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Abstract

Endurance tests of carbonate fuel cell stacks (up to 10,000 hours) have shown that hardware corrosion and electrolyte losses can be reasonably controlled by proper material selection and cell design. Corrosion of stainless steel current collector hardware, nickel clad bipolar plate and aluminized wet seal show rates within acceptable limits. Electrolyte loss rate to current collector surface has been minimized by reducing exposed current collector surface area. Electrolyte evaporation loss appears tolerable. Electrolyte redistribution has been restrained by proper design of manifold seals.

1.0 Introduction

Carbonate fuel cell technology is a highly efficient and environmentally clean source of power generation. Many organizations in the USA, Europe and Japan are actively pursuing the development of the carbonate fuel cell with the aim of commercializing this unique technology before the turn of the century. Excellent BOL (beginning-of-life) performance has been demonstrated by several developers. However, long-term stack endurance needs to be demonstrated for commercial acceptance. A useful life of 40,000 hours is desired for large scale commercialization.

Because the carbonate fuel cell is operated at 650°C in the presence of molten Li/K carbonate, sufficient long-term stability of stack components against oxidation and molten salt fluxing attack is required. In addition, a low electrolyte loss is desired to ensure sufficient electrolyte inventory for long-term performance stability. Status of these important endurance issues has been reported by several research organizations[1-3]. During the past two years, ERC has tested five carbonate fuel cell stacks for 5,000 to 10,000 hours. Detailed post-test chemical and metallographic analyses have been performed on these stacks to evaluate endurance issues. These results, together with out-of-cell test data, have been used to predict the long-term behavior of ERC's stacks. In this paper, ERC's experience with respect to important endurance issues: hardware corrosion and electrolyte loss management, is discussed.

2.0 Corrosion and Material Stability

A schematic of a carbonate fuel cell package is shown in Figure 1. The anode corrugated current collector (ACC), perforated current collector (PCC) and anode face of the bipolar plate are exposed to a reducing atmosphere while the cathode corrugated current collector (CCC), and the cathode face of the bipolar plate are exposed to an oxidizing atmosphere. Hot corrosion of these components in the presence of molten carbonate at 650°C presents a challenge to material selection. Hot corrosion attack degrades mechanical properties of current collectors, accelerates electrolyte loss and contributes to ohmic resistance increase. Therefore, a slow corrosion attack is desired for 40,000h stack operation.

The hot corrosion phenomena of the cathode-side appear to be reasonably well understood[4-10]. Ni-base high-temperature alloys are sufficiently corrosion resistant but not feasible for commercial use due to their high cost. The Fe-Cr ferritic stainless steels are low cost but not adequately corrosion resistant. The Fe-Ni-Cr austenitic stainless steel 310S and 316L are currently the choice for their acceptable cathode-side corrosion resistance and relatively low cost. In addition, Ni coating is generally used in the anode environment for sufficient corrosion resistance (discussed in Section 2.2).

2.1 Cathode-Side Materials

The oxide scale formed at 310S and 316L in the oxidizing cathode atmosphere has a multi-layered structure ($LiFeO_2$ outer and Cr-rich inner scales), as shown in Figure 2. The outer scale formed at the cathode-CCC interface contains a large amount of Ni (>20 mole%), originating mainly from the NiO cathode, and a small amount of Mn (<3 mole%) from the stainless steel substrate. The Cr content in the outer scale is generally very low (<2 mole%). The Cr-rich inner scale also contains significant amounts of Fe and Ni; Cr_2O_3, $FeCr_2O_4$ and $NiCr_2O_4$ have been identified by XRD. The thin Cr_2O_3 layer is present at the metal-scale interface and appears more compact in 310S (containing 25% Cr) than in 316L (containing 18% Cr)[10].

The corrosion resistance of 316L appears to improve with decreasing grain size. A smaller grain size may promote grain-boundary diffusion of Cr from the substrate to the metal-scale interface to form a more compact chromia protective layer[11]. Metallographic analysis of the 316L cathode-side current collectors has shown that the corrosion resistance of 316L appears acceptable for 40,000h use (Figure 3). The 310S, due to its higher Cr content, has shown better corrosion resistance than 316L[6,8,10]. However, more electrolyte loss has been observed for 310S. This will be discussed in Section 3.1.

Several out-of-cell 650°C ohmic resistance experiments (test durations of up to 6,000 hours) have been performed to investigate the stability of cathode-CCC interfacial resistance[10]. The average scale specific resistivity, normalized for contact area and NiO cathode porosity, is shown in Table 1. The oxide formed in 310S is thinner but more resistive, likely due to the presence of a more compact inner chromia scale having a relatively high specific resistivity of ~100 Ωcm. The inner scale at 316L is thicker and higher in Fe content than at 310S; therefore, it is less protective and more electronically conductive. The oxide formed at large-grained 316L is slightly thicker than at fine-grained 316L but has a somewhat lower specific resistivity. Therefore, the overall oxide ohmic losses are similar.

