***The effects of halides on the
performance of coal gas-fueled
molten carbonate fuel cells: Final
report, October 1986-October 1987***

Magee, T.P.; Kunz, H.R.; Krasij, M.; Cote, H.A.

Oct 1987

International Fuel Cells Corp., South Windsor, CT (USA)

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The Effects of Halides on the Performance of Coal Gas-Fueled Molten Carbonate Fuel Cells

Final Report, October 1986-October 1987

**T.P. Magee
H.R. Kunz
M. Krasij
H.A. Cote**

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
International Fuel Cells Corporation
195 Governor's Highway
P.O. Box 739
South Windsor, Connecticut 06074

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ABSTRACT

This report presents the results of a program to determine the probable tolerable limits of hydrogen chloride and hydrogen fluoride present in the fuel and oxidant streams of molten carbonate fuel cells that are operating on gasified coal. A literature survey and thermodynamic analyses were performed to determine the likely effects of halides on cell performance and materials. Based on the results of these studies, accelerated corrosion experiments and electrode half-cell performance tests were conducted using electrolyte which contained chloride and fluoride. These data and the results of previous in-cell tests were used to develop a computer model for predicting the performance decay due to these halides. The tolerable limits were found to be low (less than 1 ppm) and depend on the power plant system configuration, the operating conditions of the fuel cell stack, the cell design and initial electrolyte inventory, and the ability of the cell to scrub low levels of halide from the reactant streams. The primary decay modes were conversion of the electrolyte from pure carbonate to a carbonate-halide mixture and accelerated electrolyte evaporation.

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EXECUTIVE SUMMARY

The Department of Energy (DOE), Morgantown Energy Technology Center (METC), is sponsoring several programs aimed at the development of the coal gasifier/molten carbonate fuel cell power plant. Several of these programs are aimed at defining and improving the tolerance of molten carbonate fuel cells (MCFC) to impurities present in coal-derived gases. Other programs have as their objective the development of hot gas cleanup systems for the removal of impurities to enable the mating of the coal gasifier and molten carbonate fuel cell. This report describes the results of a study conducted at International Fuel Cells (IFC) on the effects of halides present in coal-derived gases on the performance of molten carbonate fuel cells.

The program consisted of several tasks. First, a literature survey and thermodynamic analyses were performed to determine the anticipated effects of halides. These results were used to formulate a test plan. The tests included laboratory out-of-cell measurement of the performance of anodes and cathodes with halides present in the electrolyte and corrosion measurements on materials of construction. These data and previous data from in-cell tests were used to develop a model for the prediction of the effects of halides on cell performance. The following paragraphs describe the results obtained in the various tasks.

Task 1 - Literature Survey and Analysis

Halides present in reactant gases are expected to affect molten carbonate fuel cells in several ways. Effects observed in short-term tests performed by the General Electric Company and the United Technologies Corporation include hardware corrosion, presumed anode poisoning, electrolyte con-

tamination, enhanced electrolyte loss, changes in cathode morphology and chlorination of the LiAlO_2 matrix.

Thermodynamic calculations show that halides, in the form of HCl and HF , in the presence of molten lithium and potassium carbonates, are converted almost completely to carbon dioxide, water and lithium and potassium halides. This means that molten carbonate cells are effective scrubbers in removing HCl and HF from the reactant streams. Chlorides are expected to increase the rate of electrolyte loss in the cell due to the high vapor pressures of LiCl and KCl and perhaps pose an electrolyte contamination problem at ppm levels in the gas phase.

Fluorides are expected to cause less of an electrolyte loss problem due to lower KF and LiF vapor pressures. However, the slower rate of fluoride evaporation will convert the electrolyte more readily. The inlet concentration of both halides will have to be maintained at a level low enough so that loss of electrolyte and conversion of the electrolyte will not reduce cell performance excessively.

Nickel anode corrosion due to HCl in the fuel was not seen in any prior in-cell test. Thermodynamic calculations confirm these observations and show that anode corrosion will not be a concern. Anodes were shown to be able to tolerate up to 100 ppmv chlorides, at least in the short term.

Cathode hardware corrosion was considerable even at 10 ppmv HCl . Changes in cathode morphology and a loss of adherence of particles were seen after only six days of 100 ppmv HCl . Thermodynamic confirmation of these observed results was not possible due to the lack of appropriate data.

The LiAlO_2 matrix from a cell operated with HCl in the reactants was found to contain HCl , LiCl , and/or LiAlOCl_2 . These observations could also not be confirmed thermodynamically because of the lack of appropriate

data, but calculations did show that the conversion of the matrix to Li_3AlF_6 is possible.

Post-test analyses of cells that operated with HCl in the oxidant and results of the literature survey indicate that halides in a molten carbonate fuel cell will accelerate the corrosion rate of structural alloys such as AISI 316 stainless steel used in separator plates.

Task 2 - Test Plan

The test plan was based on the understanding of the effects of chlorides and fluorides obtained in the literature survey and thermodynamic analyses.

Hydrogen chloride in a molten carbonate reactant gas is anticipated to react quantitatively with the electrolyte to form chlorides. These chlorides will accelerate the corrosion of cathode-side components and lead to conversion of the electrolyte until the rate of chloride loss balances the rate of input. The vapor pressure of the chlorides is expected to be high enough for these rates to be balanced with a relatively small conversion of the electrolyte from carbonate to chloride. The loss of electrolyte will be greatly accelerated due to the chloride.

Hydrogen fluoride in the reactant gases is anticipated to have somewhat different effects. The effect on corrosion of cathode-side components is unknown. Since the vapor pressures of lithium and potassium fluoride are much less than those of the chlorides, they will not evaporate from the electrolyte as rapidly, and more conversion of the electrolyte may take place. Compared to chlorides, fluorides will affect performance more through electrolyte conversion than through electrolyte loss.

Because of these anticipated effects, out-of-cell tests were planned for Task 3 to determine the effects of chloride and fluoride in the electrolyte

on the corrosion of cathode-side components and to determine the short-term effects of halides on the performance of half-cell tests of both anode and cathode-side components.

Task 3 - Out-of-Cell Investigation

Experiments planned in Task 2 were implemented to determine the effects of chloride and fluoride on the performance of cathodes and on the corrosion of materials of construction. In order to determine the effect of halide in the electrolyte on electrode open circuit potential, a series of open circuit voltage measurements were made between electrodes in halide-free and halide-containing electrolytes. For both chloride and fluoride, the open circuit voltages increased due to the presence of halides, as would be expected, accounting for the reduced carbonate ion activity in the Nernst equation. These data were needed to predict the concentration polarization present in the thin layer of halide-containing electrolyte that is expected to develop in the anode when halide enters the cell through the fuel or oxidant.

Three anode and nine cathode half-cell performance tests were run in which electrolyte content was varied. The content was varied in each test because electrolyte loss is considered to be a major decay mode which is accelerated in the presence of halides. One anode and six cathode tests were performed using 72 mole percent Li_2CO_3 and 28 mole percent K_2CO_3 electrolyte containing no halide. This electrolyte composition was selected because it is the electrolyte composition used in present IFC single cells and stacks. The other two anode tests and three cathode tests were performed using the same electrolyte having various halide contents: 23 anion percent chloride and 23 anion percent fluoride in the anode electrolyte, and 3.1 anion percent chloride, 23 anion percent chloride and 23 anion percent fluoride in the cathode electrolyte.

Initial tests on halide-free electrolyte indicated that the data were not reproducible enough to accurately determine the effects of halides. Modi-

fications incorporated into the half-cell improved reproducibility.

Performance results from tests having halide in the electrolyte clearly showed that chloride is detrimental to the cathode performance and the greater the concentration of chloride, the greater the effect. Fluoride, however, had little effect on the cathode. Anodes were not affected by halide in the electrolyte. Diagnostic tests performed in half cells indicated the presence of halide ion concentration gradients which resulted in concentration polarizations in agreement with the results measured earlier in the open circuit tests.

Visual observations were made on the half-cell test components after testing was completed. The thicknesses of components and the electronic resistivities of the electrodes were measured.

The cathode side stainless steel components were found to be significantly corroded by chloride, but not by fluoride. Fluoride, however, caused the nickel-oxide cathode components to swell more than usual. Halides appeared to lower post-test electrolyte chromate which comes from the oxidation of chromium in the stainless steel. The surface of the nickel-oxide components was softened.

Corrosion testing was performed on three structural materials (AISI 310 stainless steel, AISI 316 stainless steel, and Incoloy 825[®]) in the cathode environment using halide-free electrolyte and electrolyte containing 3.1 anion percent chloride or fluoride. Results of these tests indicate that the presence of these halides accelerates the corrosion rate of all three alloys. In a halide-free and chloride-containing environment, the AISI 310 alloy was the most resistant of the three. However, in a fluoride-containing molten carbonate environment, the resistance to corrosion of AISI 310 alloy was comparable to that of AISI 316 and somewhat lower than that of Incoloy[®] 825.

Metallographic and weight change data suggest that the halides accelerate the corrosion of the alloys by detrimentally affecting the adherence of the protective scales. This is evidenced by more oxide spalling in samples tested in the halide-containing environments than in the control samples.

SEM/Microprobe analyses showed that the oxide scales formed on the three alloys were similar in composition. The resistance of the alloys to corrosion appeared to be related to the uniformity, continuity, and compactness of the chromium-rich oxide protective layer. Breakdown of this layer resulted in increased corrosion. In the presence of fluoride, the corrosive attack appeared to be more intergranular in nature for all three alloys. This is evidenced by the appearance of a chromium-rich oxide phase in the outermost grain boundaries of the base metal and by chromium depletion of the grain boundaries.

Task 4 - In-Cell Investigation

The in-cell test data used in this contract were obtained previously under Contract No. DE-AC01-79ET15440 between the Department of Energy and International Fuel Cells. Those experiments consisted of ambient pressure endurance tests with 10 ppm and 60 ppm HCl added to the fuel gas. Both tests were run until a large decay in performance was experienced, about 40 mv in 522 hours for the 10 ppm test and 80 mv in 10 hours for the 60 ppm test.

Task 5 - Post-Test Analysis

After the completion of the half-cell tests, post-test observations were made on each component. Observations included thickness and resistivity measurements and visual inspection of each part. The most significant effect found in the half-cell post-test analysis was the corrosion and

spalling of the cathode side stainless steel in the presence of chloride. A similar effect was observed to be not as pronounced in the presence of fluoride.

A potentially significant effect was observed in the case of nickel oxide in the presence of fluoride. In this case the nickel oxide swelled in thickness twice as much as in any other test, even more than the nickel oxide in the presence of chloride. The fluoride may have affected the oxidation and lithiation of the nickel, but the fluoride itself may have entered the lattice structure of the NiO. Under external component compression, this could lead to a denser cathode and a change in electrolyte distribution throughout a cell.

Other important observed effects included a possible interaction between the chromium in the stainless steel and halides, and softening of the nickel oxide components.

Task 6 - Develop a Model to Predict Effect of Halides on MCFC

Using the results of the literature survey, thermodynamic analyses and out-of-cell tests, the mechanisms by which halides cause decay were postulated. A computer model was developed including the major decay modes of conversion of the electrolyte from carbonate to halide and electrolyte loss due to increased vapor pressures. This model was compared to the results of the in-cell tests and found to agree with that data.

The model indicates that halide present in the electrolyte tends to be concentrated in the anode, resulting in a different electrolyte composition between the electrodes. This composition difference results in a concentration polarization and liquid-junction potential and a performance loss. The higher volatility of the halides increases the rate of electrolyte loss. Because the electrolyte is shared between the anode, cathode,

and matrix, electrolyte loss results in some loss from all of these components. The relative amounts depend on the component pore size distributions. Most of the polarization increase due to electrolyte loss for the present cell design was found to be due to the anode.

The tolerance limit of the stack to halides was found to depend on the operating conditions of the stack and the system which incorporates the stack. For example, with halide present in the fuel gas, the halide flow in the fuel vent will increase with time. If that fuel is completely burned to provide carbon dioxide for the oxidant, the halide in the fuel exhaust may reenter the cell in the oxidant inlet. If the halide is scrubbed from the oxidant and transported to the anode, the halide may be trapped within the stack. The tolerance level of such a system would be different from that in which part of the fuel effluent is recirculated.

For a stack operating at 172 ma/cm^2 and 10 atm pressure using a fuel gas obtained from an O_2 -blown Texaco gasifier at 85 percent $\text{H}_2 + \text{CO}$ utilization and an oxidant dilute in CO_2 (to provide long cathode life) at 37 percent CO_2 utilization, the tolerance levels to both HCl and HF are about 0.1 ppm based on a performance loss of 20 mv in 40,000 hours. This result applies to a system in which the oxidant is free of halides. This tolerance level pertains to the present cell package design and initial electrolyte inventory. Tolerance can be increased by increasing cell tolerance to electrolyte loss, by increasing the initial electrolyte inventory, and by adding electrolyte during the power plant life.

This low a tolerance level to halide casts doubts on the assumption made in the model that complete scrubbing of HCl and HF occurs within the stacks and that complete saturation with the alkali metal halides occurs at the fuel exit. At this low halide content, the stack may not be an efficient scrubber and saturator.

Increase in contact resistances between components in the cell due to accelerated corrosion was not included in the model because of the results of the corrosion tests and the low tolerance level in the absence of this loss.

Task 7 - Management and Documentation

All management functions were performed including contract administration, technical control, schedule control, cost control, subcontract management, documentation and communications.

TASK 1 - LITERATURE SURVEY AND ANALYSIS

LITERATURE SURVEY

A literature survey was conducted to obtain any pertinent information on the effects of chloride and fluoride on the performance of molten carbonate fuel cells. The subjects surveyed consisted of experimental tests in which halides had been introduced into cells, properties of mixtures of lithium and potassium carbonate with chloride and fluoride, and the effects of chlorides and fluorides on the corrosion of molten carbonate cell materials. Thermodynamic data obtained in this survey were used to make calculations to determine the modes of decay to be anticipated. These anticipated modes were then compared with observations from the cell tests in which chlorides were introduced.

Observed Effects of Halides in Cells

Chloride, in the form of HCl, was found to be detrimental in short-term subscale molten carbonate fuel cells in two independent studies. General Electric studied the effects of 10 ppmv HCl and 100 ppmv HCl in the fuel and in the oxidant [1]. One cell ran for 24 days with 10 ppmv HCl in the fuel, without any loss in performance necessarily attributable to the halide. A second cell, which ran with 100 ppmv HCl in the fuel for 60 days, suffered slight increases in anode polarization. However, this same cell when run with 100 ppmv HCl in the oxidant for 6 days showed a dramatic loss in cathode performance. A third cell ran for 26 days with 100 ppmv HCl in the fuel and 10 ppmv HCl in the oxidant. Anode and cathode performance started to deteriorate after about 12 days with HCl in the reactant gases.

UTC studied the effects of HCl in the fuel [2]. After 60 ppmv HCl was added to the fuel, the cell decayed 81 mV at 160 ASF in ten hours. Cell

performance recovered quickly and completely after the introduction of halide-free fuel. Later, 10 ppmv HCl was introduced into the fuel causing an immediate loss of 12 mV at 160 ASF followed by 21 days of slow decay. The section describing Task 4 discusses these data in greater detail.

Both GE and UTC found evidence of anode poisoning by large amounts of HCl (60 ppmv or greater). HCl, at low levels of 0.5 to 2 ppm, is known to poison catalysts for the methanation reaction, but poisoning of the shift reaction or the electrochemical oxidation reaction has not been demonstrated in electrochemical cells [3]. Park and O'Brien expected the anode to dissolve by the reaction: $\text{Ni(s)} + 2\text{HCl(g)} \rightarrow \text{NiCl}_2\text{(s)} + \text{H}_2\text{(g)}$ [4], but neither the GE or the UTC study noticed any corrosion of the nickel anode or of the wet seal. GE, however, did find a buildup of corrosion products from the stainless steel hardware in the anode exit gas channel.

The cathode is expected to dissolve by the reaction: $\text{NiO(s)} + 2\text{HCl(g)} \rightarrow \text{NiCl}_2\text{(s)} + \text{H}_2\text{O(g)}$ [4]. The GE study found that with 100 ppmv HCl in oxidant that the NiO cathode showed signs of changes in morphology and a loss of adherence of particles. The cathode hardware was severely corroded and the stainless steel current collector corroded extensively near the inlet side of the cathode. A buildup of corrosion products developed in the cathode exit port, causing the third GE test cell to fail.

Halides react with the electrolyte by: $2\text{HX(g)} + \text{M}_2\text{CO}_3\text{(l)} \rightarrow 2\text{MX(l)} + \text{H}_2\text{O(g)} + \text{CO}_2\text{(g)}$ where X is either F or Cl (or other halide) and M is either Li or K. The GE study, in an out-of-cell test, found that at 923 K with 100 ppmv HCl in the oxidant and fuel, the anode electrolyte tile contained 3.6 wt. percent chlorides after 30 hours and the cathode electrolyte tile contained 1.2 wt. percent chlorides after 58 hours. Electrolyte loss rates through evaporation are expected to increase because of alkali halides in the melt. The UTC test cell, which used considerably less electrolyte

than any of the GE test cells, lost 62 percent of its original electrolyte after 62 days of testing. Kruglov et al. found that Na_2CO_3 and K_2CO_3 in the presence of NaX or KX , respectively, where X is either Cl or F , dissociated, giving off CO_2 [5]. The degree of dissociation of K_2CO_3 at 973 K remained below 16 percent when KX content was below 60 mole percent. GE also conducted X-ray diffraction studies of the LiAlO_2 matrix which revealed that chlorides were present in the form of HCl and LiCl and/or LiAlOCl_2 .

