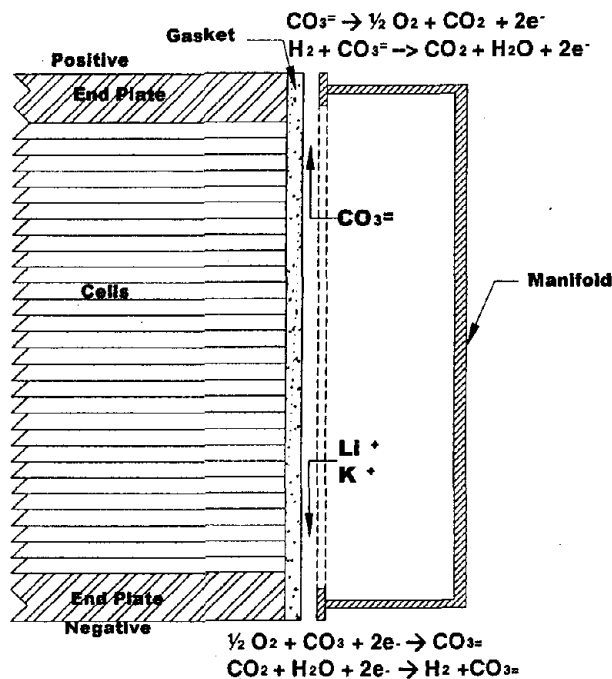


Figure 10. ELECTROLYTE MIGRATION IN A FUEL CELL STACK:
Electrolyte Migrates from the Positive to the Negative End-Cells, Drying Out the Top Cells

3. CONCLUSIONS

- The fuel cell loses ~10% of its electrolyte reservoir in the first 2,000h of operation. Delayed electrolyte addition during the first 2,000h of operation was achieved by storing either lithium or sodium carbonate to the cathode current collector, depending upon the temperature region of the cell.
- The ribbed cathode has been shown to be superior to the baseline current collector in performance and cell longevity. It promises to more than double cell life. A manufacturing method has been development. Implementation into the stack design is proceeding.
- The electrolyte loss on the baseline cathode current collector was reduced in half by aluminizing one side of the collector. An alternate current collector material has not yet

been identified that is superior to the baseline 316L material, although Nitronics 30 is a promising candidate.

- Electrolyte migration, which reduces the life of the end cells, has been significantly mitigated by the "mosaic" design and by increasing the density of the protective coating on the bipolar plate.