2.2 Anode-Side Materials

In the reducing anode atmosphere, an unprotected stainless steel surface forms a very thick multi-layered oxide scale. The inner layer is rich in $LiCrO_2$ and the compact chromia layer is absent[5,6]. Some Ni-base alloys such as Inconel 600 have demonstrated better corrosion resistance than stainless steels. However, they are not attractive for commercial application because they are expensive and consume Li during the selective internal oxidation of Cr to $LiCrO_2$. Ni is thermodynamically noble in the anode environment. Therefore, surface protection of stainless steels by Ni coating has generally been adopted by fuel cell developers. With the protection provided by the Ni coating, the anode-side bipolar plate has shown virtually no corrosion attack for up to 10,000h operation (Figures 3 and 4). Consequently, no significant ohmic loss due to anode-side contact interfacial resistance was observed. Although a small amount of Cr-rich oxide forms at the grain boundaries of the Ni layer (diffused into the coating from the substrate stainless steels), no deleterious effect on the corrosion protection is observed. The interdiffusion profiles in the Ni coating during the 5,000-10,000h testing is shown in Figure 5. The diffusion of Fe and Cr into the coating appears tolerable. Using the analytical solution available for a one-dimensional unsteady-state diffusion system[12], the diffusion profiles after 40,000h operation can be estimated. Based on this estimation, the Ni thickness of 0.002" may be adequate for 40,000h use. As a point of caution for long-term protection, the Ni coating also should be consistently defect-free.

2.3 Wet-Seal Stability

The wet-seal simultaneously experiences reducing and oxidizing environments; only aluminum-containing alloys possess sufficient corrosion resistance under such environments. Aluminizing has generally been selected as the technique for enhancing surface aluminum content for protection[7,8]. Aluminizing methods include painting, thermal spraying or vacuum deposition, followed by diffusion heat treatment. The resultant diffused coating on stainless steel surface generally consists of a MAl-M_3Al structure (M = Fe, Ni, plus 5-15 mol% Cr). A hard Cr-rich phase and an inner layer with secondary phase inclusions (possibly carbide and σ phases) are also present. The coating has been shown to provide sufficient protection for the substrate stainless steels during a 5,000h out-of-cell and the 10,000h stack testing [Figure 6]. The X-ray microprobe analysis showed that the aluminized coating did not change significantly in 10,000h testing. Based on these results, it could be projected that the aluminized coating is sufficient for 40,000h use provided that a coating of consistent quality is used. The development drive now is to investigate various low-cost aluminizing processes for cost reduction.

3.0 Electrolyte Management

Electrolyte loss mechanisms during carbonate fuel cell operation have been previously reviewed [2,13,14]. The in-situ oxidized hardware surface is ideal for carbonate creepage. The formation of Li- and K-containing corrosion products, such as $LiFe_xO_y$, $LiCrO_2$, K_2CrO_4 and $LiAlO_2$, and the subsequent absorption of electrolyte into the porous oxide scale further increase the loss. Excessive electrolyte loss can cause matrix drying, resulting in increased gas cross-over, electrode polarization and ohmic resistance.

Post-test hardware (both internal and external) has been thoroughly washed and digested to determine the electrolyte loss associated with corrosion and creepage. Electrolyte losses to the external hardware (manifolds, end plates, etc.) and the anode-side internal hardware were found to be very low (<5% of BOL inventory after 40,000 hours projected). On the other hand, electrolyte loss to the cathode-side internal hardware, either by creepage or by incorporation into the oxide scale contributes significantly to the total electrolyte loss (~20% of BOL Inventory).

3.1 Electrolyte Loss to Cathode-Side Internal Hardware

In terms of the creeping electrolyte, the farther away the hardware surface from the cathode, the higher the potassium concentration of the creeping electrolyte (Figure 7). Therefore, the potassium concentration in the creeping electrolyte is highest at the bipolar plate surface (>90 mol%). In the oxide scale, the Li content is significantly higher than K (Li>90 mol%), expected because lithium ferrite is the main corrosion product. These results suggest that Li is consumed into the oxide scale, leaving mainly K (as carbonate and chromate) to continue to creep away on the hardware surface. Vapor phase electrolyte transport (mainly as KOH) also may have contributed to such an electrolyte composition gradient on the cathode-side hardware surface. The creeping electrolyte on the current collector surface also contains substantial Cr, particularly at the bipolar plate surface which is farthest away from the cathode. In fact, almost all the K and Cr found at the bipolar plate surface could be corresponded stoichiometrically to the K_2CrO_4 compound. The formation of K_2CrO_4 may have enhanced the wetting behavior or decreased the melting point (preventing the solidification) of the creeping electrolyte. This may explain the higher electrolyte creepage loss on 310S than on 316L; 310S alloy has a higher Cr content for promoting the formation of K_2CrO_4.