Halide Properties

Thermodynamic property data for most of the species involved in the reaction of halides with the electrolyte were found in JANAF Thermochemical Tables [6]. Other thermodynamic property data were found in Barin and Knacke [7]. Janz et al. has compiled vapor pressure data for Li_2CO_3 , K_2CO_3 , LiCl , KCl , LiF , and KF in their pure states and has also compiled phase diagrams for $\text{LiCl} - \text{KCl}$, $\text{LiF} - \text{LiCl}$, $\text{Li}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ and others involving alkali metals and halides [20]. Janz, also gave references and some data for various physical, thermodynamic and electrochemical properties for numerous molten salts [35]. Janz also assisted in obtaining references through the Rensselaer Polytechnic Institute Molten Salt Data Base.

Materials Corrosion

A computer literature search was conducted to determine the effect of halides on the corrosion of stainless steels, nickel-base alloys, and pure nickel in a molten carbonate environment. Chemical Abstracts (1967-1986), the Metals Index (1966-1986), and the Engineering Index (1970-1986) were searched. No references dealing specifically with the subject of interest were found. A number of references were noted in which the effect of halides on metal corrosion in air at elevated temperatures, in $(\text{Na}, \text{K}) \text{NO}_3$ melts, and in gas turbine hot corrosion environments were addressed.

Since molten carbonate salt mixtures are used in the heat treating industry and in air clean-up systems for scrubbing sulfur oxides, it is improbable that no data were published on the interaction of structural alloys with carbonate/halide salt mixtures. It was deduced, therefore, that the bulk of the work in these areas was conducted before computer files were established. As a result, a manual search of literature published prior to 1966 was conducted. A report on the survey results obtained follows.

In molten salt mixtures of lithium, sodium, the potassium carbonates, austenitic stainless steels and nickel-base alloys form three types of passivated oxide films: metal oxides, spinels, and alkali metal - metal oxides [8]. Cr_2O_3 is normally not found on metal surfaces exposed to the melt. In a study conducted by Grantham et al. [8], at a temperature range of 930 - 1290°F (499 - 699°C) it was determined that the metal oxides were predominantly iron and nickel oxide, the spinels were predominantly iron chromite, FeCr_2O_4 , and lithium chromite, LiCrO_2 , was the major constituent of the alkali metal - metal oxide film. The metal oxide films were found to be more prevalent at lower temperatures and in longer duration tests. The spinel structure was the dominant film at 930°F (499°C) even after one year of exposure. A cubic, disordered LiCrO_2 film as observed at lower temperatures and shorter times.

These investigators noted that the metal oxide film initially formed transforms into cubic LiCrO_2 which in turn transforms into the hexagonal LiCrO_2 film by the action of the melt. The protectiveness of the LiCrO_2 film was attributed to the compactness and tenacity of this material. Of the three alkali metals in the melt, only lithium was small enough to get into the LiCrO_2 octahedral interstice without distorting the lattice. It was suggested that LiCrO_2 was formed from two precursors: the metal oxide film, containing lithium, and the cubic oxide alkali metal - metal oxide film. The corrosion process was believed to be diffusion controlled.

In another study [9] conducted in a binary $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ fuel cell electrolyte at 1205°F (652°C), LiCrO_2 and LiFeO_2 were found to be the major constituents of the corrosion product on an AISI 316 anode housing. It was also found that a LiAlO_2 coating on AISI 316 hardware offered good corrosion protection in a molten carbonate environment, especially in the wet seal areas.

Since the corrosion resistance of alloys subjected to a mixture of molten carbonate salts appears to be dependent on the formation of a protective LiCrO_2 film, any contaminant which interferes with the formation of this protective layer would be expected to lower the alloys corrosion resistance. The detrimental effects of sulfide in mixtures of alkali metal carbonate melts in the Molten Carbonate Process for removal of the oxides of sulfur from power plant stack gases [1] and in recovery processes for spent pulping liquors in the paper industry [10-12] is documented in the literature. The corrosion rates in sulfur-containing melts was found to be orders of magnitude higher than in pure carbonates. The effect of halides on metal corrosion in a molten carbonate environment is not as well documented, at least in recent literature, but the available data also indicates that accelerated corrosion rates can be expected.

Investigators at General Electric [1] found that in a fuel cell molten carbonate environment addition of 100 ppm of HCl caused severe corrosion problems of cathode AISI 316 hardware at 1200°F (650°C). The corrosion was severe enough to cause almost complete plugging of the gas passages with corrosion products. The corrosion was extensive at the inlet side of the current collector and extended for only a few millimeter downstream. Addition of 10 ppm HCl was not a problem on the cathode side at 1200°F (650°C) but was expected to cause corrosion problems at lower temperatures.

On the anode side, there was no evidence of chloride induced corrosion of the anode or cell hardware after one month of exposure to a melt containing

10 ppm HCl. Thermodynamic calculations supported these results at 1200°F (650°C). However, it was predicted that 100 ppm HCl would cause chlorination of anode hardware at 662°F (350°C).

In the heat treating industry, molten mixtures of carbonates, chlorides, and other salts are used for heat treating baths for steels and non-ferrous alloys. For example, the Metals Handbook [13] lists a salt bath conforming to a military specification, MIL-S-10699, which consists of a mixture of equal amounts of Na_2CO_3 and KCl, and is used for tempering steel in the temperature range 1150 - 1700°F (621 - 927°C). Compatibility studies conducted on alloys of which contaminant vessels for these molten salt mixtures are made should provide pertinent information to the present study. Although no specific references are given in the Metals Handbook, the recommended materials of construction for salt bath pots are alloys with 30 - 40 percent Ni and 15 - 23 percent Cr, such as RA 330 and Incoloy. The Corrosion Handbook [14] recommends the use of 14 - 18 percent Cr, nickel-base alloys as materials of construction for fused salt pots to contain KCl/ Na_2CO_3 .

Jackson and LaChance [15] evaluated a number of Fe-Ni-Cr cast alloys in molten neutral heat treatment salts with 50 percent Na_2CO_3 - 50 percent KCl salt differed significantly from that in the NaCl-KCl or NaCl-KCl- BaCl_2 salt mixtures. They plotted the corrosion rate vs. percent of chromium or nickel in the alloy and showed that in the Na_2CO_3 - KCl molten salt alloys which had a chromium concentration of 26 - 36 percent were most susceptible to corrosion as were alloys with 10 - 15 percent nickel. The HH alloy (25 Cr-12 Ni) was, therefore, ruled out as a material of construction for salt pots. The HK-40 (25 Cr-20 Ni), HT (15 Cr-35 Ni), and HW (12 Cr-60 Ni) performed well in this service.

In their study of iron in melts containing sodium halides and carbonates at 700 C, Kochergin and Ignat'eva [16] found an activating effect of Cl^- and F^- ions on oxidation of iron which was attributed to their adsorptive

displacement of oxygen from the iron surface. They found that the rate of oxidation in a Na_2CO_3 - 50 percent NaF melt was slightly higher than in a Na_2CO_3 - 50 percent NaCl melt. They also noted that the thermal dissociation of sodium carbonate at 800°C increased with halide addition. The fluoride had a more pronounced effect than the chloride.

Baraka and Baraka [17] studied the behavior of nickel in halide-containing (Na,K) NO_3 melts at 752°F (400°C). They found that corrosion of nickel increased in the presence of Cl^- and Br^- but decreased in the presence of I^- . They noted that the oxidation interaction at constant temperature occurs at a rate which was dependent on the nature of the halide ion present. The rate of this oxidation process increased generally in the order Cl^- , Br^- , I^- and was attributed to the increase of O^{2-} in the melt. The presence of F^- greatly increased the rate of Ni corrosion. This was attributed to the small size of the fluoride ion and its high reactivity. It was postulated that fluoride penetrates the oxide layer and forms insoluble nickel fluoride.

Several references were found in which the effects of gaseous HCl on oxidation of Fe-Cr-Ni alloys were studied. Although in a molten carbonate fuel cell environment incoming gaseous HCl would be expected to be converted to lithium and potassium chlorides, these data provide pertinent information relating to corrosion problems which will be encountered in the inlet lines to the fuel cell. Ellcott and Marsh [18] have shown that introduction of 500 ppm HCl(g) into moist air significantly reduces the oxidation resistance of Incoloy 800 alloy at 1472°F (800°C), especially during temperature cycling. The accelerated corrosion was attributed to the combined presence of voids and chloride-enriched phase at the alloy-oxide interface. This resulted in reduced adhesive strength of the oxide and severe oxidation rates in presence of HCl (g) were increased. This was attributed to enhanced rates of transport of reactive components to the oxidizing surface and to some reactive

volatization. It was suggested that the presence of a chloride-rich region beneath the oxide facilitated such transport.

Similar results were obtained by Hossain and Saunders [19] in their study of the oxidation of a Ni-Cr-Al alloy at 1562°F (850°C) in air containing HCl gas. In moist air, HCl gas caused the oxide formed on the Ni-Cr-Al alloy to crack during the early stages of growth and extensive blistering and spalling of the oxide occurred on cooling. In dry air containing HCl, no cracking was observed but the oxide blistered and spalled on cooling. In dry or moist air free from HCl, an adherent protective oxide formed which did not spall. They attributed the oxide cracking at temperature to the production of H_2 by reaction to Cr and Al in the alloy with water vapor and removal of NiO as $NiCl_2$ by reaction with HCl gas. The H_2 , thus produced, dissolved in the alloy at temperature; but on cooling, hydrogen was released causing the oxide to blister and spall. Pre-oxidation of the alloy before subjecting to an HCl-containing environment eliminated the effects of HCl in short-term, isothermal tests.

Results of this survey indicate that halides in a molten carbonate fuel cell will accelerate the corrosion rate of structural alloys. The survey also shows that very little work was done to specifically evaluate the effects of halide contamination in a molten carbonate fuel cell environment. This points out the need for additional work in this area to characterize better and define the mechanisms involved.

THERMODYNAMIC ANALYSIS

Although thermodynamics cannot be used alone to determine the modes of decay due to halides, it does provide a guide to the modes to be anticipated. Where thermodynamic properties were found, calculations were performed to determine the equilibrium composition of fuel cell components in the presence of chloride and fluoride. Data were available to calculate the equilibrium

composition of the electrolyte in the presence of hydrogen chloride and fluoride, the vapor pressures of the alkali metal chlorides and fluorides over the electrolyte, nickel anode potential for chloride formation, and lithium aluminate matrix material composition.

Electrolyte

Halides in the form of either HCl or HF are anticipated to react with the molten carbonate electrolyte by:

where M represents either lithium (Li) or potassium (K).

Halides accelerate electrolyte loss by converting the carbonate to gaseous carbon dioxide and by vaporization of MCl or MF. In the gaseous state, MCl and MF can polymerize. Equilibrium constants for reactions 1-1, 1-2, vaporization and polymerization were calculated and are given in Appendix A.

From these equilibrium constants, the equilibrium vapor pressures can be determined and compared with available data or correlations. In Figure 1-1, these calculated vapor pressures, $P_{\text{KCl}} + P_{\text{K}_2\text{Cl}_2}$ and $P_{\text{LiCl}} + P_{\text{Li}_2\text{Cl}_2} + P_{\text{Li}_3\text{Cl}_3}$ are plotted as a function of anion fraction chloride $\{\text{Cl}^-\}$ with $\{\text{Li}^+\} = 1$, $\{\text{K}^+\} = 1$ and $\{\text{K}^+\}/\{\text{Li}^+\} = 0.38/0.62$. Here $\{\text{Li}^+\}$ and $\{\text{K}^+\}$ are the cation fractions of lithium and potassium respectively. The pure alkali-metal chloride data were obtained from Janz et al. [20]. The value for KCl is an extrapolation out of the range given by Janz et al.

As can be seen from Figure 1-1, the calculated vapor pressure of the pure chlorides are in reasonably good agreement with data. A similar plot for

fluoride is found in Figure 1-2. The experimental results for fluorides shown in Figure 1-2 are extrapolations and are in less satisfactory agreement with calculations.

Figure 1-1. Alkali-Metal Chloride Vapor Pressure as a Function of Chloride in Melt

Figure 1-2. Alkali-Metal Fluoride Vapor Pressure
as a Function of Fluoride in Melt

At steady state, the amount of halide reacting with the electrolyte will equal the amount of halide leaving the electrolyte. Therefore, at any given halide concentration in the gas phase, it is possible to calculate the anion fraction halide in the melt.

In order to obtain an estimate of the steady state halide concentration in a cell, a set of operating conditions and a system configuration were selected which include reactant compositions associated with an O_2 -blown Texaco coal gasifier molten carbonate fuel cell power plant. The operating conditions are:

Temperature = 650°C

Pressure = 1 atm

Oxidant composition: 8.9% CO₂, 11.7% O₂, 79.5% N₂ - 55°C dew point

Oxidant utilization = 37%

Fuel composition = 56.2% H₂, 10.5% CO, 33.4% CO₂ - 80°C dew point

Fuel utilization = 85% (H₂ + CO)

Current density = 172 ma/cm²

Halide was assumed to enter the stack in the fuel gas. The fuel effluent from the stack was then completely burned in the inlet oxidant without venting so all of the halide leaving in the fuel would be returned to the stack in the oxidant stream. Under this situation, when steady state is reached in the stack, the mass flux of halide leaving the stack in the oxidant stream must be equal to that in the inlet fuel. The concentration of halide in the oxidant effluent is much less than that in the fuel inlet because the ratio of oxidant-to-fuel volume flow rates is 10.7 in this case.

The electrolyte was considered to be homogeneous in composition in this calculation. In actual practice, the halides would be preferentially scrubbed from the fuel inlet stream near the fuel inlet location. Also, a gradient in halide concentration would exist between the anode and cathode due to different concentrations in the gas streams, the production of carbonate ions at the cathode, and the consumption of carbonate ions at the anode. The oxidant effluent was considered to be in equilibrium with this uniform electrolyte composition.

The steady state compositions obtained using these assumptions are presented in Table 1-1 as a function of the halide concentration in the fuel inlet. For the case of 10 ppm chloride and 10 ppm fluoride in the fuel inlet stream, 0.933 ppm chloride and 0.933 ppm fluoride would be present in the oxidant effluent. These effluent concentrations are in equilibrium

with an electrolyte containing 0.031 anion fraction chloride and 0.56 anion fraction fluoride. Results for other concentrations in the oxidant gas are presented in Figure 1-3.

Table 1-1. Steady State Halide Concentrations
in Electrolyte

<u>ppmv Halide in Fuel</u>	<u>ppm Halide in Oxidant</u>	<u>$\{Cl^{-}\}$ in Cathode Melt</u>	<u>$\{F^{-}\}$ in Cathode Melt</u>
1	0.0933	<0.01	0.067
5	0.4665	0.016	0.31
10	0.933	0.031	0.56
50	4.665	0.13	1
100	9.33	0.23	1

Figure 1-3. Steady State Halide Balance

At these operating conditions, assuming that the cell contains 13g of $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ (62/38 molar %) electrolyte and that no halide leaves the cell in the oxidant effluent prior to reaching steady state, the inlet flux of each halide in the fuel is sufficient to completely convert the electrolyte in 16,200 hours. Since the steady state concentration of chloride is only 0.031 ion fraction, steady state for chloride would be reached in the order of 500 hours. For fluoride, since the steady state ion fraction is much higher at 0.56, the time for fluoride conversion is of the order of 9000 hours.

These results indicate that chloride and fluoride may have different decay modes. Chloride will achieve steady state relatively quickly with a small chloride ion concentration. Electrolyte will be lost by evaporation into the oxidant effluent. Conversely, fluoride will reach steady state slowly with a large electrolyte conversion and a slow rate of electrolyte loss. The large electrolyte conversion could result in a gradient in electrolyte composition between the anode and cathode as mentioned previously. This composition difference would result in a performance loss due to an electrolyte concentration polarization, a liquid-junction-potential effect, and perhaps increased cell internal resistance and electrode polarizations.

This case considered an operating pressure of 1 atm. At 10 atm, the volume flux of oxidant from the cell would be reduced by a factor of 10 due to the increased oxidant density. A much higher electrolyte conversion would result before the flow of halide from the cell would balance the input flow.

Anode

The nickel anode is expected to react with HCl by: $\text{Ni(s)} + 2\text{HCl(g)} \rightarrow \text{NiCl}_2\text{(s)} + \text{H}_2\text{(g)}$ [4].