During the past several years, current collectors having different surface areas have been evaluated. The total electrolyte loss to the cathode-side hardware, based on the geometric surface area, is shown in Figure 8. The hardware with the larger surface area experienced proportionately larger total electrolyte loss. Therefore, current collectors of low surface area design are desired.

3.2 Evaporative Electrolyte Loss

The continuous loss of electrolyte by evaporation of electrolyte in the fuel and oxidant streams has always been a concern as a possible cause of long-term performance deterioration. The major evaporated species are KOH and K in the anode gas stream and KOH in the cathode gas stream[14]. Electrolyte evaporative loss rate from stack testing has been reported to be $<5\%$ of the BOL electrolyte inventory after 40,000 hours. Based on this result, electrolyte evaporative loss rate appears tolerable.

Recently, thermodynamic calculation of vapor pressure of volatile species using a modified SOLGASMIX computer program[15] has been performed. The program, expanded using Conforming Ionic Solution Theory[16] to represent ionized species in the liquid carbonate phase, has been used at ERC to study the effect of contaminants on carbonate fuel cell[17]. In the anode exit gas stream of a typical natural gas power plant, only KOH is the major volatile species (Figure 9), agreeing with the reported mechanisms[14]. The partial pressures of LiOH and K are significantly lower. Stack temperature has a very strong effect; therefore, about 95% of the evaporated species are expected to condense out of the exit gas stream by cooling to 550°C. Using the calculated partial pressures, the evaporative loss from the anode side is estimated to be $<3\%$ of BOL electrolyte inventory after 40,000h operation. On the other hand, the calculation showed that the evaporative loss from the cathode side could be higher than from the anode side, primarily due to the much higher cathode gas flow rate. However, cell and stack tests have not shown such a high evaporative loss from the cathode side[14].

3.3 Electrolyte Migration

Electrolyte redistribution by migration has been an important electrolyte management concern. Without electrolyte migration mitigation, stack end-cell life of only 2,000-3,000 hours has been observed. Recent manifold seal design improvements have resulted in significant reduction of electrolyte redistribution by electrolyte migration[18], as evidenced by the performance of a lab-scale stack AL-0.15-3 tested over 7,000 hours; the end-cells in this stack did not show any more decay than the central cells[19]. Extrapolating from the life of this small-area stack (250-cm^2), it is expected that the life of the full-area cells ($>$5000-cm^2) can be extended to more than 40,000 hours (as projected in Figure 10). Long-term stack verification of this design is planned.

4.0 Conclusion

Based on the post-test results of the stack components tested for up to 10,000 hours, the ERC's carbonate fuel cell repeat hardware (bipolar plate, current collectors, Ni coating, and wet-seal aluminizing) appears adequate for 40,000h use. Also, BOL electrolyte inventory appears sufficient for 40,000h life.

Acknowledgement

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TABLE 1. AVERAGE SPECIFIC OHMIC RESISTIVITY OF OXIDE FORMED AT CURRENT COLLECTOR-CATHODE INTERFACE AFTER 2,000h TESTING:

The Specific Resistivity of SS 310S is Higher But
The Overall Resistance of SS310S and SS316L is Similar