This reaction will occur only if $P_{\text{H}_2}/P_{\text{HCl}}^2 < K_{\text{eq}}$, where

$$K_{\text{eq}} = \exp \left[\frac{1}{RT} (\mu_{\text{Ni}}^{0,s} + 2\mu_{\text{HCl}}^{0,g} - \mu_{\text{NiCl}_2}^{0,s} - \mu_{\text{H}_2}^{0,g}) \right] \quad (1-3)$$

At a given hydrogen pressure the anode will be at a potential defined by the equation:

$$E = E^\circ + \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{P_{\text{H}_2}} \right) - \frac{RT}{2F} \ln (P_{\text{O}_2}^{1/2} P_{\text{CO}_2})_{\text{REF. ELECTRODE}} \quad (1-4)$$

where the potential is referenced to an O_2/CO_2 reference electrode,

E° = potential at standard states of unity activities

F = Faraday's constant (96487 coulombs/equivalent)

Combining (1-3) and (1-4):

$$E = E^\circ + \frac{RT}{2F} \ln \left(\frac{P_{H_2O} P_{CO_2}}{P_{HCl}^2} \right) - \frac{RT}{2F} \ln (P_{O_2}^{1/2} P_{CO_2})_{REF. ELECTRODE}$$

$$\text{where } E^\circ = \left(\mu_{NiCl_2}^{0.5} + \mu_{H_2O}^{0.5} - \mu_{Ni}^{0.5} - 2\mu_{HCl}^{0.5} - \frac{1}{2} \mu_{O_2}^{0.5} \right) / 2F$$

Figure 1-4 presents the potential at which nickel chloride will form at the anode as a function of HCl concentration in the gas phase using a 2/3 atm CO_2 , 1/3 atm O_2 reference gas. The oxidation potential of the anode is shown for comparison. Similar calculations for the cathode are impossible because of the lack of thermodynamic data on reaction products of lithiated nickel oxide and the halides. For example, chloride ions may enter the crystal lattice of lithiated nickel oxide and change its properties.

Figure 1-4. Nickel Electrode Degradation by HCl

Matrix

Two possible matrix-halide reactions were studied thermodynamically:

The equilibrium constant for equation (1-5) is given by:

$$K_{15} = \frac{P_{LiAlF_6} P_{H_2O}^2}{P_{HF}^4} = \exp \left[\frac{1}{RT} \left(\mu_{LiAlO_2}^{0,S} + 4\mu_{HF}^{0,G} + 2\mu_{LiF}^{0,L} - \mu_{LiAlF_6}^{0,S} - 2\mu_{H_2O}^{0,G} \right) \right]$$

At 900° K, $K_{1-5} = 0.0863$, but because P_{HF} is taken to the fourth power, equation (1-5) will not be important at the HF concentrations of interest.

The equilibrium constant for equation (1-6) is given by:

$$K_{16} = \frac{P_{H_2O}^2}{P_{HF}^4 \{Li^+\}^2 \{F^-\}^2} = \exp \left[\frac{1}{RT} \left(\mu_{LiAlO_2}^{0,S} + 4\mu_{HF}^{0,G} + 2\mu_{LiF}^{0,L} - \mu_{Li_2AlF_6}^{0,S} - 2\mu_{H_2O}^{0,G} \right) \right]$$

At 900° K, $K_{1-6} = 8.9 \times 10^6$, meaning that the reaction for equation (1-6) could be significant.

DISCUSSION

The literature survey and thermodynamic analyses indicate that hydrogen chloride and hydrogen fluoride present in gasified coal can affect the performance of molten carbonate fuel cells in several ways.

- o Electrolyte conversion -- The thermodynamic calculations indicate that HCl or HF will tend to react essentially completely with the molten carbonate electrolyte to form chlorides and fluorides. The presence of chloride formation was confirmed by the presence of chlorides in the post-test electrolyte of a cell which was tested with HCl in the reactants.
- o Electrolyte vaporization -- Theoretical and experimental vapor pressures of pure KCl and LiCl agree reasonably well, giving confidence that the calculated vapor pressures of chlorides and fluorides above partially converted molten carbonate electrolyte are reasonably accurate. These calculations indicate that conversion of the electrolyte will result in an increased rate of vaporization. For the case of chloride, the increased vaporization will take place with a relatively small degree of conversion at 1 atm pressure; whereas for fluoride, a large conversion could take place before increased vaporization would occur. Conversion becomes more important as a decay mode as pressure is increased. The importance of vaporization as a decay mode is attested to by the large electrolyte loss experienced in the cell tested at United Technologies Corporation (UTC) with HCl in the fuel.
- o Anode poisoning -- Although the thermodynamic analysis and post-test inspection of anodes which operated on HCl - containing fuel indicate that nickel chloride should not form, poisoning of the anode reaction apparently occurred in both the General Electric (GE) and UTC tests. Since carbonate ions are consumed at the anode, the replacement of some of the carbonate ions by chloride ions may slow the anode reaction.

- o Cathode Current Collector Corrosion -- The literature survey on the effect of chlorides in the corrosion caused by alkali metal salts indicates that the chlorides increase corrosion. The post-test inspection of cell components tested with HCl in the reactants confirm that this increased corrosion also occurs in the fuel cell environment.
- o Cathode Changes -- Thermodynamic calculations indicate that NiCl_2 can form at cathode potentials with adequately high HCl pressures. Prior to the formation of chloride from the oxide, however, some chloride may enter the lattice of the lithiated nickel oxide and change its properties. A change in cathode morphology was noted in a GE cell test.
- o Matrix Material Changes -- Both thermodynamic calculations and post-test analysis of a GE cell indicate that lithium aluminate may not be stable above certain concentrations of halide in the electrolyte.

CONCLUSIONS

Molten carbonate fuel cells are anticipated to be very sensitive to the presence of chlorides and fluorides in the fuel gas. Conversion of the electrolyte from carbonate to chloride and fluoride is anticipated. For the case of chloride, an accelerated rate of electrolyte loss will occur; whereas for fluoride, the electrolyte loss rate will not be increased as much. The conversion of the electrolyte in both cases, however, might lead to anode poisoning, cathode and matrix material changes, and increased cathode current collector corrosion, depending on the degree of electrolyte conversion. An electrolyte concentration polarization, liquid junction potential effect and increased internal resistance can occur due to the different electrolyte composition in the anode and cathode.

TASK 2 - TEST PLAN

Using the understanding of the effects of chlorides and fluorides obtained in the literature survey and thermodynamic analyses as presented in the previous section, a test plan was formulated for investigating the effects of these halides in Tasks 3 and 4 of this contract. Task 3 involved out-of-cell testing and Task 4 in-cell testing. These test plans were modified during the program to reflect changes in program emphasis and scope.

Hydrogen chloride in a molten carbonate reactant gas is anticipated to react quantitatively with the electrolyte to form chlorides. These chlorides will accelerate the corrosion of cathode-side components and lead to a conversion of the electrolyte until the rate of chloride loss balances the rate of input. The vapor pressure of the chlorides is expected to be high enough for these rates to be balanced with a relatively small conversion of the electrolyte from carbonate to chloride. The loss of electrolyte will be greatly accelerated due to the chloride.

Hydrogen fluoride in the reactant gases is anticipated to have somewhat different effects. The effect on corrosion of cathode-side components is unknown. Since the vapor pressures of lithium and potassium fluoride are much less than those of the chlorides, they will not evaporate from the electrolyte as rapidly, and conversion of the electrolyte will take place with much less electrolyte loss. Therefore, fluorides will affect performance more through electrolyte conversion than through electrolyte loss compared to chlorides.

Because of these anticipated effects, the out-of-cell tests in Task 3 were aimed at determining the effects of chloride and fluoride content in the electrolyte on the corrosion of cathode-side components and the measurement

of the short-term performance effects in half-cell tests of both anode-side and cathode-side components.

In the out-of-cell corrosion experiments, three cathode current collector materials were corrosion tested for 1000 hours in molten carbonate electrolyte containing chloride and fluoride. The three materials were AISI 316 stainless steel, AISI 310 stainless steel, and Inconel 825. The temperature of the test (700°C) was above that of the cell (650°C) in order to accelerate the corrosion rate. The electrolyte halide content was 3.1 anion percent halide, which corresponds to one ppm halide in the gas phase for chloride and 0.04 ppm halide in the gas phase for fluoride. The material samples were exposed to an oxidant gas which simulates that anticipated in a Texaco O₂-blown coal gasifier fueled molten carbonate fuel cell power plant. Details of these plans can be found in Appendix B.

The anode-side half-cell performance tests consisted of the measurement of the overpotential as a function of current density for halide-free electrolyte and electrolyte containing 23 anion percent of each halide. For the chloride, this electrolyte composition results in a gas phase chloride concentration of 10 ppm, as shown in Figure 1-3. For fluoride, the gas phase concentration is 0.3 ppm. The anode tests included all of the components on the anode side of the cell including the anode, bubble barriers, current collectors and matrix.

The cathode-side half-cell performance tests also consisted of the measurement of overpotential as a function of current density for halide-free electrolyte and electrolyte containing 23 anion percent of each halide. In addition, a test was performed with 3.1 anion percent of chloride to determine the trend of performance change with chloride content. The cathode tests included all of the components on the cathode side of the cell including the cathode, current collector and matrix. Details of the components can be found in Appendix B. Both the anode and cathode tests

were performed using reactants which simulated those in the Texaco O₂-blown coal gasifier power plant.

Post-test analyses were planned on the corrosion samples and components from the half-cell tests. Because the purpose of the corrosion tests was to determine the effect of halides in the surface corrosion layers, an extensive post-test analysis was planned for those layers including sectioning the samples and investigating the thickness, composition and conditions of the corrosion layers. Because of the shortness of the tests and the variable conditions in the half-cell tests, only visual inspection and component thicknesses were planned for post-test components.

For the in-cell tests in Task 4, data were desired on the performance decay of a bench-scale cell while operating with halide in the reactants. Some of these data were already available from the IFC Contract No. DE-AC01-79ET15440 with DOE. Although additional tests were initially planned, these tests were later removed from the plan.

TASK 3 - OUT-OF-CELL TESTS

HALF-CELL TESTS

Introduction

A series of molten carbonate half-cell experiments were conducted to determine how chloride and fluoride in the electrolyte affect cell performance and the individual cell components. The objectives of the half-cell test program were: to measure how a concentration gradient of carbonate would affect cell performance, to determine how the amount of electrolyte in an electrode affects anode and cathode polarization in the presence of halides, and to obtain electrode overpotential as a function of current data for several chloride and fluoride concentrations for both anodes and cathodes. Half-cell testing also allowed a larger matrix of conditions to be tested in a given amount of time than could be done with full-cell subscale testing. Parts tested in the half-cell were the same as those that were used in full-cells and are described in the Test Plan given in Appendix B.

Experimental

Two individual half-cell rigs were constructed: one to act as an anode half-cell, the other to act as a cathode half-cell, thereby enabling both electrodes to be run simultaneously. A schematic of a half-cell test rig is shown in Figure 3-1. Oxygen, nitrogen and carbon dioxide were supplied to the cathode half-cell through in-house gas lines. Hydrogen and carbon dioxide were supplied to the anode half-cell through in-house gas lines as well. Carbon monoxide was supplied to the anode half-cell through bottled gas. Both rigs also had the capability of running under diagnostic oxidant (a 1:2 $O_2:CO_2$ mixture). Running an anode and a cathode half-cell at the same time had several advantages over running either two anode or two cathode tests at the same time. This arrangement made optimum

Figure 3-1. Half-Cell Schematic

use of the available gas flow controllers, minimized the number of times that the flow meters had to be calibrated and allowed both cells to use the same electrolyte at the same time. A separate oven was set up to manufacture electrolyte. Each gas flow rate was regulated and monitored by Matheson Gas Flow Controllers/Measurers. All tests were performed at 1 atm pressure and 650°C cell temperature.

Gases flowed in parallel through two saturators: one containing only water and the other containing a water-halide solution. This approach allowed for individual control of the dew point and halide concentration in the gas stream. After considering halide-containing gas bottles and permeation tubes, gas saturators were chosen to introduce halide into the gas stream because of their low cost. A computer program was developed, using halide and water vapor pressure vs. concentration and temperature tables, that defined the required flow rates of gases through each saturator, the

temperature of each saturator, the concentration of halide solution in the halide saturator, and the method to maintain the halide concentration in the halide saturator in order to give the desired final flow rate, dew point and halide concentration in the combined gas stream. The water saturator used in each rig was a two-zone water saturator. The liquid in the lower half of the saturator was heated to 0.6°C above the desired dew point. The upper half of the saturator, which contained no liquid, was held at the desired dew point. The gas going into the saturator was dispersed into the liquid using a porous spherical stone. This arrangement kept superheated water from entering the gas phase and gave very good control of the water dew point. The saturator was tried using the halide-water solution, but the fitting holding the gas-dispersion stone was made of brass and readily dissolved in 40°C , 10 weight percent HCl solution. The halides saturator was replaced with an all-glass, single-zone saturator to introduce HCl into the cell. The single-zone saturator can be as accurate as the two-zone saturator if carefully calibrated and the liquid kept at a constant level. It was determined that an HF saturator was unnecessary, due to the low rate of fluoride loss from the cell, because of the low vapor pressures of KF and LiF. Gas-phase halide concentration was occasionally checked by bubbling the gas through a column of distilled water. Glass beads in the column assured good liquid-vapor contact. The gas was bubbled through the column for a known length of time and the water in the column analyzed by Dionex ion chromatography for halide content. After the concentration of halide initially in the distilled water was subtracted from the Dionex results, the halide concentration in the gas phase could be calculated, assuming that all the halide in the gas phase was scrubbed out by the water and that the gas stream flow rate was known. Flow rates and halide saturator solution concentration were chosen so that the gas phase halide concentration would not vary by more than 5 percent over 350 hours of expected test life. Only CO_2 flowed through the halides-water saturator in all the tests.

Cell temperature was maintained using Lindberg Sola Basic crucible furnaces. Cell performance was monitored with a potentiostat/galvanostat designed and built at International Fuel Cells.

A sketch of the cathode half-cell configuration is shown in Figure 3-2. An AISI 310 stainless steel, shielded slot plate was placed on top of an alumina base to allow gases to escape from the counter electrode (CE). The counter electrode was a fine mesh gold screen with a small hole in the center, filled with an insulating material to support the tapes on top. The hole minimized undesired electric field lines between the working and counter electrode. Two LiAlO_2 type matrices were placed on top of the counter electrode and were filled to capacity with electrolyte. On top of the tapes was the nickel oxide cathode working electrode (WE). A hole was cut in the middle of the working electrode so that the gold wire reference electrode could contact the electrolyte. The reference electrode was shielded by an alumina tube. On top of the working electrode was another piece

Figure 3-2. Cathode Half-Cell Configuration

of AISI 310 stainless steel shielded slot plate, which functioned as a current collector. A hollow stainless steel push rod and perforated plate maintained contact between all the parts by applying pressure to the package and served as the working electrode's connection to the potentiostat/galvanostat. The oxidant flowed through the inside of the push rod. Cell temperature was monitored with alumina-covered thermocouples. An area of tape was left exposed so that electrolyte could be added or removed by the operator using a piece of fine pore CeO_2 attached to the end of an alumina rod. Table 3-1 describes each component in more detail.

TABLE 3-1: HALF-CELL COMPONENTS

<u>COMPONENT</u>	<u>MATERIAL</u>	<u>THICKNESS</u>	<u>POROSITY</u>
Anode Current Collector	Nickel	50 mils	0
Anode (Ribbed)	Nickel + 2% Cr	60 mils (27% open cross-sectional area)	0.50
Fine Pore	Nickel + 2% Cr	4 mils	0.36
Cathode Current Collector	310 stainless steel	Base = 6 mils Rib = 4 mils	----
Cathode	In-Situ Lithiated Nickel-Oxide	40 mils	0.773
Matrix	LiAlO_2	2 Pieces 9 mils each	0.42

After the eighth cathode half-cell test, cathode material was placed under the matrix, as well as on top of it, to function as a better matrix support and counter electrode. The gold screen was retained as a counter electrode current collector. The anode half-cell configuration was similar to this cathode half-cell configuration and is shown in Figure 3-3.

Figure 3-3. Anode Half-Cell Configuration

Results and Discussion

Prior to measuring the performance of anodes and cathodes in the half-cell, a series of experiments were performed to determine the effect of halides on the potential of the reference electrode. The effect of halide content on the reference electrode is important in determining the true potential of the working electrode. The halide effect is also important in determining whether any difference in potential between the reference electrode and working electrode is due to a difference in electrolyte composition.

An electrolyte halide ion concentration difference can also exist in a fuel cell. Halides may enter the fuel cell system in the fuel and air supply and react with the electrolyte. Since carbonate ions are produced within the cell at the cathode and consumed at the anode, the cathode may be richer in carbonate than the anode.

A set of experiments was performed to determine if a carbonate ion concentration gradient would follow theoretical predictions. The results from these experiments is useful in modeling how halides affect molten carbonate fuel cells.