MATERIAL	SPECIFIC OHMIC RESISTIVITY (Ω cm)
310S	30 - 40
316L FINE-MEDIUM GRAINED	15-25
316L LARGE-GRAINED	~ 15

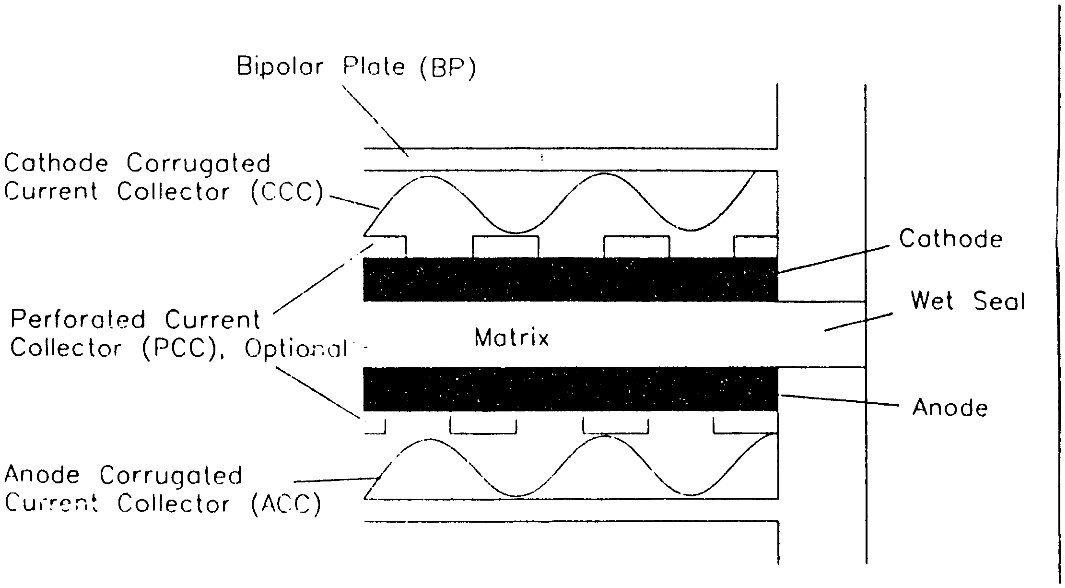

FIGURE 1. SCHEMATIC OF CARBONATE FUEL CELL PACKAGE: The Bipolar Plate, Corrugated As Well As Perforated Current Collectors Are Exposed to Hot Corrosion in Presence of Carbonate Electrolyte