The experimental setup shown in Figure 3-4 was used to perform these experiments. Four LiAlO_2 matrices, each 3.18 cm by 2.54 cm by about 0.023 cm thick, were placed on an alumina sheet so that there was a 0.03 cm gap between two pairs of matrices. Matrices were stacked on top of each other so that a crack in any matrix would not separate a piece of matrix from the rest. Thick-walled alumina tubes were placed over each matrix. A 1:2 $\text{O}_2:\text{CO}_2$ gas mixture flowed through each tube at 10 standard cc/min. A small hole was cut near the bottom of each tube to allow the gas to exit. Each tube also contained a thermocouple, completely enclosed in an alumina tube, and a gold wire connecting a voltmeter with the matrix. This wire was also enclosed in alumina within the rig except for the tip in contact with the matrix. All experiments were performed at 650°C and ambient pressure and ran for 16 to 24 hours.

Figure 3-4. Experimental Half-Cell Setup

Halide-free electrolyte was introduced through one tube and halide-contaminated electrolyte through the other. Both halide-free and halide-contaminated electrolyte had a 72:28 Li:K molar ratio. Enough electrolyte was introduced into each tube to fill each matrix to about 100 percent.

In the first trial, it was hoped that electrolyte would wick across the alumina to bridge the gap between the two pairs of matrices, but this never occurred. In the second trial, the gap was eliminated but results were inconclusive since it was not known whether the KCl, LiCl, K_2CO_3 and Li_2CO_3 melted and wicked into the electrolyte at the same rate. Finally, the gap was bridged by dropping a piece of zirconia across the gap after all the electrolyte had melted. Four chloride concentrations (23, 50, 78 and 92 anion percent chloride) and two fluoride (23 and 44 anion percent fluoride) concentrations were tested. The potential difference using a continuous matrix containing halide-free electrolyte was measured to be 2.5 mV. Results are plotted in Figure 3-5. All but one potential difference shown are peak values. Peak occurred briefly (15 minutes to 30 minutes) after the gap was closed. After that, polarization slowly dropped to zero, approximately overnight. Also shown in Figure 3-5 is a point taken from a study on the effects of sulfur, and a line representing the Nernst equation which accounts for the ratio of carbonate ion activities between the two electrodes.

The cause for the data differing from the Nernst equation is not known. Possible reasons are that a liquid junction potential effect is significant, that an unknown reaction is taking place, that a complex is forming (such as $K_2CO_3 - KF$), or that the carbonate ion is dissociating to CO_2 , as is suggested by Kruglov, et al. [5]. The data seem to follow the Nernst equation for anion fractions of halide less than 0.23.

Figure 3-5. Concentration Difference Test Results Vs. Nernst Equation

All previous half-cell performance tests were conducted using tile matrices that were about 70 mils thick [21]. The present full cells used tape matrices that are 18 mils thick. It was desirable to use the same components from present day full cells in the half cells. Therefore, prior to performance testing in the presence of halides, several tests were performed to demonstrate reproducible results with tape matrices.

Shown in Table 3-2 is a brief description of each of the twelve half-cell tests to measure performance. Although twelve tests were conducted, five tests were used in rig development. Besides two baseline tests, only those tests yielding results on halide effects will be dealt with in depth.

Table 3-2. Half-Cell Test Summary

<u>Test</u>	<u>Objective</u>	<u>Operating Time (Hours)</u>
Cathode Test #1	Repeat prior half-cell data. Cell failed when RE* broke through tape.	0
Cathode Test #2	Repeat Test #1 only using CeO ₂ block to prevent RE breakthrough.	427
Cathode Test #3	Use LiAlO ₂ powder to promote better contact between WE and matrix.	305
Cathode Test #4	Test a new half-cell rig. To be compared to Test #3.	90
Cathode Test #5	Bind tape and WE together by softening tape with isopropanol.	308
Cathode Test #6	Test cell with 3.1 anion percent chloride in the electrolyte.	210
Cathode Test #7	Bind tape and WE together by hot pressing WE into tape. No halide.	506
Cathode Test #8	Test cell with 23 anion percent chloride in the electrolyte. Used NiO CE.	173
Cathode Test #9	Test cell with 23 anion percent fluoride in the electrolyte. Used NiO CE.	269
Anode Test #1	Baseline anode test. Used Ni CE.	142
Anode Test #2	Test cell with 23 anion percent chloride in the electrolyte. Used Ni CE.	145
Anode Test #3	Test cell with 23 anion percent fluoride in the electrolyte. Used Ni CE.	117

*RE = Reference electrode; WE = working electrode; CE = counter electrode

Cathode Test #3 - This test ran without halide in the electrolyte in order to reproduce prior data, only using a tape matrix instead of the tile matrices used previously. Since erratic performance changes in Cathode Test #2 were attributed to a loss of contact between the cathode and tape, in this test 173 mg of fine LiAlO_2 powder was placed between the electrode and the tape to maintain electrolyte contact. Electrolyte was removed from the wick area using a piece of porous CeO_2 attached to an alumina rod. The CeO_2 has a finer pore structure than the matrix, and electrolyte preferentially wicks into the CeO_2 from the matrix. The CeO_2 was allowed to remain in contact with the matrix for about half of an hour, after which the CeO_2 was removed from the cell, cooled and weighed. At each electrolyte content in the rig, open-circuit potential, the iR -free cathode overpotential, the cell iR at 160 mA/cm^2 , and cell temperature were measured. The data did not repeat the Cathode Test #2 data and the cell iR was high (120 to 171 mV at 160 mA/cm^2), but the overpotential data compared favorably with previous data. Figure 3-6 shows the data from Test #3. The mass of electrolyte was converted to percent fill, assuming that the added LiAlO_2 powder had properties similar to the tape matrix (same pore spectra, same void volume) and that it had a bulk density of 1.09 g/cc .

The experimental data obtained in Test #3 were obtained using an oxidant gas consisting of 0.67 atm CO_2 and 0.33 atm O_2 . In order to compare the data with that obtained previously with tile matrices and other tests run with halides, the cathode Test #3 data were corrected to the test plan oxidant by multiplying the overpotential under the $1:2 \text{ O}_2:\text{CO}_2$ oxidant by 1.2. The value of 1.2 was determined by comparing old data under the test plan oxidant to old data under the $1:2 \text{ O}_2:\text{CO}_2$ oxidant. The results are shown in Figure 3-7. For the old 44 mil cathode the correction was 1.12 ± 0.01 at fills less than 22 percent, and for the old 33 mil cathode the correction was 1.33 ± 0.02 at fills less than 31 percent. A weighted average of these two values gives a correction factor of 1.2 for a 40 mil cathode. The present halide-free electrolyte data compares favorably with the old data.

Current = 160 mA/cm²
 $O_2/CO_2 = 1:2$
 Temp = 1200°F
 0.040" Thick Cathode
 Solid symbols indicate
 electrolyte addition.

Figure 3-6. Half-Cell Cathode Test #3

Figure 3-7. Effect of Halide on Cathode Half-Cell

Cathode Test #6 - The purpose of this test was to determine the effect of a low chloride concentration in the electrolyte. To maintain electrolyte contact between the cathode and the tape, the tapes were softened with isopropanol and pressed onto the cathode prior to cell assembly. The cell was then heated to 704°C to burn impurities out of the tape. The cell temperature was reduced to 649°C and 72 mole percent Li_2CO_3 , 28 mole percent K_2CO_3 electrolyte containing extra Li_2CO_3 for component lithiation was added to the cell. The electrolyte contained 3.1 anion percent chloride, as described in the test plan, while maintaining a 72:28

Li:K cation ratio. The cell started with a low amount of electrolyte (22 percent cathode void volume fill) based on an estimation of the electrolyte content to result in the minimum overpotential. The matrix was filled to capacity with electrolyte. An electrolyte density of 1.88 g/cc at 649°C was used, calculated using Amagat's Law ($\bar{V}_{\text{mix}} = \sum_{i=1}^n X_i \bar{V}_i$ and $\rho = 1/\bar{V}_{\text{mix}}$). The extra Li_2CO_3 for component lithiation was added to the electrolyte to account for 4 atomic percent Li in the NiO cathode, lithiation of the matrix (350 hours times the initial rate of lithiation of a stack matrix), and lithium in the oxides formed in the stainless steel perforated push plate and current collector. The cell started using a two-zone saturator to introduce HCl, but a brass fitting dissolved and the saturator was replaced with an all-glass, one-zone saturator, as described earlier. Ion chromatography confirmed that the expected 1 ppm HCl was introduced into the oxidant. The oxidant was a 9.5 mole percent O_2 , 7.2 mole percent CO_2 , 64.6 mole percent N_2 , 18.7 mole percent H_2O mixture flowing at 600 sccm (wet flow) at 1 atm pressure. The data are plotted in Figure 3-8. The weight of electrolyte in the cell was converted to percent fill and the overpotential plotted as a function of percent fill (Figure 3-7). The chloride present in this cell appears to have increased the overpotential by about 100 mV. The cell failed when one of the flow controllers failed during an electrical power surge, resulting in water being blown out of one of the saturators and into the cell, cracking the matrix.

T = 1200°F
0.040" Thick Cathode
HCl = 10 ppm

Figure 3-8. Half-Cell Cathode Test #6

Several current versus potential sweeps were taken, two at a slow sweep rate (Figures 3-9 and 3-10) (25 mA/min) and two at a fast sweep rate (Figures 3-11 and 3-12) (400 and 800 mA/min). When slow sweep rates were used, a wavy polarization curve resulted, followed by rapid polarization changes. When fast sweep rates were used, smoother performance curves were obtained. The effect of sweep rate is thought to be due to halide ion concentration gradients building up among the working, counter, and reference electrodes during the slow sweep rates. Since carbonate ions are produced in the working electrode and consumed in the counter electrode, the halide ion concentration will decrease in the working electrode and increase in the counter electrode with time. Eventually, the halide ion concentration might reach a point where chloride evolution can occur from the counter electrode, resulting in the rapid oscillations in the polarization data.

Cathode Test #8 - The purpose of this test was to determine the effect of a high chloride concentration in the electrolyte. Because of the fragility of unsupported tape matrix and poor electrode contact with the matrix in the half-cell rig in contrast to the excellent tape matrix properties seen in fuel cells, Cathode Test #8 started using some of the start-up procedures used in full cells. To minimize tape cracking and tape separation during the test, the tape was hot pressed between two pieces of cathode at 204°C and 100 psi resulting in a configuration similar to the anode configuration shown in Figure 3-3, with the exception that a sheet of AISI 310 stainless steel current collector was placed between the alumina base plate and the gold screen so that gases could escape from the NiO counter electrode.

After assembly, the cell was heated in a manner similar to that used in a full-cell start-up. The cell was heated to 204°C and held at 204°C under O₂/CO₂/N₂ overnight (or 8 hours minimum) to burn binder out of the tape. The cell was then heated to 470°C and the electrolyte added.

Figure 3-9. Cathode Test #6 Slow Sweep Performance Curve #1

Figure 3-10. Cathode Test #6 Slow Sweep Performance Curve #2

Figure 3-11. Cathode Test #6 Fast Sweep Performance Curve #1

T = 1207°F
 800 mA/min
 Cathode: 10 ppm HCl
 minimum
 electrolyte

Figure 3-12. Cathode Test #6 Fast Sweep Performance Curve #2

The electrolyte added in this test contained 23 anion percent chloride, maintaining a 72:28 Li:K cation ratio. Extra Li_2CO_3 was added in similar amounts to Cathode Test #6. The cell was held at 470°C overnight (or 8 hours minimum), heated to 650°C and allowed to equilibrate for a day. The oxidant was that described in the test plan and flowed at 600 sccm with 10 ppm HCl introduced through the saturators. Relatively low cell iR 's were achieved in this test (44 to 90 mV at 160 mA/cm²). The data is shown in Figure 3-13 and the overpotential is plotted as a function of percent fill in Figure 3-7. Overpotential as a function of current was measured twice and is shown in Figures 3-14 and 3-15.

$I = 160 \text{ mA/cm}^2$
100 ppm HCl

Figure 3-13. Half-Cell Cathode Test #8

Figure 3-14. Cathode Test #8 Fast Sweep Performance Curve #1

T= 1205°F
 400 mA/min
 Cathode: 100 ppm Cl⁻
 823 mg electrolyte
 OC = - 17 mV

Figure 3-15. Cathode Test #8 Fast Sweep Performance Curve #2

This test and Cathode Test #6 clearly show that chloride has a detrimental effect on the cathode itself. Several reasons for the loss in performance have been suggested: chloride entering the NiO lattice, changes in morphology and a change in the wetting angle. The relatively stable performance of each test at each percent fill and the increase in overpotential due to an increase in chloride concentration suggests that whatever phenomenon occurs, it occurs rapidly and is strongly concentration dependent, especially at chloride concentrations below 3.1 percent.

Cathode Test #9 - This test was similar to Cathode Test #8, except that the electrolyte contained 23 anion percent fluoride instead of 23 anion percent chloride. An electrolyte density of 1.91 g/cc at 650°C was used. A saturator to introduce fluoride was not used; it had been calculated that the vapor pressures of LiF and KF were so low that fluoride loss would be small and a fluoride make-up was unnecessary (fluoride content was calculated to drop from 23 anion percent fluoride to 21.4 anion percent fluoride after 350 hours of operation). The test plan oxidant flowed at 600 sccm (wet) with no halide. The cell was assembled in the same manner as Cathode Test #8. The data are shown in Figure 3-16 and the electrolyte weight was converted to percent fill in Figure 3-7. Note that high concentrations of fluoride do not seem to adversely affect the cathode. Several overpotential vs. current curves were taken (Figures 3-17 to 3-24). Figures 3-17 and 3-18 show repeatability at the first point in Figure 3-16. Figures 3-19 and 3-20 are repeatable, even though the curve in Figure 3-19 was taken at a fast sweep rate (400 mA/min) and the curve in Figure 3-20 was taken at a slow sweep rate (25 mA/min). The irregularities seen in the Cathode Test #6 with chloride and slow sweeps are not present in this test. Figure 3-21 was taken when the cell contained 643 mg of electrolyte. Figures 3-22 to 3-24 show repeatability at the last point in Figure 3-16. There is very little difference between any of these sweep curves. Figure 3-25 shows the results of a current step test. The electrode was held at 160 mA/cm² for 5 minutes, resulting in 91 mV overpotential. The current was then interrupted and the potential was recorded on a strip chart recorder. The curve shows a rapid drop in potential until about 12 mV is reached, after which the potential drops to zero in about 2 minutes, 30 seconds. This curve suggests that a diffusion process is responsible for the slow drop in potential below 12 mV. The working electrode, which produces carbonate ions, is free of fluoride, while the reference electrode is surrounded by 23 anion percent fluoride. The 12 mV difference was also found in the concentration gradient polarization study discussed earlier for this anion percent fluoride.

Figure 3-16. Half-Cell Cathode Test #9

T = 1202° F
 400 mA/min
 Cathode: 0.34 ppm F⁻
 OC = -17 mV
 660 mg electrolyte

Figure 3-17. Cathode Test #9 Fast Sweep Performance Curve #1
 With 660 mg of Electrolyte in the Cell.

Figure 3-18. Cathode Test #9 Fast Sweep Performance Curve #2
With 660 mg of Electrolyte in the Cell

Figure 3-19. Cathode Test #9 Fast Sweep Performance Curve #3
With 660 mg of Electrolyte in the Cell

T = 1208°F
25 mA/min
Cathode - 0.34 ppm F⁻
660 mg electrolyte
OC = -17 mV

Figure 3-20. Cathode Test #9 Slow Sweep Performance Curve

Figure 3-21. Cathode Test #9 Performance Curve With 643 mg of Electrolyte in the Cell

Figure 3-22. Cathode Test #9 Performance Curve #1 With 629 mg of Electrolyte in the Cell

T = 1201°F
400 mA/min
Cathode - 0.34 ppm F⁻
629 mg electrolyte
OC = -14 mV

Figure 3-23. Cathode Test #9 Performance Curve #2 With 629 mg of Electrolyte in the Cell

T = 1201°F
400 mA/min
Cathode - 0.34 ppm F⁻
629 mg electrolyte
OC = -14 mV

Figure 3-24. Cathode Test #9 Performance Curve #3 With 629 mg of Electrolyte in the Cell

Figure 3-25. Cathode Test #9 Potential Sweep After Current Step

Anode Test #1 - The first anode test was designed to be a baseline test (no halide in the electrolyte) since previous anode half-cell data were scarce. The test configuration shown in Figure 3-3 was used in all three anode half-cell tests. The cells were started in a modified full-cell manner. The cell was first heated to 204°C under 1:2 O₂:CO₂ for at least 8 hours to burn out the binder in the tapes. The cell was then heated to 470 C, electrolyte was added, the cell was purged with N₂ and then the cell was put on a 29.4 mole percent H₂, 5.5 mole percent CO, 17.5 mole percent CO₂, 47.6 mole percent H₂O mixture at a flow rate of 600 sccm (wet) overnight. The cell was then heated to 650°C and given time to equilibrate. The electrolyte used in this test contained no halide and was a 72:28 molar mixture of Li₂CO₃:K₂CO₃ plus extra Li₂CO₃ to account for lithium taken up by the anode, the fine pore and the matrix (these amounts were calculated using the initial rate of component lithiation in full scale stacks times 350 hours of expected cell life). The current collector plate in the anode tests was perforated by drilling holes in the plate to match up with the holes in the nickel push rod plate. Details on the anode components are given in Table 3-1. The matrix and the fine pore were filled to capacity with electrolyte and the anode was filled to 30 percent with electrolyte. The 30 percent value was chosen based on previous anode performance vs. percent fill data. The data for Anode Test #1 are shown in Figure 3-26. The weight of electrolyte was converted to percent fill using an electrolyte distribution program which utilizes measured pore spectra for molten carbonate components. The results of overpotential vs. percent fill are shown in Figure 3-27.

Figure 3-26. Half-Cell Anode Test #1

Figure 3-27. Anode Overpotential Vs. Percent Fill

Anode Test #2 - This test was similar to Anode Test #1, except that the electrolyte contained 23 anion percent chloride (maintaining a 72:28 Li:K cation ratio) and 10 ppm HCl was introduced into the fuel. The data are shown in Figure 3-28 and are converted to percent fill in Figure 3-27. It is not clear why the data falls below the baseline data. Chloride in the electrolyte may have lowered the contract angle between the nickel and the electrolyte. Several current vs. overpotential curves were taken at a relatively fast sweep rate of 400 mA/min. Figure 3-29 shows one of three curves taken at 655 mg of electrolyte, all of which were repeatable. Figure 3-30 shows data taken with 609 mg of electrolyte in the cell.

Figure 3-28.
 Half-Cell Anode Test #2.

T = 1208°F
400 mA/min
Anode - 10 ppm Cl⁻
655 mg electrolyte
OC = -26 mV

Figure 3-29. Anode Test #2 Performance Curve With 655 mg of Electrolyte in the Cell

$T = 1208^{\circ}\text{F}$
 400 mA/min
 Anode - 10 ppm Cl^{-}
 655 mg electrolyte
 OC = -26 mV

Figure 3-30. Anode Test #2 Performance Curve With 609 mg of Electrolyte in the Cell

Anode Test #3 - This test was similar to Anode Test #2, except that the electrolyte contained 23 anion percent fluoride (maintaining a 72:28 Li:K cation ratio). No HF was introduced into the fuel since it was determined that this was unnecessary due to the low vapor pressures of LiF and KF. The overpotential data are shown in Figure 3-31 and the electrolyte weight was converted to percent anode void volume filled with electrolyte in Figure 3-27. Again, it is not clear why the data fall below the baseline data. Three current vs. overpotential curves were taken at each point in Figure 3-31 and are presented in Figures 3-32 to 3-34. A potential vs. time

curve similar to that taken under Cathode Test #9 was also taken on this test (Figure 3-35). The curve temporarily falls below 0 mV overpotential after the current was interrupted. This was not observed in repeats of this curve, but is possibly due to a slower diffusion rate away of fluoride ions away from the anode than the reference, due to the porosity of the anode and the smoothness of the reference.

Figure 3-31.
Half-Cell Anode Test #3

Figure 3-32. Anode Test #3 Performance Curve #1

Figure 3-33. Anode Test #3 Performance Curve #2

T = 1205°F
400 mA/min
Anode: 23 Anion & F⁻
697 mg electrolyte
OC = -18 mV

Figure 3-34. Anode Test #3 Performance Curve #3

Figure 3-35. Anode Test #3 Potential Sweep After Current Step

Conclusions

Anode and cathode half-cell configurations were developed which allowed half-cell tests to be conducted using LiAlO_2 tapes instead of LiAlO_2 tiles. Performance results from tests having halide in the electrolyte clearly show that chloride is detrimental to the cathode and that the greater the concentration of chloride, the greater the effect. Fluoride, however, had little affect on the cathode. Anodes were not adversely affected by halide in the electrolyte. Halide ion concentration gradients were evident in slow current-overpotential sweeps and potential-step tests repeated what was seen in the concentration polarization study.

CORROSION TESTS

Introduction

The objective of the corrosion tests was to determine the influence of chlorides and fluorides on the corrosion of cathode-side alloys of construction in molten carbonate electrolytes. The corrosion tests were conducted at 760°C for 1000 hours under a pressure of one atmosphere. Three alloys, AISI 316, AISI 310, and Incoloy[®] 825, were evaluated in an electrolyte composed of 72 mole percent Li_2CO_3 and 28 mole percent K_2CO_3 converted to contain 3.1 anion percent chloride or fluoride. The three alloys were also evaluated in an electrolyte of similar composition, but containing no halide ions, to establish a baseline corrosion rate.

Experimental

A schematic of the test set-up is shown in Figure 3-36. Two-zoned gas saturators were used to introduce water into the cell. An all glass saturator was used to introduce chloride. It was determined that for each cell, two saturators running in parallel, one filled with a halide-water solution and the other just water, would be the least expensive method to introduce halide into the gas stream.

Figure 3-36. Schematic of Retort Test

Test specimens of AISI 316 and AISI 310 stainless steels and Incoloy[®] 825 were wet ground on 240-grit paper, washed in 20 percent nitric acid solution, rinsed and dried. All samples measured 1.27 cm x 2.54 cm. The thicknesses of AISI 316, AISI 310, and Incoloy[®] 825 were 0.114 cm x 0.152 cm, and 0.033 cm, respectively. The specimens were sandwiched between prefilled nickel electrodes to simulate conditions in a stack and placed in a retort at 760°C, as shown in the schematic. The nickel electrode was prefilled with 20 grams of a molten carbonate electrolyte having a composition of 72 mole percent Li_2CO_3 , 28 mole percent K_2CO_3 converted to contain 3.1 anion percent halide.

The oxidant composition was 9.5 mole percent O_2 , 7.2 mole percent CO_2 , 64.6 mole percent N_2 and 18.7 mole percent H_2O . In addition, in one test, a portion of the N_2 flow was diverted to a saturator containing 10 percent

hydrochloric acid and held at a temperature calculated to provide 1.0 ppm chloride in the atmosphere to keep the chloride in the electrolyte from evaporating. The evaporation of fluoride from the electrolyte was calculated to be negligible over the test period. Therefore, fluoride was not added to the gas stream. All tests were interrupted at 500 hours for specimen weight determination but only the 1000 hour specimens were fully evaluated.

The post-test specimens were washed in acetic acid to remove residual electrolyte, rinsed in distilled water, dried and weighed. Metallographic cross-sections of the specimens were prepared by mounting the specimens in a phenolic resin which had been previously examined with a Scanning Electron Microscope (SEM) and determined by Energy Dispersive Spectroanalysis (EDS) to be free of chlorides. Elemental X-Ray maps of the oxide layers on the control and chloride test specimens were obtained using the SEM. The specimens were obtained using the SEM. The specimens from the fluoride test were examined with a Scanning Electron Microprobe since fluorine could not be detected with SEM. Both the SEM and Microprobe analyses were conducted at the United Technologies Research Center (UTRC).

Microstructural features of the pre-test and post-test specimens are shown in Figures 3-37 and 3-40. The post-test AISI 316 and AISI 310 specimens exposed to halide exhibited base metal microstructures similar to the control specimens, Figures 3-38 and 3-39. The Incoloy[®] 825 post-test specimens base metal microstructures which varied in appearance depending on whether the chloride, fluoride, or no halide was present. The scale morphologies of the post-test specimens varied with the test environment.

a. AISI 316

b. AISI 310

c. Incoloy[®] 825

Figure 3-37. Photomicrograph of the Pre-Test Alloys
(oxalic/electrolytic etch)

a. Halide-free

b. 10 ppm Cl

c. 10 ppm F

Figure 3-38. Photomicrographs of AISI 316 Alloy Tested for 1000 Hours in a Molten Carbonate Environment at 760°C (oxalic/electrolytic etch)

a. Halide-free

b. 10 ppm Cl

c. 10 ppm F

Figure 3-39. Photomicrographs of AISI 310 Alloy tested for 1000 Hours in a Molten Carbonate Environment at 760°C (oxalic/electrolytic etch)

a. Halide-free

b. 10 ppm Cl

c. 10 ppm F

Figure 3-40. Photomicrographs of Incoloy[®]825 Alloy Tested for 1000 Hours in a Molten Carbonate Environment at 760°C (oxalic/electrolytic etch)

The extent of metal loss, maximum oxide penetration and total metal affected were measured for each specimen by a technique described schematically in Figure 3-41. The pertinent metallographic data, as well as weight change data, are compiled in Table 3-3.

These data show that the corrosion of the test alloys was accelerated by the presence of both chloride and fluoride in the electrolyte. Apparently the halides affected the morphology and adherence of the protective scales formed. The fluoride was more aggressive than the chloride to all three alloys.

Figure 3-41. Schematic of the Metallographic Technique Used for the Corrosion Tests

Table 3-3

Summary of the 1000-Hour Metallographic and Weight Change Data

	AISI 316			AISI 310			INCO 825		
	CONTROL	10 PPM CL ⁻	10 PPM F ⁻	CONTROL	10 PPM CL ⁻	10 PPM F ⁻	CONTROL	10 PPM CL ⁻	10 PPM F ⁻
METAL LOSS, mils/side ($\frac{A-B}{2}$)	1.0	1.9	1.6	0.3	0.0	1.3	1.0	0.5	1.0
MAXIMUM OXIDE PEN ⁿ , mils/side (C)	1.3	0.6	1.4	0.6	1.4	2.0	1.3	1.9	1.6
TOTAL METAL AFFECTED, mils/side ($\frac{A-B}{2} + C$)	2.3	2.5	3.0	0.9	1.4	3.3	2.3	2.4	2.6
WEIGHT CHANGE									
500 HR - %	+3.3	-5.1	-0.9	+1.2	+0.7	+0.5	+2.2	-5.6	+2.9
1000 HR - %	+3.6	-1.2	-3.2	+1.5	+1.2	+0.4	+2.6	-1.6	+3.6

In halide-free and chloride-containing environments, the AISI 310 alloy was the most resistant of the alloys tested. However, in the presence of fluoride, attack of the AISI 310 alloy was comparable to that of AISI 316 and somewhat higher than that of Incoloy[®] 825 (Table 3-3). The Incoloy[®] 825 alloy showed the most consistent rate of attack in the three environments in which it was tested.

From the 1000-hour weight change data (Table 3-3) it is deduced that the halide ions aggravate the corrosion of the test alloys by causing the oxide layers to spall. For the AISI 316 and AISI 310 alloys, the fluoride appears to have a stronger effect on oxide spalling than does the chloride. For Incoloy[®] 825, the weight change data suggests that chloride induces spalling, whereas the fluoride does not. This is in general agreement with the appearance of the oxide scales shown in Figures 3-38 and 3-40.

SEM and Microprobe results, conducted at UTRC, show for the AISI 316 control specimen, Figure 3-42, an outer scale consisting of oxides of iron and nickel with a continuous chromium-rich oxide underlayer. An intermittent silicon-rich oxide layer is observed above the chromium-rich oxide layer. In the presence of chloride, Figure 3-43, the chromium-rich oxide layer loses its continuity, appears less compact, and is interspersed with a nickel-rich oxide. The silicon-rich oxide layer is essentially non-existent. The specimen exposed to the fluoride environment, Figure 3-44, also showed an outer layer of iron and nickel oxides with a continuous chromium oxide enriched underlayer. In addition, the grain boundaries underneath the continuous chromium-rich oxide layer show a significant amount of the same phase. Nickel enrichment is observed above and below the chromium oxide layer. As in the control specimen, an intermittent silicon oxide layer is observed above the chromium oxide layer.

BEI

Cr

Ni

Fe

Si

Figure 3-42. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 316 Control Specimen Tested for 1000 Hours at 760°C in a Molten Carbonate Environment Free of Halides

BEI

Cr

Ni

Fe

Si

Figure 3-43. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 316 Specimen Tested for 1000 Hours at 760°C in a Molten Carbonate Environment Containing 10 ppm Cl in the Oxidant Gas

Figure 3-44. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 316 Specimen Tested for 1000 Hours at 1400°F in a Molten Carbonate Environment Containing 10 ppm F in the Oxidant Gas

Figures 3-45 to 3-47 show the elemental X-Ray maps of the oxide layers on the AISI 310 alloy. The control specimen, Figure 3-45, shows an oxide composition very similar to the AISI 316 alloy specimens discussed above. In the presence of chloride, the chromium-rich oxide layer takes on a peculiar ribbed appearance which could not be explained. This layer is intermixed with iron and nickel-rich oxides in contrast to the relatively pure chromium-rich oxide layer in the control sample. Again, intermittent enrichment of silicon oxide is evident on top of the chromium-rich oxide layer. Specimens exposed to the fluoride-containing environment show similar elemental distribution, but the chromium-rich oxide layer appears thinner and extends into the outermost grain boundaries of the base metal. The grain boundaries underneath the chromium-rich oxide layers appear to be depleted of chromium.

Figure 3-45. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 310 Control Specimen Tested for 1000 Hours at 760°C in a Molten Carbonate Environment Free of Halides

BEI

Cr

Ni

Fe

Si

Figure 3-46. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 310 Specimen Tested for 1000 Hours at 760°C in a Molten Carbonate Environment Containing 10 ppm Cl in the Oxidant Gas

Figure 3-47. Backscatter Electron Image (BEI) and Elemental X-Ray Maps of the AISI 310 Specimen Tested for 1000 Hours at 1400°F in a Molten Carbonate Environment Containing 10 ppm F in the Oxidant Gas

The Incoloy[®] 825 control specimen, Figure 3-48, also shows the nickel and iron oxides in the outer layer and a continuous chromium-rich oxide underlayer. Upon exposure to the chloride-containing environment, Figure 3-49, the chromium-rich oxide layer became significantly thinner and extended into the grain boundaries of the base metal. Chromium depletion in the matrix underneath the chromium-rich oxide layer is also evident. The specimen exposed to the fluoride-containing environment, Figure 3-50, was similar in appearance, but the presence of chromium-rich oxide and depletion of chromium in the grain boundaries were also noted.

During the SEM and Microprobe analyses, a special effort was made to find halides in the oxide scales, but none could be detected. This suggests that either halides are present in concentrations below the detection limit of the instruments (<1%) or that volatile halide corrosion products were formed and evaporated. An example of a volatile corrosion product of this type is CrO_2Cl_2 which has a boiling point of 117°C , well below the 760°C test temperature.

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Conclusions

Results of the corrosion tests indicate that the presence of a halide in a molten carbonate electrolyte accelerates the corrosion of AISI 316, AISI 310, and Incoloy[®] 825 alloys. In a halide-free and chloride-containing environment, the AISI 310 alloy was the most resistant of the three. However, in a fluoride-containing molten carbonate environment, the resistance to corrosion of AISI 310 was comparable to that of AISI 316 and somewhat lower than that of Incoloy[®] 825.

Metallographic and weight change data suggest that the halides accelerate the corrosion of the alloys by detrimentally affecting the adherence of the protective scales. This is evidenced by more oxide spalling in samples tested in the halide-containing environments than in the control samples.

SEM/Microprobe analyses showed that the oxide scales formed on the three alloys were similar in composition. The resistance of the alloys to corrosion appeared to be related to the uniformity, continuity, and compactness of the chromium-rich oxide protective layer. Breakdown of this layer resulted in increased corrosion. It should be pointed out that since no X-Ray or Electron Diffraction analyses were conducted in this study, the specific make-up of the protective scales, i.e. whether spinels, mixed spinels, or metal oxides, could not be determined. In the presence of fluoride, the corrosive attack appeared to be more intergranular in nature for all three alloys. This is evidenced by the appearance of the chromium-rich oxide phase in the outermost grain boundaries of the base metal and by chromium depletion of the grain boundaries.

Although a special effort was made to find halides in the oxide scales, none could be detected. This suggested that either the halides were present in concentrations below the detection limit of the instrument ($<1\%$) or that volatile corrosion products were formed and then lost by evaporation in the course of the test. The presence of voids in the oxide scales lends credence to the latter hypothesis.

TASK 4 - IN-CELL INVESTIGATION

Experimental in-cell data on the effects of hydrogen chloride present in the fuel gas of a molten carbonate fuel cell were previously obtained by IFC under Contract DE-AC-01-79ET15440 with DOE. The experimental conditions and reactant compositions used in those tests are listed in Table 4-1. Two different hydrogen chloride contents were introduced into the fuel gas at atmospheric pressure, first 60 ppm and then 10 ppm. Between the introduction of the 60 ppm and the 10 ppm, the performance of the cell was allowed to recover. In these tests, the HCl was introduced in the fuel by adding the appropriate amount of HCl to the fuel-gas water saturator.

TABLE 4-1

EXPERIMENTAL CONDITIONS FOR PREVIOUS CHLORIDE TESTS*
(CELL NO. 319)

Pressure = 1 atm

Temperature = 650°C

Fuel Composition:

51.0 mole % H₂, 9.6 mole % CO, 10.6 mole % CO₂
28.8 mole % H₂O

Oxidant Composition:

11.7 mole % O₂, 17.1 mole % CO₂, 64.1 mole
% N₂, 7.1 mole % H₂O

Current Density = 172 ma/cm²

Fuel (H₂ + CO) Utilization = 81%

Oxidant (CO₂) Utilization = 30%

Fuel HCl Content = 10 ppm and 60 ppm

*DOE Contract No. DE-AC01-79ET15440

The experimental cell voltage data at a constant current density of 172 mA/cm^2 after the introduction of the HCl into the fuel gas are presented as a function of time in Table 4-2 for 10 ppm HCl and Table 4-3 for 60 ppm HCl. A graph of the data for these tests is presented in Figure 6-5.