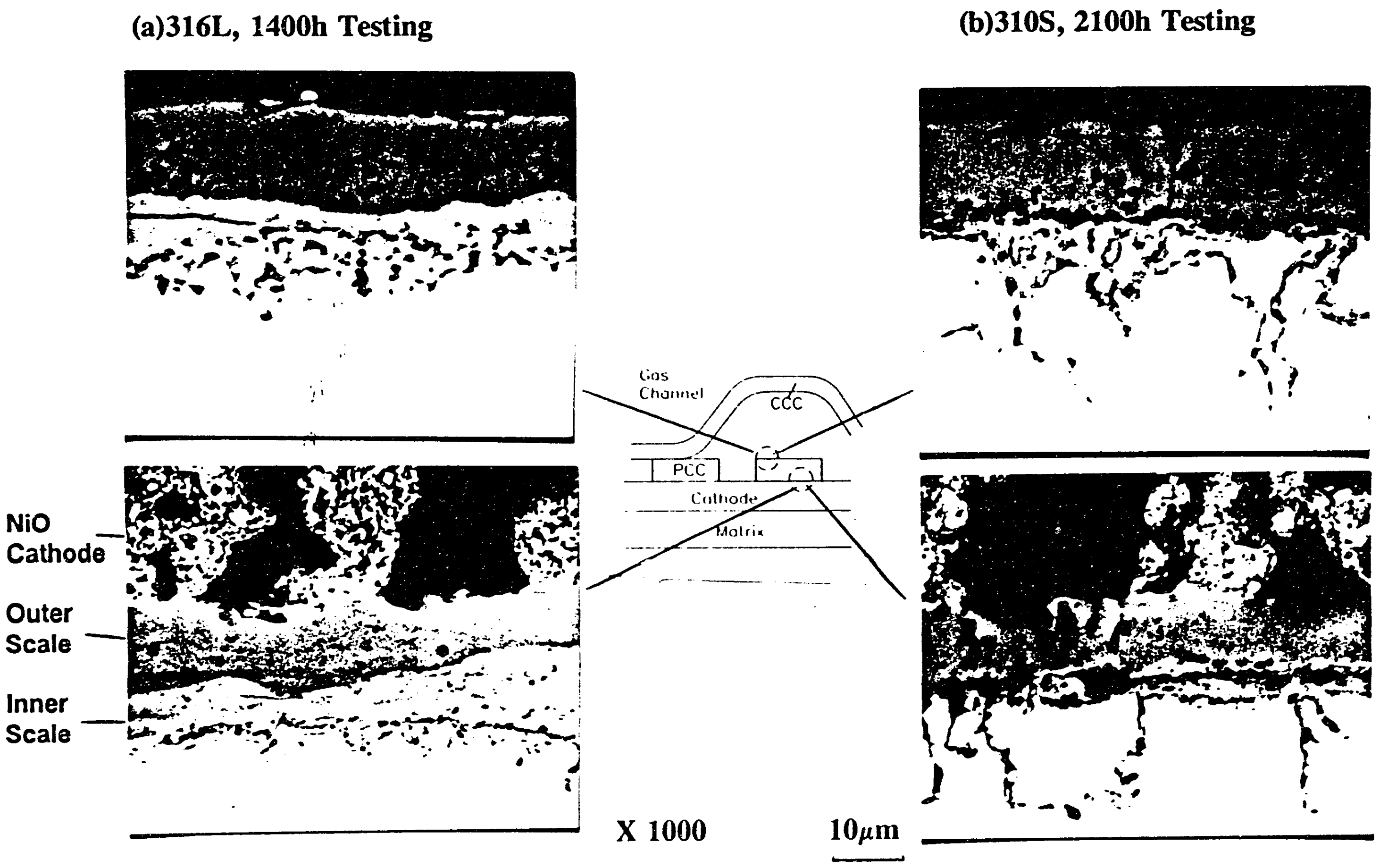

FIGURE 2. POST-TEST OXIDE MORPHOLOGY:
Cr-Rich Inner Protective Layer is Much Thinner in Case of SS310S

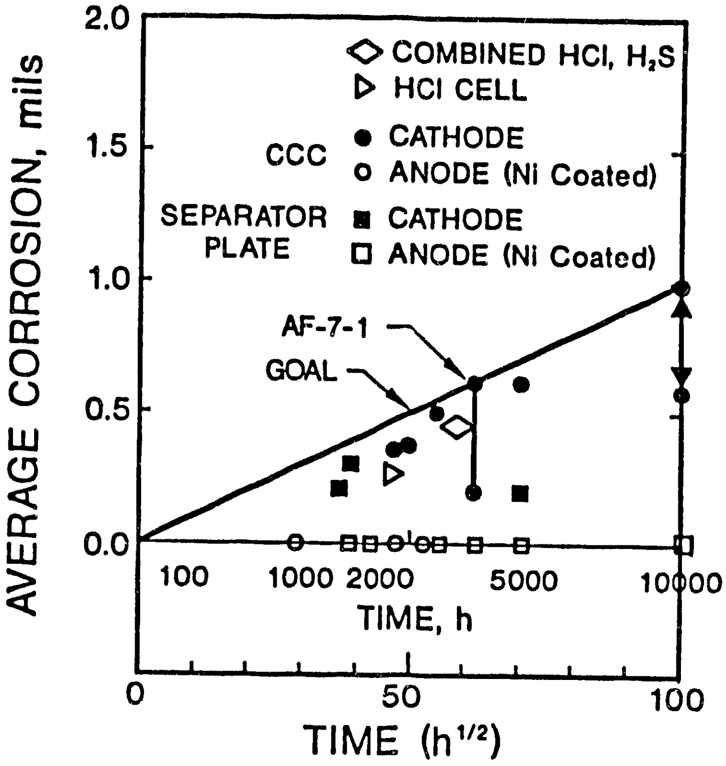

FIGURE 3. CORROSION OF CURRENT COLLECTION HARDWARES:
The Rates Are Within Acceptable Limit