TABLE 4-2

EXPERIMENTAL DATA FOR TEST WITH 10 PPM HCl IN FUEL

<u>CELL TIME</u> (HRS)	<u>TIME AFTER HCl INTRODUCTION</u> (HRS)	<u>CELL VOLTAGE</u> (VOLTS)	<u>VOLTAGE DECAY</u> (VOLTS)
790	0	0.681	0
810	20	0.667	0.014
834	44	0.670	0.011
858	68	0.662	0.019
929	139	0.658	0.023
953	163	0.660	0.021
977	187	0.663	0.018
1001	211	0.651	0.030
1025	235	0.652	0.029
1097	307	0.630	0.051
1121	331	0.642	0.039
1145	355	0.643	0.038
1169	379	0.643	0.038
1193	403	0.643	0.038
1265	475	0.652	0.029
1288	498	0.639	0.042
1312	522	0.648	0.033

TABLE 4-3

EXPERIMENTAL DATA FOR TEST WITH 60 PPM HCl IN FUEL

<u>CELL TIME</u>	<u>TIME AFTER</u>	<u>CELL VOLTAGE</u>	<u>VOLTAGE DECAY</u>
(HRS)	<u>HCl INTRODUCTION</u>	(VOLTS)	(VOLTS)
	(HRS)		
629	0	0.678	0
	0.16	0.675	0.003
	1.83	0.623	0.055
	10.25	0.597	0.081

The cell design used in this cell test was the same as that described previously under out-of-cell testing except that the cathode-side current collector consisted of a perforated plate and Kintex fabricated from AISI 316 stainless steel rather than single-piece 310 AISI stainless steel.

Additional in-cell tests were attempted under this contract as described in the Test Plan. Since elevated pressure operation was desired, the method of halide introduction was changed from a halide solution in a gas saturator to bottles containing halide. Hydrogen and nitrogen were used as the carrier gases to introduce halides into the fuel and oxidant, respectively. Because of adsorption or reaction of the halides with the walls of the bottles during the time necessary to modify the test stands for the safe handling of the halide gases, no useful data were obtained with this injection system.

TASK 5 - POST-TEST ANALYSIS

POST TEST OBSERVATIONS FROM HALF-CELL PERFORMANCE TESTS

Experimental Procedure

The half-cell performance tests are summarized in Table 3-2. After the completion of each half-cell test, the cell chamber was flushed with an inert gas and allowed to cool. Most often, the cell was removed from the furnace while it was at about 650°C and allowed to cool rapidly under ambient conditions. The cell chamber was opened almost immediately after it was removed from the furnace and the cell holder placed on a stand to cool down to room temperature and then stored in a desiccator containing a water absorbant.

After all the half-cell tests had been completed, visual observations were made of all the components tested. These observations included the condition of each component and the degree of contact between components. Thickness and resistivity measurements were also performed on cell components. Thickness was determined by using calipers whenever possible, or by breaking the sample in half, setting it on edge and comparing the thickness with a calibrated scale on the eyepiece of a microscope under 4X magnification. Errors between the two methods were less than 5 percent.

Resistivity was measured using the method of L. J. van der Pauw [22], summarized by J. L. Smith and J. R. Stapay [23]. The sample to be measured was sanded flat and its thickness, d , measured by calipers. The sample was then placed on a clean 7.5 cm diameter alumina plate. Four spring-loaded 0.038 cm diameter platinum wires were orientated so that the tips of the wires made contact with the edge of the sample, each wire tip as far apart from the other tips as possible. The platinum wires were held onto

the alumina with new alligator clips, which were attached to silver wire leads. Current was first passed through two adjacent wires and the potential measured across the other two wires, and a resistance calculated, $R_1 = V_1/I_1$. Then current was passed through two other adjacent wires, one of the wires being the same as that used to give I_1 , and the potential across the remaining two wires measured. The second resistance, $R_2 = V_2/I_2$ was then used with R_1 to determine the resistivity, ρ , by iteratively solving:

$$\exp\left(\frac{-\pi R_1 d}{\rho}\right) + \exp\left(\frac{-\pi R_2 d}{\rho}\right) = 1$$

This method gave a resistivity of $0.00119 \, \Omega \, \text{cm}$ for a graphite sheet (literature values range from $0.0010 \, \Omega \, \text{cm}$ to $0.0019 \, \Omega \, \text{cm}$).

Component conditions noted included the color, the degree of cracking, mechanical strength, hardness and any other unusual features. Hardness was determined by comparing the depth and ease in which a scratch could be made using a razor blade in the sample relative to new component material not tested in the half-cell.

The degree of contact between components was determined by how easily components could be separated using a razor blade. Components that were separated when received were considered to have poor contact, unless one component left marks or indentations on the entire surface on the other, in which case contact was considered probably good. Components that were attached together when received but were not in full contact or took little effort to separate were considered to have poor contact. Samples that could not be separated at all or without a dedicated effort were considered to have good contact.

Thickness Measurements

The results of the pre-test and post-test component thickness measurements are given in Table 5-1. Pre-test thicknesses were obtained on all matrices, all working electrodes, some of the counter electrodes, parts of the current collectors, but none of the fine pores. All pre-test components had relatively consistent thicknesses. The matrix used in Cathode Test 6 consisted of three layers of tape, but would have fallen into the range of the other values if it had only two layers. Post-test matrix thicknesses varied greatly, depending on the amount of compression placed on the tape before or during the test and on electrolyte on the surface of the tape, which may have interfered with the measurements. The tape and the working electrode in Cathode Test 3 could not be separated, so the cathode thickness was subtracted away from the thickness of both cathode and tape to obtain the matrix thickness, and this may have introduced errors. Note that the active area matrix thicknesses are much smaller than either the wick area or pre-test thicknesses. This is probably a result of the method in which the three tests shown in Table 5-1 were assembled, where the working electrode was pressed into the tape. Matrix layer thicknesses were probably not significantly affected by the presence of halide in the electrolyte.

Pre-test working electrode thicknesses were very consistent. The counter electrodes used in Cathode Tests 8 and 9 and Anode Tests 1, 2 and 3 were of the same material as the working electrodes.

TABLE 5-1 HALF CELL POST-TEST OBSERVATIONS SUMMARY

	Pre-Test Matrix	Post-Test Wick Area Matrix	Post-Test Active Area Matrix	Pre-Test Working Electrode	Post-Test Working Electrode	Pre-Test Counter Electrode	Post-Test Counter Electrode
	Thickness (mils)	Thickness (mils)	Thickness (mils)	Thickness (mils)	Thickness (mils)	Thickness (mils)	Thickness (mils)
Cathode Test #2	19.14	20	-	40	-	-	-
Cathode Test #3	19.04	30.5	-	40	44.5	-	-
Cathode Test #4	19.04	-	-	40	-	-	-
Cathode Test #5	17.54	-	15	40	33	-	-
Cathode Test #6	26.4	29.5	-	40	44.3	-	-
Cathode Test #7	17.54	-	-	40	45	-	-
Cathode Test #8	17.94	-	12.3	40	41.8	40	42
Cathode Test #9	17.94	17.2	-	39	51.7	40	48
Anode Test #1	17.94	17.2	12.3	66	64	-	54.1
Anode Test #2	17.94	19	-	66	66	-	66
Anode Test #3	18.7	19.7	-	66	63	-	59.1

	Pre-Test Current Collector Base	Post-Test Current Collector Base	Pre-Test Current Collector Rib	Post-Test Current Collector Rib	Post-Test Current Collector Rib	Post-Test Fine Pore
	Thickness (mils)	Thickness (mils)	Thickness (mils)	Thickness (mils)	Height (mils)	Thickness (mils)
Cathode Test #2	-	8	-	6	6	-
Cathode Test #3	-	9	-	-	54	-
Cathode Test #4	-	-	-	-	-	-
Cathode Test #5	-	-	-	-	-	-
Cathode Test #6	7	-	4	-	-	-
Cathode Test #7	7	9	4	9	56	-
Cathode Test #8	-	-	-	-	-	-
Cathode Test #9	-	12.3	-	9.8	57	-
Anode Test #1	-	36	-	-	-	3.7
Anode Test #2	50	-	-	-	-	5
Anode Test #3	50	49	-	-	-	4

	Resistivity (ohm-cm)				
	Working Electrode	Counter Electrode	Tape Color	Tape Condition	Working Electrode Condition
Cathode Test #2	-	-	yellow	finely cracked and very brittle	-
Cathode Test #3	11.75	-	yellow	finely cracked-no loss of contact	brittle
Cathode Test #4	-	-	-	-	-
Cathode Test #5	14.15	-	yellow	large cracks-loss of contact in places	uncracked
Cathode Test #6	14.55	-	light-yellow	layer near cath. rubbed-large cracks	soft, very brittle, extra porous
Cathode Test #7	3.445	-	-	-	tab broken off, brittle
Cathode Test #8	3.518	3.116	white-yellow	large cracks-some loss of contact	not soft like CE, not cracked
Cathode Test #9	11.505	2.956	dull white	large cracks-some loss of contact	very soft, brittle, has small cracks
Anode Test #1	0	0	white	cracked in wick but not in active area	tan colored film on surface
Anode Test #2	0	0	white	uncracked	thick soft brown coating on surface
Anode Test #3	0	0	white	uncracked-blistered wick area	tan colored film on surface

The anodes appear to have thinned slightly from testing, probably due to the external pressure applied to the cell package to ensure good contact between components. Halide did not seem to affect anode thicknesses greatly. The cathodes on the other hand thickened from testing, especially the fluoride test (Cathode Test 9) where both the working electrode and the counter electrode thicknesses increased significantly. The increase in thickness may have been due to electrolyte on the electrode surface, thus interfering with the thickness measurements. However ignoring Cathode Test 5 which lost thickness probably because of the assembly procedure, there is a weak correlation between the increase in thickness and the total operating time (Figure (5-1)). Cathode compaction has been noted in molten

Figure 5-1. Effect of Fluoride on NiO Expansion

carbonate stacks where swelling is restrained by externally applied pressure. The nickel cathodes swelled due to reactions with oxygen, lithium, and possibly halide. The cathodes normally convert to lithiated nickel oxide in the absence of halide. Fluoride appears to enter the nickel oxide lattice, or change the manner of nickel oxidation, while chloride did not, resulting in the Cathode Test 9 working and counter electrodes swelling more than those used in other tests. Fluoride entering the lattice structure is possible because the fluoride ion is about the same size as oxygen, while the chloride ion is larger (atomic radii: $F^- = 1.36 \text{ \AA}$, $Cl^- = 1.81 \text{ \AA}$, $O^{2-} = 1.40 \text{ \AA}$, $Li^+ = 0.60 \text{ \AA}$). In a situation where the expansion would be constrained, such as in a stack (or to some extent, in the half-cell), this would result in a decrease in the porosity of the cathode and would affect electrolyte distribution in the cell.

Not all the pre-test current collector dimensions were recorded, but can probably be considered to be uniform from test to test. Pre-test rib height is not included in the table, but is about 59 mils. These results cannot be considered accurate because thickness could only be determined at the edge of the sample and the edge may or may not have had burrs. Often electrolyte was found on the surface of the current collector. Nevertheless, it appears that the AISI 310 stainless steel shielded slot current collectors used in cathode tests have increased in thickness, probably due to electrolyte on the surface or corrosion of the current collector. The nickel plate used in Anode Test 3 is unchanged.

Pre-test fine pore thicknesses are about 4 mils. The post-test values indicated in Table 5-1 show that the thicknesses did not change significantly.

Resistivity

Resistivity measurements were made on all lithiated nickel oxide components that were available. All nickel components used in the anode tests had immeasurably small resistivities. The working electrode used in Cathode Test 6 (3.1 anion percent chloride) has a high resistivity, relative to the other values in the table. Yet the working electrode in Cathode Test 8 (23 anion percent chloride) has a low resistivity, which is about equal to the resistivity of the Cathode Test 8 counter electrode. The Cathode Test 9 working electrode has a high resistivity, while its counter electrode has a low resistivity. The resistivity values may indicate how much lithium has entered the lattice. A low resistivity may indicate that the NiO was fully lithiated. This would explain why Cathode Test 7, which ran the longest of any test and may have had sufficient time to lithiate, has a low resistivity. Lithium also enters the lattice more readily at high potentials. This might explain the difference in resistivity between the working and counter electrodes used in Cathode Test 9. It is not understood why Cathode Test 6 has a high resistivity, while Cathode Test 8 has low resistivities in both the working and counter electrodes. It was hoped that the resistivity values would indicate whether or not halide had entered the lattice structure, but conclusions were difficult to draw from this set of data.

Condition of Matrix

Unfilled tape that has been heated to cell operating temperature of 650°C is brittle and white. Most of the matrices used in cathode tests ended with a yellow color. The yellow color is thought to be due to chromate (CrO_4^{-2}) in the electrolyte. Chromium in the stainless steel components of the cathode side of a cell oxidizes and diffuses into the electrolyte. Chromium in the nickel anodes did not give the electrolyte a yellow

color because of the reducing atmosphere in the anode half-cell chamber and the method of anode fabrication. However, the cathode tests that had halide in the electrolyte did not have as deep a yellow color in the matrix as those that ran with halide-free electrolyte. The chloride cathode tests (Tests 6 and 8) had matrices that had a yellow tint, with the tint lighter in the test having more chloride in the electrolyte. The fluoride cathode test (Test 9) had a matrix that showed hardly any yellow coloring. The most likely reason for the lack of yellow coloring in the matrix in the presence of halide is that the chromate ion reacted with the halide, forming a volatile compound (for example, CrO_2Cl_2 , which has a boiling point (117C) that is much less than cell operating temperature). This is because all chromium compounds have some color with the exception of CrCl_2 , which is white. If this compound was formed, then CrF_2 , which is green, would have been expected to form in the fluoride test, and this color would be seen on the white matrix. Other explanations include a change in the oxidation state of chromium or the formation of a passivation layer impermeable to oxygen or chromate ion.

The matrices themselves were almost always found to have some cracks and were very brittle. This would probably be due to the method of cell assembly, the electrolyte removals during the test, or the cooling down process. Tape layer cracking was especially profound in Cathode Test 6. In Test 6, the layer of tape nearest the cathode was severely cracked or broken up, looking more like large grains of sand rather than a layer of fine particles. However, the same thing was not observed in Cathode Test 5, which was assembled in a similar fashion, or was it observed in any of the other halide tests leading to the conclusion that the layer was broken up because three tape layers were used in the configuration, instead of two.

The wick area of the matrix used in Anode Test 3 (23 anion percent fluoride in the electrolyte) had several large blisters. These blisters were easily broken to reveal several small air pockets, either partially or wholly en-

closed by white material. It is possible that these blisters were undistributed electrolyte.

Condition of Working Electrode

All the cathodes used in the half-cell tests were made brittle through use in the half-cell. Some cathodes contained small cracks which may have developed outside the Test 7, except the tab used in Cathode Test 7, used for electrolyte removal, which broke off during the test. The cathodes used in the halide tests (Cathode Tests 6, 8, 9) were soft in comparison to those tests which ran without halide in the electrolyte. This softness was determined by noting how easily a sample could be scratched with a scalpel. The NiO in the halide test cathodes did not flake away like the NiO in the clean electrolyte test cathodes when scratched. This soft layer was fairly thick, but did not go all the way through the cathode because the cathodes in the halide tests were just as brittle as the cathodes in the rest of the tests. The soft layer may be similar to the loss of adherence of particles observed in the General Electric full cell tests having chloride in the oxidant.

The anodes, unlike the cathodes, retained their original mechanical strength. A soft tan-colored film developed on the surface of all the anodes, even the anode used in the baseline cell. This film was found to be much thicker in Anode Test 2, the chloride test. It is possible that chromium in the anode may have reacted with an impurity present in all cells, possibly chloride, resulting in the soft tan layer.

Counter Electrode Condition

Wherever a nickel counter electrode was used in a half-cell configuration, rather than a gold counter electrode, the counter electrode was observed in the same condition as the working electrode (see Table 5-2). The only exception is that in Cathode Test 8 where the counter electrode was softer than the working electrode.

TABLE 5-2 HALF CELL POST-TEST OBSERVATIONS SUMMARY

	<u>Nickel Counter Electrode Condition</u>	<u>Gold Screen Condition</u>	<u>Fine Pore Condition</u>	
Cathode Test #2	-	smooth, has spotty film on surface	-	
Cathode Test #3	-	-	-	
Cathode Test #4	-	-	-	
Cathode Test #5	-	some gold left on tapes	-	
Cathode Test #6	-	not in contact with entire tape	-	
Cathode Test #7	-	-	-	
Cathode Test #8	normal appearance, very soft	pitted in areas	-	
Cathode Test #9	very brittle, cracked, very soft	appears unchanged	-	
Anode Test #1	tan colored film on surface	slightly pitted, spotty film on surface	tan colored film, has a crack	
Anode Test #2	thick soft brown coat, cracks at edge	slightly pitted	thick soft brown coating on surface	
Anode Test #3	tan colored film on surface	unpitted, small cracks in wires	tan colored film on surface	
=====				
	<u>Ni Current Collector Condition</u>	<u>310 SS Shielded Slot Plate Condition</u>	<u>Miscellaneous</u>	
Cathode Test #2	-	gold screen left impression in current collector	elyte wicked away 1.5 mm from tape	
Cathode Test #3	-	electrolyte on the surface of current collector	some elyte on current collector	
Cathode Test #4	-	-	-	
Cathode Test #5	-	-	-	
Cathode Test #6	-	-	no loss of adherence of particles in WE	
Cathode Test #7	-	electrolyte on the surface of current collector	some elyte on current collector	
Cathode Test #8	-	310ss ribs corroded, flat side blisters w/deep pits	blisters contain red and tan layers	
Cathode Test #9	-	310ss bare metal+black coat, CC-elyte+some blisters	black coat not same thing as blisters	
Anode Test #1	tan colored film on surface	-	elyte seen on gold screen	
Anode Test #2	made impression into flat side of WE	-	lots of elyte on 310 ss plate	
Anode Test #3	tan colored film on surface	-	tape blisters are mostly air	
=====				
	<u>Contact Between Current Collector & Working Electrode</u>	<u>Contact Between Cathode or Fine Pore and Tape</u>	<u>Contact Between Tape and Counter Electrode</u>	<u>Contact Between Anode and Fine Pore</u>
Cathode Test #2	-	probably poor	-	-
Cathode Test #3	good	good	-	-
Cathode Test #4	-	-	-	-
Cathode Test #5	-	good	-	-
Cathode Test #6	-	easily separated	poor	-
Cathode Test #7	probably good	-	-	-
Cathode Test #8	left marks in WE	good	easily separated	-
Cathode Test #9	good	good	fair	-
Anode Test #1	good	easily separated	poor, none in wick	good
Anode Test #2	left marks in WE	probably poor	probably poor	poor
Anode Test #3	good	easily separated	easily separated	good

Fine Pore Condition

The fine pores in all the anode tests were in the same condition as the corresponding working electrode and counter electrode.

Gold Screen Condition

The gold wire screen was used as the counter electrode in Cathode Tests 2-7 and was used to connect the counter electrode to out-of-cell electronic equipment in Cathode Tests 8, 9 and Anode Tests 1-3. In cases where the gold screen was used as a counter electrode, a gold film was often found on the matrix in places where the gold contacted the matrix. Some electrolyte was found on all the gold screens observed, which appeared as a spotty film. Some of the screens were pitted, which is not necessarily due to the presence of halide, since Anode Test 1 (baseline test) had a pitted gold screen. The gold screens used in the fluoride anode and cathode tests, however, appeared unchanged.

Nickel Current Collector Condition

The nickel current collectors in the anode tests (see Table 5-2) were in the same condition as the corresponding working electrode and counter electrode.

Stainless Steel Current Collector Condition

The AISI 310 stainless steel shielded slot plates were used in cathode tests both as current collectors and as a method of allowing gases to escape from the counter electrode. In some tests both plates were not available for post-test observations. The most significant observations

were made on the plates used in Cathode Tests 8 and 9 (23 anion percent chloride and fluoride in the electrolyte, respectively).

In Cathode Test 8, the current collector was not available but the AISI 310 stainless steel plate under the counter electrode was. The flat side of the plate (which was next to the counter electrode) was covered with a shiny black brittle material that was easily scraped away. Underneath it was a tan-colored layer; underneath which was a red-brown colored layer, underneath which was what appeared to be bare metal. Some areas had large blisters, which when scraped away, revealed a great deal of the red-brown material and deep pitting. The blisters were located where the plate made contact with the counter electrode, in some areas counter electrode material was found attached to the blisters. The ribbed side of the plate did not have the blisters, but still had the shiny black material and was covered with electrolyte.

Both the current collector and the plate under the counter electrode from Cathode Test 9 were available for post-test analysis. Bare metal was seen on both parts. The plate under the counter electrode had areas covered with the same shiny black material found on the Cathode Test 8 plate but no blisters were found. The shiny black material was difficult to scrape away, but where it could be done, tan material and deep pitting were found. In some areas on the ribbed side, gray-silver blisters were found, but these were mostly air pockets that were easily flaked away. Underneath the air pockets was a thin brown layer. The current collector's flat side (facing the working electrode) had a few of the blisters that were noted on the Cathode Test 8 plate. The ribbed side was covered with electrolyte, but no blisters or tan material was found.

Contact Between Components

In all cases the contact between the current collector and the working

electrode was good. On the other hand, contact between the working electrode (or fine pore) and the matrix was only good in the cathode tests where special steps were taken to ensure good contact. In Cathode Test 3, LiAlO_2 powder was applied between the tape and the working electrode, which gave good contact. In Cathode Tests 5 and 6, the tape was softened with isopropanol and the working electrode was pressed into the tape. Cathode Test 5 had good contact between the two components but Cathode Test 6 did not, probably because of the broken up third layer. Hot pressing the matrix and working electrode together resulted in good matrix-working electrode contact in the case of Cathode Tests 8 and 9, but did not in the case of the anode tests. The fine pores were easily separated from the matrix. Contact between the matrix and the counter electrodes was generally poor. The gold screen in Cathode Test 6 was not in contact with the entire tape, while the nickel counter electrodes and tapes were easily separated. Contact between the anode fine pores and working electrodes were good except in the case of Anode Test 2 where the ribbed side of the anode was facing the fine pore, giving less than 50 percent contact. Contact between components did not seem to be affected by the presence of halide in the electrolyte.

Conclusions

Chloride and fluoride in the electrolyte affected both anode and cathode half-cell components in several ways. The most significant effect was the corrosion and spalling of the cathode side stainless steel in the presence of chloride. A similar effect was observed to be not as pronounced in the presence of fluoride. This visually observed effect differs from the corrosion experiments which found fluoride to be more aggressive than chloride in corroding AISI 310 stainless steel. This is explained by the way the two experiments were conducted. The corrosion experiments were conducted at a higher temperature for a much longer period of time, under a much lower halide concentration than the half-cell experiments. Fluoride

may or may not be more aggressive than chloride in the half-cell experiment environment. Observations made on the half-cell components were not as rigorous as those made on the corrosion test specimens; the half-cell observations may have missed the development of an oxide layer or a change in mass of a component from corrosion and spalling. The half-cell tests showed that stainless steel is strongly attacked by halide; the corrosion tests quantified these observations, but at different conditions.

A potentially significant effect was observed in the case of nickel oxide in the presence of fluoride. In this case, the nickel oxide swelled in thickness twice as much as in any other test, even those having chloride in the electrolyte. The fluoride may have affected the oxidation and lithiation of the nickel, and the fluoride itself may have entered the lattice structure of the NiO. Under external component compression, this could lead to a denser cathode, changing how the electrolyte is distributed throughout a cell.

Other important halide effects included an interaction between the chromium in the stainless steel and halides, and softening of the nickel oxide components.

TASK 6 - MODEL DEVELOPMENT

Based on the literature survey, thermodynamic analyses, and experimental results, halides can affect the performance of molten carbonate fuel cells in several ways. The performance of each component, anode, cathode, and matrix, can be affected, and an electrolyte concentration polarization can occur due to different halide ion concentrations in the anode and cathode. These results were used to develop a model of the performance decay of molten carbonate fuel cells in the presence of halides. The electrolyte composition difference between the electrodes is described first because it affects the concentrations within the anode, cathode, and matrix and hence their performances as well.

Electrolyte Concentration Polarization

Halide present in a molten carbonate electrolyte migrates between the electrodes due to three effects: diffusion, ionic transference, and bulk flow. In equation form, the flux from the cathode toward the anode is:

$$\dot{M} = -D \frac{dc}{dx} + CW \frac{d\phi}{dx} + CV \quad (6-1)$$

where the symbols are defined in the Table of Nomenclature. If a higher halide ion concentration is present on the anode side than the cathode side of a cell, the first term on the right represents the diffusion of halide toward the cathode as expressed by Fick's first law. The second term represents the flux of halide ion toward the anode due to the potential gradient in the electrolyte and the negative charge on the halide ion. The third term represents the bulk flow of halide ion toward the anode since the flux of carbonate ions across the cell when current flows results in a net bulk velocity in the electrolyte [24].

Since the rate at which halide enters and leaves cells is very low in the ppm range, this equation can be used to calculate a pseudo steady state concentration profile by assuming that the flux across the cell is zero. A true steady state is not achieved because of the loss of electrolyte with time. Equation (6-1) becomes:

$$\frac{dc}{c} = \frac{W}{D} d\phi + \frac{V}{D} dx \quad (6-2)$$

The potential difference across the cell, $\Delta\phi$, is equal to the matrix IR plus an IR contribution within the electrodes. The velocity of the electrolyte is dependent on the current using Faraday's law [24]:

$$V = \frac{30 (I/A)}{96,500 \rho} \quad (6-3)$$

Using these relationships,

$$\ln \frac{C_A}{C_c} = \frac{WIR}{D} + \frac{\delta}{D} \left(\frac{30 (I/A)}{96,500 \rho} \right) \quad (6-4)$$

For an 18 mil matrix, $\delta = 0.018$ (2.54 cm.) For a porosity of .042, a tortuosity = (porosity)^{-0.5} from the Bruggeman equation [25], an assumed diffusion coefficient of 10⁻⁵ cm²/sec and an electrolyte density of 1.93 g/cc, the last term on the right becomes

$$\frac{0.018 (2.54)}{(10^{-5})(0.42)^{1.5}} \times \frac{30 (I/A)}{96,500 (1.93)} = 2.70 \left(\frac{I}{A} \right) \quad (6-5)$$

for the contribution from the matrix. If a lumped parameter analysis is considered, contributions from the anode and cathode to this term can be estimated by dividing the total possible contribution from each by two. This assumes that the electrochemical formation or consumption of carbonate ions occurs in the center of each electrode. These terms are (for a 40 mil cathode of 0.75 porosity with an electrolyte content of 30 percent and a 56 mil anode with a 0.42 porosity and an electrolyte content of 30 percent)

$$\left[\frac{1}{2} \frac{(0.040 \times 2.54)}{[(0.75 \times 0.30)]^{1.5}} + \frac{1}{2} \frac{(0.056 \times 2.54)}{[(0.42 \times 0.30)]^{1.5}} \right] \frac{30 (I/A)}{96,500 (1.93) (10^{-5})} \quad (6-6)$$

The total last term is therefore

$$35.9 \left(\frac{I}{A} \right)$$

The two expressions in (6-6) are more significant than that in (6-5) because the velocities in the electrodes are higher than in the matrix.

The first term on the right of Equation (6-4) can be estimated if the mobility of the chloride is considered to be related to that of the carbonate ion by the ratio of the charge on the ion to its ionic radius [26].

From the conductivity of the carbonate, the carbonate ion mobility is $1.17 \times 10^{-5} \text{ cm}^2/\text{volt sec}$. The ratio of the charge to ionic radius of the carbonate is 0.67, and for the chloride, 0.552. The chloride mobility is then $0.96 \times 10^{-5} \text{ cm}^2/\text{volt sec}$. Using an iR of 20 mV at 100 mA/cm^2 and a diffusion coefficient of $10^{-5} \text{ cm}^2/\text{sec}$,

$$\frac{WiR}{D} = 0.30 \left(\frac{I}{A} \right) \quad (6-7)$$

Since this term is much less than (6-5), ionic transference can be seen to be negligible.

Substituting the sum of (6-5), (6-6), and (6-7) into Equation (6-4),

$$\ln \frac{C_A}{C_c} = 36.2 \left(\frac{I}{A} \right) \quad (6-8)$$

The differences in open circuit potential between two electrodes in electrolyte of different halide concentrations were measured in this program and are shown in Figure 6-1. That data can be fit by the equation

$$\eta_{conc} = 0.060 \ln \frac{C_{CARB C}}{C_{CARB A}} \quad (6-9)$$

or

$$\eta_{conc} = 0.060 \ln \left(\frac{1 - C_c}{1 - C_A} \right) \quad (6-10)$$

Eliminating C_c between Equations (6-8) and (6-10)

$$\eta_{conc} = 0.060 \ln \left(\frac{1 - C_A e^{-36.2(I/A)}}{1 - C_A} \right) \quad (6-11)$$

The large exponent of 36.2 indicates that during operation on load, the cathode will be essentially free of halide and all of the halide will be located on the anode side. This means that halide will leave the cell only in the fuel effluent and C_A , the concentration of halide in the electrolyte at the anode will be directly dependent on the concentration of halide in the fuel exit gas. The variation of C_A over the surface of the electrode area is assumed to be relatively small at steady state. This result is different from the assumption used in the estimation of electrolyte equilibrium composition in Task 1 that the halide will leave in the oxidant effluent.

Figure 6-1. Potential Difference Due To
 Difference in Electrolyte Composition

The relationship between the gas- and liquid-phase concentrations (vapor pressures) were calculated in this program and are presented in Figure 6-2. These graphs were curve fit by the equations:

$$C_{ACL} = 923.43 \exp \left[-10.199 (LO \times 10^6)^{-0.09212} \right] \quad (6-12)$$

for chloride where LO is the mole fraction of chloride in the fuel effluent and

$$C_{AF} = 1.8178 - 1.8173 \exp \left[-0.3942 (FO \times 10^6) \right] \quad (6-13)$$

for fluoride where FO is the mole fraction of fluoride in the fuel effluent.

The steady-state concentrations of chloride and fluoride in the fuel effluent can be calculated from the inlet concentrations in the fuel and oxidant if the concentration in the oxidant exhaust is assumed to be negligibly small. The resulting equations are:

$$LO = \frac{\frac{(x_H + x_{CO} + x_C + x_{HO})}{(x_H + x_{CO})} \frac{(F_{CL})}{(F_{UT})} + \frac{(x_O + x_{OC} + x_N + x_{OH})}{x_{OC}} \frac{(O_L)}{(O_{UT})}}{\frac{x_C + x_{HO} + 2(F_{UT})(x_H + x_{CO})}{(x_H + x_{CO})(F_{UT})} + \frac{1 - (F_{UT})}{(F_{UT})}} \quad (6-14)$$

and

$$FO = \frac{\frac{(x_H + x_{CO} + x_C + x_{HO})}{(x_H + x_{CO})} \frac{(F_F)}{(F_{UT})} + \frac{(x_O + x_{OC} + x_N + x_{OH})}{x_{OC}} \frac{(F)}{(O_{UT})}}{\frac{x_C + x_{HO} + 2(F_{UT})(x_H + x_{CO})}{(x_H + x_{CO})(F_{UT})} + \frac{1 - (F_{UT})}{(F_{UT})}} \quad (6-15)$$

Prior to steady state being reached, a different relationship than that used in Equations (6-11), (6-12), (6-13), (6-14), and (6-15) must be used. If all of the halide is assumed to be stored in the anode, the anion fraction of the halide in the anode will build up with time during an initial transient period. The initial moles of carbonate in the anode is

$$\frac{0.01792 \text{ g } (1.93 \text{ g/oc})}{91.89 \text{ g/mole}} = 3.76 \times 10^{-4} \frac{\text{MOLES}}{\text{cm}^3} \quad (6-16)$$

Figure 6-2. Calculated Vapor Pressures of Halides

Some fraction of this (Z) may be present in thin films which will react with the halide and introduce concentration polarizations before the entire anode reaches steady-state. The moles of chloride from the fuel increases with time as:

$$(MFC) = \frac{2 (\cancel{IA})(3600)}{F} \left(\frac{x_H + x_{CO} + x_C + x_{HO}}{x_H + x_{CO}} \right) \frac{(P_{CL})}{(F_{UT})} T \quad (6-17)$$

The moles of fluoride from the fuel increases as:

$$(MFF) = \frac{2 (\cancel{IA})(3600)}{F} \left(\frac{x_H + x_{CO} + x_C + x_{HO}}{x_H + x_{CO}} \right) \frac{(PF)}{(F_{UT})} T \quad (6-18)$$

Similarly for the oxidant gas, the moles of chloride from the oxidant is:

$$-(MOC) = \frac{2 (\cancel{IA})(3600)}{F} \left(\frac{x_O + x_{OC} + x_N + x_{OH}}{x_{OC}} \right) \frac{(CL)}{(OUT)} T \quad (6-19)$$

and for fluoride:

$$(MOF) = \frac{2 (\cancel{IA})(3600)}{F} \left(\frac{x_O + x_{OC} + x_N + x_{OH}}{x_{OC}} \right) \frac{(F)}{(OUT)} T \quad (6-20)$$

The concentration polarization for chloride is then, from Equation (6-10):

$$\eta_{\text{CONC CHLORIDE}} = 0.060 \ln \left[\frac{1}{1 - \frac{(MFC)}{2(3.76 \times 10^{-4})} - \frac{(MOC)}{2(3.76 \times 10^{-4})}} \right] \quad (6-21)$$

and for fluoride is:

$$\eta_{\text{CONC FLUORIDE}} = 0.060 \ln \left[\frac{1}{1 - \frac{(MFF)}{2(3.76 \times 10^{-4})} - \frac{(MOF)}{2(3.76 \times 10^{-4})}} \right] \quad (6-22)$$

In this transient analysis, assumptions are made that all of the halide is stored in a fraction of the electrolyte in the anode, and that no halide leaves the cell during the transient period. The first assumption will affect the length of the transient time and must be verified using experi-

mental data. The second assumption is based on the probable manner in which the halide will be scrubbed from the reactant gases by the cell. The high effectiveness of the cell as a scrubber will probably result in halide in the fuel being removed near the fuel flow inlet, with little appearing in the fuel exhaust until breakthrough occurs. The case is not as simple with the cathode reactant and a crossflow configuration, but, with a lumped parameter analysis, this assumption is considered to be better than the assumption of uniform composition used in a homogeneous reactor model.