X400 10μm

FIGURE 4. NI COATING AFTER 10,000h TESTING:
Excellent Protection Is Provided by Ni Coating

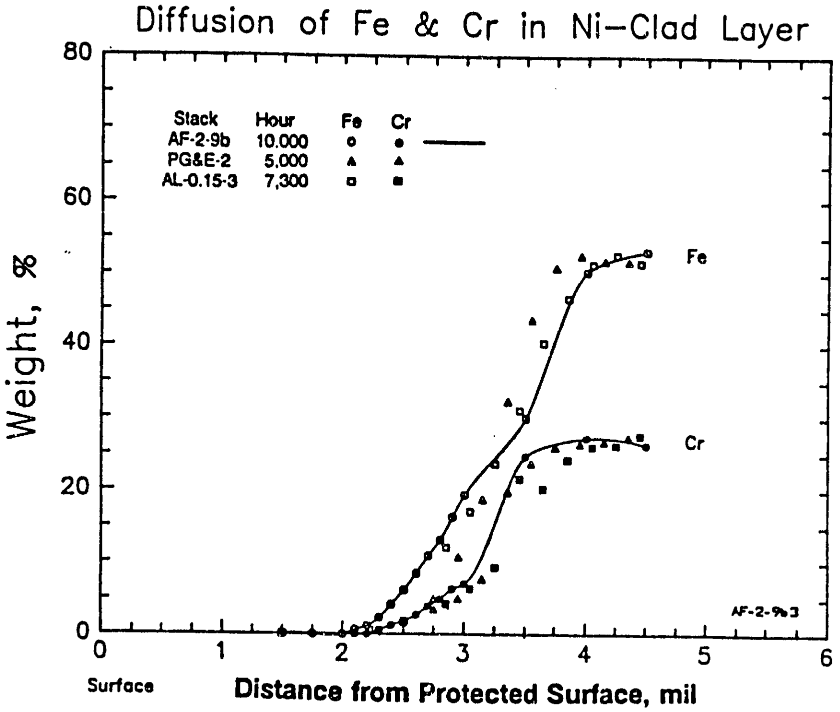

FIGURE 5. Fe & Cr WT% DIFFUSION IN Ni CLAD LAYER:
Protection of Stainless Steel by Ni is Evident

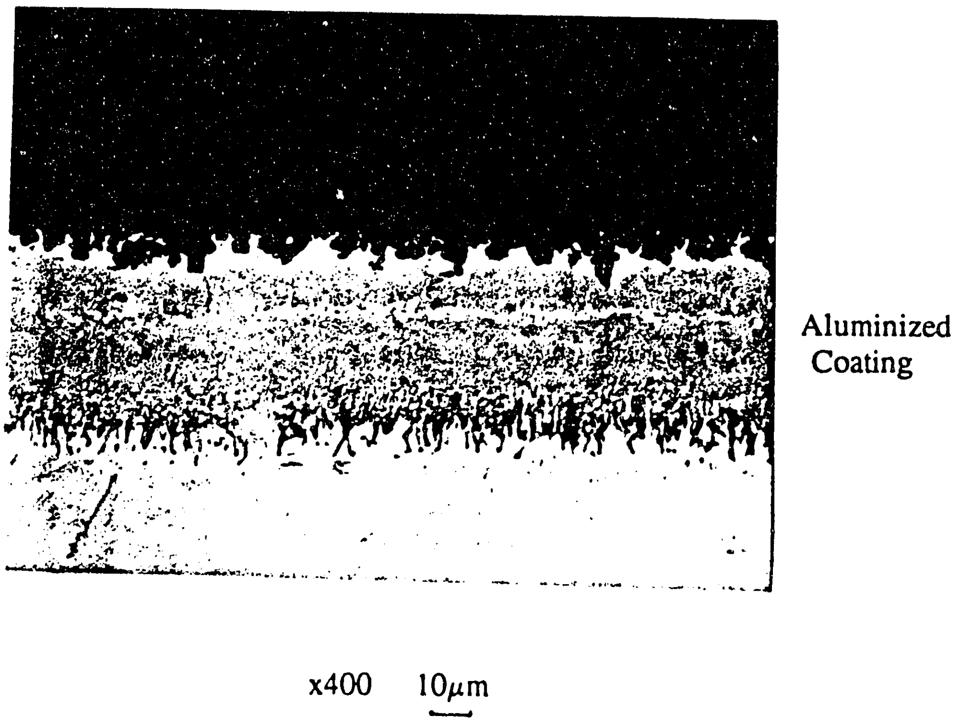

FIGURE 6. PHOTOMICROGRAPH OF 10,000-HOUR STACK WET SEAL:
Wet Seal Appears Stable

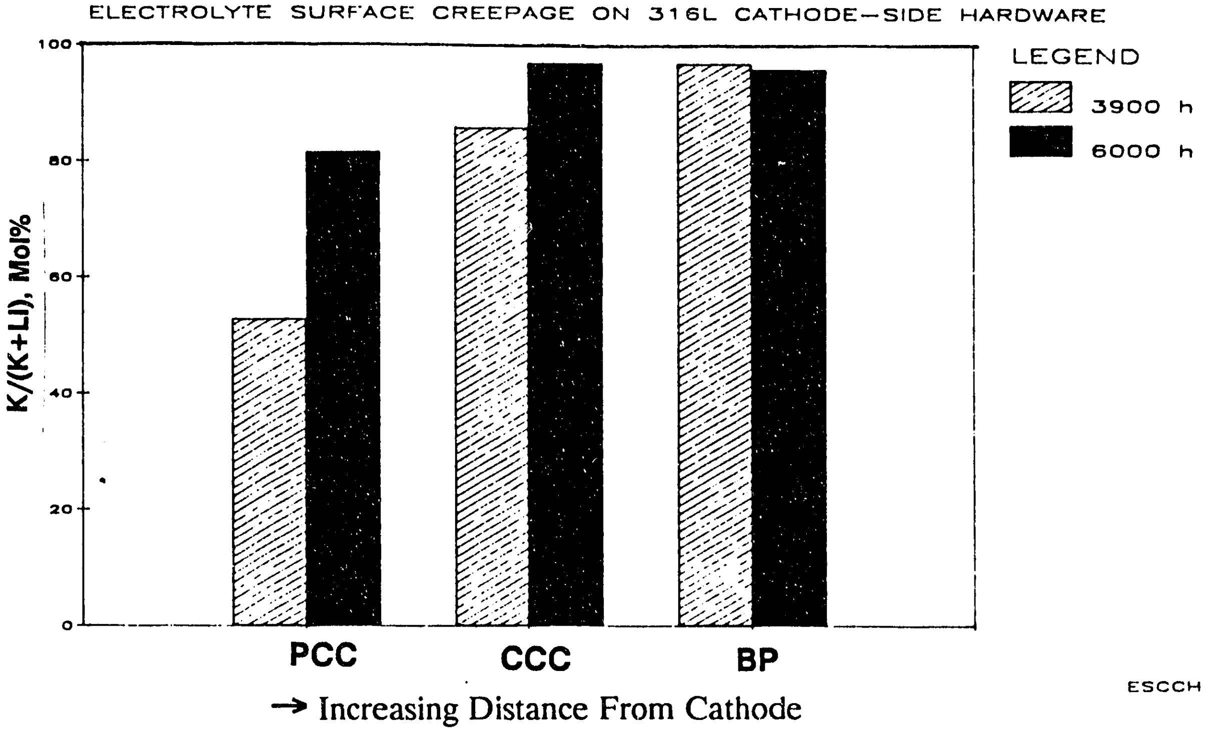

FIGURE 7. POTASSIUM MOLE FRACTION ALONG CATHODE-SIDE HARDWARE SURFACE:
Potassium Mole Fraction of Creeping Electrolyte Increases Farther Away from Cathode

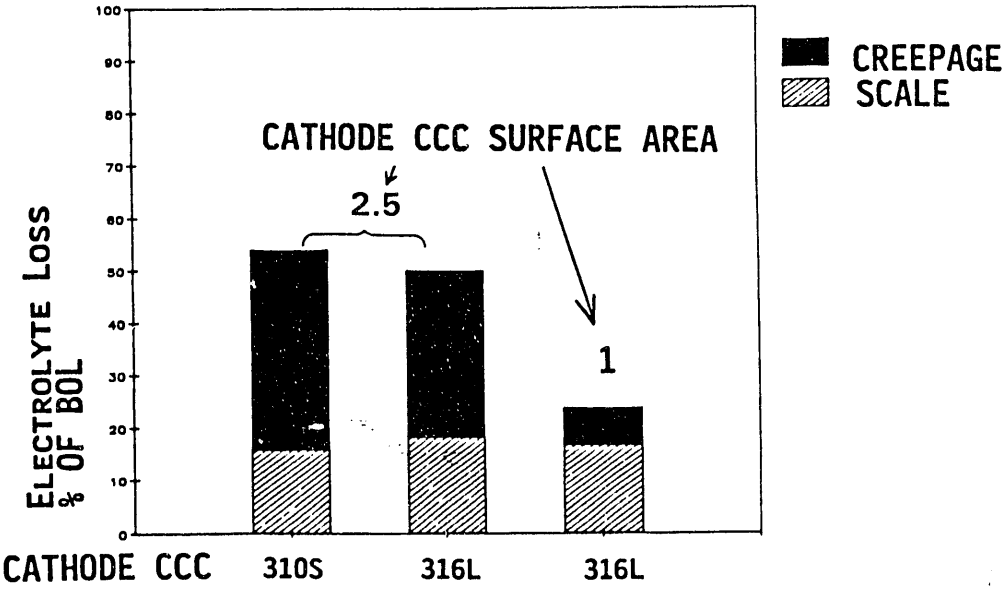

FIGURE 8. PROJECTED ELECTROLYTE LOSS TO INTERNAL HARDWARE (40,000h):
≤25% BOL Loss to Internal Hardware can
be Achieved with Current Collectors
of Reduced Surface Area

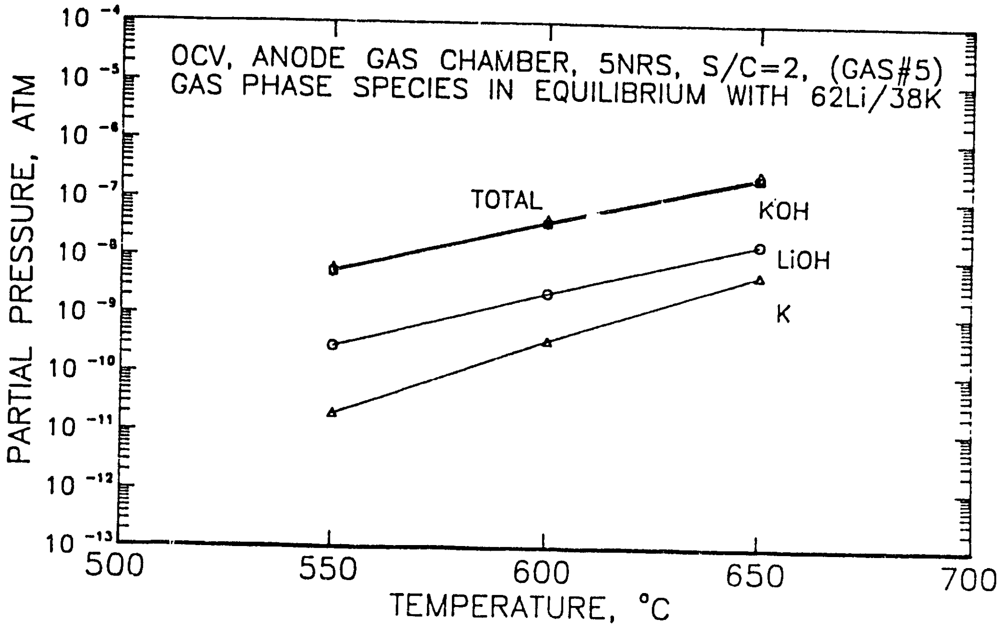

FIGURE 9. CALCULATED VAPOR PRESSURE OF VOLATILE SPECIES IN ANODE ATMOSPHERE:
KOH Is The Major Volatile Species

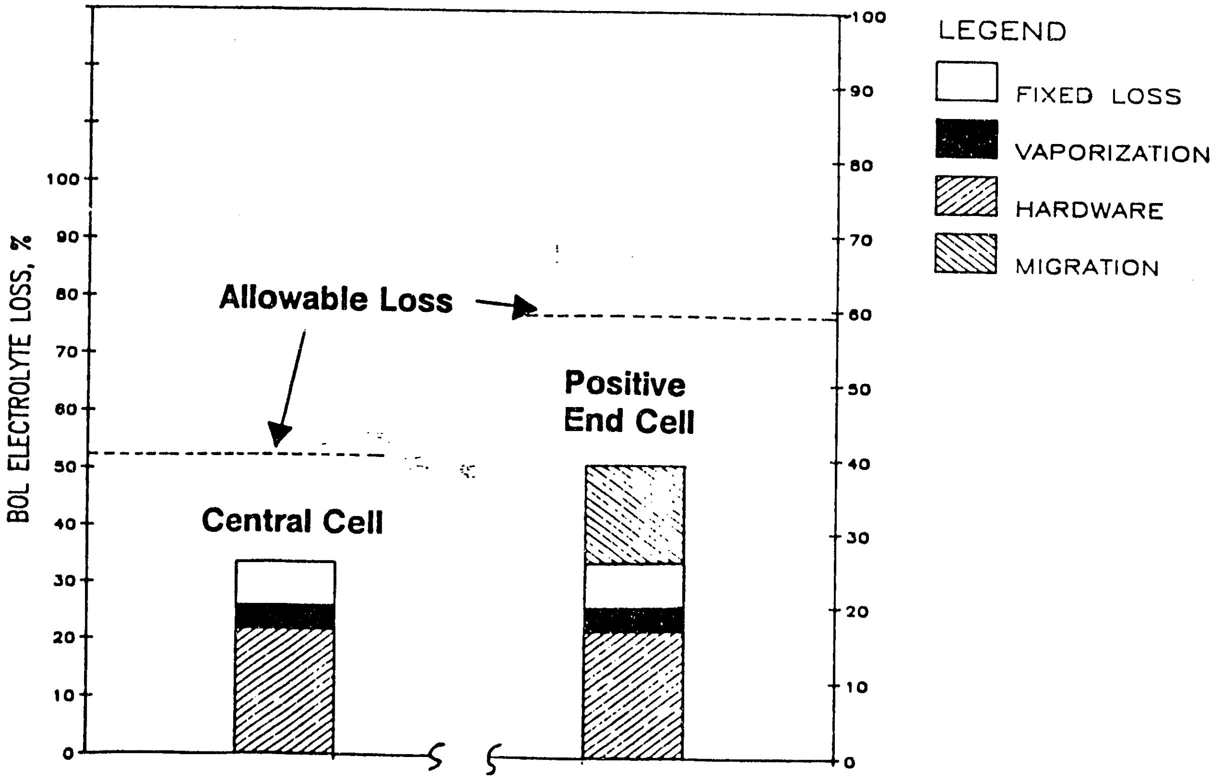

FIGURE 10. PROJECTED ELECTROLYTE LOSS IN 40,000 HOURS:
Projected Loss Well Within Allowable Loss Limit

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