The concentration polarizations from Equations (6-21) and (6-22) are used until they exceed the values calculated from the steady-state Equations (6-11), (6-12), (6-13), (6-14), and (6-15). Then the steady-state equations are used.

Anode Polarization

Halides can affect the performance of anodes in three ways: loss of electrolyte from the anode, reduction in the anode kinetics for the H_2 oxidation reaction at the inlet hydrogen pressure, and an increase in the utilization loss due to increased sensitivity to hydrogen pressure.

Experimental half-cell anode overpotential data previously obtained at 160 mA/cm^2 for a ribbed anode and fine pore are shown as a function of electrolyte percent fill in Figure 6-3. Points from the data graph are tabulated in Table 6-1 and are used to obtain a functional relationship for anode polarization.

$$\eta_a = f(MA) \quad (6-23)$$

where MA is the mass of the electrolyte in the anode per unit frontal area. Linear interpolation is used to obtain values of polarization at values of MA between those listed in Table 6-1. This mass can be obtained from the total mass of electrolyte in the cell, assuming that the capillary pore radius in each component is the same.

Figure 6-3. Performance Versus Electrolyte Fill for Anode

TABLE 6-1

ANODE POLARIZATION VALUES

<u>(Volts)</u>	<u>% Fill</u>	<u>mA (g/cm²)</u>
0.085	2.5	0.002883
0.058	5.0	0.005765
0.038	10.0	0.01153
0.033	15.0	0.017295
0.031	20.0	0.02306
0.0295	25.0	0.028825
0.0285	30.0	0.03459
0.028	35.0	0.040355
0.0285	40.0	0.04612
0.032	50.0	0.05765
0.046	60.0	0.06918

The total mass of electrolyte in the cell decreases with time because of the accelerated evaporation caused by the halides. This rate of loss at pseudo steady state can be calculated by noting that the inlet halide flow in both the fuel and oxidant contribute to the loss. The resulting equation for electrolyte mass per unit frontal area is:

$$M = 0.1066 - \frac{3600(91.89)(I/A)}{96,500} \left(\frac{x_H + x_{CO} + x_C + x_{HO}}{x_H + x_{CO}} \right) \left(\frac{P_{CL} + P_F}{F_U} \right) T - \frac{3600(91.89)(I/A)}{96,500} \left(\frac{x_O + x_{OC} + x_N + x_{OH}}{x_{OC}} \right) \left(\frac{F + C_L}{O_U} \right) T \quad (6-24)$$

where 91.89 is the molecular weight of the electrolyte and 96500 is Faraday's constant. The relative loss rates of lithium and potassium halides are near the relative lithium and potassium contents in the electrolyte, so no change in composition of the electrolyte is assumed.

The quantity 0.1066 in Equation (6-24) is the initial mass of electrolyte in the cell per unit area, calculated in the manner shown in Table 6-2.

The polarization of this anode at optimum fill at 160 mA/cm² was measured as a function of fuel composition [27] and found to vary with the concentration of hydrogen in the fuel gas according to the equation.

$$\eta_A = \frac{2.418 \times 10^{-2}}{(P_{H_2})^{1/2}} + 8 \times 10^{-3} \quad (6-25)$$

The square root dependence is considered to be present because of the importance of surface diffusion in the anode. This equation predicts a somewhat higher overpotential (42 mV) compared to the data in Figure 6-3 (28 mV). Correcting for this difference, the overpotential of the anode in the absence of halides, accounting for the effects of hydrogen pressure and electrolyte content is:

$$\eta_A = \left[\frac{2.418 \times 10^{-2}}{(P_{H_2})^{1/2}} + 8 \times 10^{-3} \right] \left[\frac{f(MA)}{0.028} \right] \quad (6-26)$$

TABLE 6-2

<u>Component</u>	<u>Average Thickness (cm)</u>	<u>X</u>	<u>Porosity</u>	<u>X</u>	<u>Percent Fill</u>	<u>Electrode Volume Area</u>
Cathode	0.040 (2.54)	x	0.75	x	0.22 =	0.01676
Anode	0.056 (2.54)	x	0.42	x	0.30 =	0.01792
Fine Pore	0.004 (2.54)	x	0.36	x	0.37 =	0.00135
Matrix	0.018 (2.54)	x	0.42	x	1.00 =	0.01920
						<hr/> 0.05523 ₂ cc/cm ²

With Electrolyte Density of 1.93 g/cc, Initial
Mass of Electrolyte Is

$$1.93 \times 0.05523 = 0.1066 \text{ g/cm}^2$$

The halides are suspected to poison the anode reaction because of the rapid loss of performance experienced by cells in which chloride was introduced into the anode gas. Not enough chloride was introduced to convert much electrolyte to chloride in the time period in which the performance loss occurred. Enough chloride was introduced, however, to considerably cover the anode catalyst surface area. Chloride has been found to poison fuel reforming nickel catalyst which had been activated with alkali [28].

The adsorption of halide on the surface of the anode catalyst competes with the adsorption of hydrogen.

For hydrogen,

where M is an alkali metal and S is a surface site.

The equilibrium constants for these reactions are, respectively:

$$K_1 = \frac{(S \cdot H)^2}{P_{H_2} S^2} \quad (6-30)$$

$$K_2 = \frac{S \cdot MCl}{P_{MCl} S} \quad (6-31)$$

$$K_3 = \frac{S \cdot MF}{P_{MF} S} \quad (6-32)$$

For the competitive adsorption of hydrogen and one halide, say chloride,

$$S + S \cdot H + S \cdot MCl = 1 \quad (6-33)$$

Equations (6-30), (6-31), and (6-33) can be solved to give

$$S \cdot H = \frac{P_{H_2}^{1/2}}{P_{H_2}^{1/2} + \frac{K_2}{K_1^{1/2}} P_{MCl} + \frac{1}{K_1^{1/2}}} \quad (6-34)$$

If the empirically determined dependency of anode overpotential on the square root of hydrogen pressure in Equation (6-25) is considered to be due to the square root dependency of hydrogen coverage seen in Equation (6-34), the manner in which chloride affects the anode polarization can be estimated. If the rate of anode reaction depends on $S \cdot H$, Equation (6-25) implies that K_1 may be small. Then

$$S \cdot H = \frac{K_1^{1/2} P_{H_2}^{1/2}}{1 + K_2 P_{MCl}} \quad (6-35)$$

With both halides present,

$$S \cdot H = \frac{K_1^{1/2} P_{H_2}^{1/2}}{1 + K_2 P_{MCl} + K_3 P_{MF}} \quad (6-36)$$

Therefore, $P_{H_2}^{1/2}$ in Equations (6-25) and (6-26) are replaced by $P_{H_2}^{1/2}$ times a multiplier of

$$FG = \frac{1}{1 + K_2(P_T)(LO) + K_3(P_T)(FO)} \quad (6-37)$$

for pseudo steady-state.

For short times, the nickel catalyst is assumed to adsorb all of the halides that enter the cell. No coupling with halide converting the electrolyte or leaving the cell is assumed. These assumptions are made because of the previous cell data with halides in the reactant and the scrubbing of

halides from the fuel until breakthrough occurs as described under the section on concentration polarization. For these short times, the area is reduced by the factor

$$FF = 1 - \frac{\text{Fraction of Area Covered by Chloride}}{\text{Fraction of Area Covered by Fluoride}} \quad (6-38)$$

$$FF = 1 - \frac{6.023 \times 10^{23} \left(\frac{\text{MOLECULES}}{\text{MOLE}} \right) \cdot T(\text{HR}) \cdot \frac{\text{AREA}}{\text{MOLECULE}}}{\frac{A_{\text{NICKEL}}}{\text{CM}^2 \text{ FRONTAL}}} \times \left\{ \frac{2(3600)(I/A)}{96,500} \left[\left(\frac{PF+PCL}{FUT} \right) \frac{1}{(X_H+X_{CO})} + \left(\frac{CL+F}{OUT} \right) \frac{1}{X_{OC}} \right] \frac{\text{MOLES}}{\text{HR CM}^2} \right\} \quad (6-39)$$

where 6.023×10^{23} molecules moles is Avagadro's number. The area of nickel covered per molecule of halide was obtained from Reference [28] as $6.28 \times 10^{-6} \text{ cm}^2/\text{site}$. The surface area of the nickel per unit frontal area is 531, considering a 0.142 cm thick anode of 0.42 porosity with a surface area of $0.1 \text{ m}^2/\text{g}$ and a density of 8.9 g/cc. Equation (6-39) then becomes

$$FF = 1 - 7.37 \times 10^{-5} T \left\{ \frac{2(3600)(I/A)}{96,500} \left[\left(\frac{PF+PCL}{FUT} \right) \frac{1}{(X_H+X_{CO})} + \left(\frac{CL+F}{OUT} \right) \frac{1}{X_{OC}} \right] \right\} \quad (6-40)$$

For short time periods, while the halide is adsorbed and approaching steady-state coverage, FF should be used as the multiplier for $P_{H_2}^{1/2}$ in Equations (6-25) and (6-26). This multiplier is used until it exceeds FG. Then FG is used.

Increases in anode polarization can lead to changes in the adsorption characteristics of species on the anode surface due to its increasing potential. Eventually the nickel will oxidize. These effects are not included.

The increase in utilization loss on the fuel side can be determined by calculating the difference in anode polarization at the inlet hydrogen pressure with halide-containing reactants to that at the average hydrogen pressure with halide-containing reactants.

The exit hydrogen pressure is:

$$P_{H_2 \text{ out}} = P_T \left[\frac{(1 - F_{UT}) X_H}{(1 + F_{UT})(X_H + X_{CO}) + X_{CO_2} + X_{H_2O}} \right] \quad (6-41)$$

The average hydrogen pressure is:

$$\bar{P}_{H_2} = \left[(P_T X_H) + P_{H_2 \text{ out}} \right] / 2 \quad (6-42)$$

The anode polarization at this pressure in the presence of halides is, from Equation (6-26),

$$\eta_B = \left[\frac{2.418 \times 10^{-2}}{(\bar{P}_{H_2})^{1/2} (E)} + 8 \times 10^{-3} \right] \left[\frac{f(MA)}{0.028} \right] \quad (6-43)$$

where E is FF or FG depending on whether steady state has been reached with respect to poisoning of the anode reaction. The utilization loss is then

$\eta_B - \eta_A$, where η_A is obtained from Equation (6-26).

Cathode Polarization

The performance of cathodes is also affected by both conversion of the electrolyte composition and loss of electrolyte. As described under the section on concentration polarization, the cathode electrolyte is considered to be essentially free of any halides during cell operation because of the production of carbonate ions there. The overpotential of the cathode as a function of electrolyte is shown in Figure 6-4. The composite graph shown is fit by the equation

$$\eta_c = 26.82 (MC)^2 - 2.76 (MC) + 0.120 \quad (6-44)$$

Figure 6-4. Summary of Cathode Performance on Halide-Free Electrolyte

at 160 mA/cm² where MC is the mass of electrolyte in the cathode per unit frontal area. This mass is calculated from the total mass of electrolyte in the cell using Equation (6-24) and the electrolyte sharing analysis.

Matrix Polarization

The matrix is also assumed to operate relatively free of halide to the point that the electrolyte conductivity there will not be significantly changed. The matrix resistance will increase due to loss of electrolyte, however. The relationship between matrix polarization and electrolyte content is:

$$\eta_m = 0.020 \left[\frac{(0.01920 \times 1.93)}{MM} \right]^{1.5} \quad (6-45)$$

where MM is the mass of electrolyte in the matrix per unit frontal area. This equation holds at 100 mA/cm² and is based on an initial volume of 0.01920 cc of electrolyte in a 100 percent filled matrix, a density of 1.93 g/cc, and an initial polarization of 20 mV due to the matrix. At 150 mA/cm², this expression becomes:

$$\eta_m = \frac{2.28 \times 10^{-4}}{(MM)^{1.5}} \quad (6-46)$$

The exponent 1.5 accounts for both the change in area for ion flow in the matrix and the increase in tortuosity of the matrix based on the Bruggeman Equation [25].

Computer Model Description

Using the equations presented in the section on model development, a computer program, MCHALIDE, was developed which calculates the performance decay of the present molten carbonate fuel cell due to the presence of hydrogen

chloride and hydrogen fluoride in the fuel or oxidant. The performance decay is caused by the loss of electrolyte, which affects the performance of the anode, cathode, and matrix, the conversion of the electrolyte to a halide/carbonate mixture, and the possible poisoning of the anode catalyst by halide.

The design of the cell and its initial electrolyte content are built into the program. The loss of electrolyte is assumed to be caused only by the presence of a halide in the reactant, even though electrolyte loss occurs in actual cells in the absence of halides.

The operating pressure, current density, fuel inlet composition, and oxidant utilization, and the chloride and fluoride content in the inlet fuel and oxidant are all input variables. The fuel utilization is based on the consumption of both H_2 and CO , while the oxidant utilization is based on the consumption of CO_2 . These input variables are printed out with the program results.

The various sources of performance loss are calculated using the model and tabulated as a function of time from 0 to 40,000 hours. These polarization components are:

- o The anode polarization including the fuel utilization loss.
- o The cathode polarization including the oxidant utilization loss.
- o The matrix resistance loss.
- o The concentration polarization and liquid-junction potential loss caused by chloride in the electrolyte.
- o The concentration polarization and liquid-junction potential loss caused by fluoride in the electrolyte.
- o The total of all these losses.
- o The electrolyte content in the cell active area per unit active area.
- o The cell performance loss due to halides caused by the change in the total of these losses.

The HCl and HF present in the fuel and oxidant inlet gases are considered to be completely scrubbed from the gases within the stack and converted into lithium and potassium chlorides and fluorides. The halide content is assumed to increase in the cell with time until a pseudo steady-state is reached, where the halide influx as HCl and HF match the outflow as Li and K salts. These salts are assumed to be concentrated in the anode during cell operation and saturate the fuel exhaust gas. No halides are assumed to leave in the oxidant effluent. It is assumed that the fuel exhaust gas is not used to provide CO₂ to the oxidant inlet, thereby permanently removing the halide from the cell in the fuel effluent. This method of operation duplicates that used in subscale cell tests, but not that in present system configurations.

The condition at which the influx and outflux are equal is only a pseudo steady-state because the electrolyte content in the cell decreases with time after this state is reached.

Comparison of Model Results with Cell Data

Experimental data on the effects of hydrogen chloride present in the fuel gas of a molten carbonate fuel cell were previously obtained by IFC under Contract DE-AC-01-79ET15440 with DOE. The experimental conditions under which those tests were performed are listed in Table 6-3. Two different hydrogen chloride contents were introduced into the fuel gas, first 60 ppm and then 10 ppm. Prior to the introduction of the 10 ppm HCl, the performance of the cell was allowed to recover.

The measured increases in polarization with time after the introduction of the HCl for both of these cases are shown in Figure 6-5. The data for the 60 ppm case show that over a 50 mV increase in cell polarization occurs in less than two hours. Such a rapid performance loss might be

TABLE 6-3

EXPERIMENTAL CONDITIONS FOR
PREVIOUS CHLORIDE TESTS
(Cell No. 319)

Fuel Composition:

51.0 mole % H_2 , 9.6 mole % CO, 10.6 mole % CO_2
28.8 mole % H_2O

Oxidant Composition:

11.7 mole % O_2 , 17.1 mole % CO_2 , 64.1 mole
% N_2 , 7.1 mole % H_2O

Current Density = 172 mA/cm²

Fuel (H_2 + CO) Utilization = 81%

Oxidant (CO_2) Utilization = 30%

Fuel HCl Content = 10 ppm and 60 ppm

Figure 6-5. Comparison of Preliminary Model with Existing Cell Data for Early Time Periods with HCl in Fuel

expected to be caused by a poisoning of the anode by chloride. However, experimental anode half-cell data obtained in this contract indicate that anodes are not poisoned by the presence of chloride.

An alternative explanation for the rapid polarization increase is a rapid conversion of a fraction of the electrolyte in the anode to a mixture of carbonate and chloride. As defined in the section on Model Development, a fraction Z of the total anode electrolyte is considered to be present in thin films in the anode and introduce concentration polarization and liquid junction potential before the electrolyte in total anode reached pseudo steady state. A value of Z equal to 0.01 was found to lead to very good agreement with the experimental data in early time periods for both the 60 ppm and 10 ppm cases, as can be seen in Figure 6-5. The steady state concentration polarizations for these two cases are 63 mV and 12 mV respectively. The levels of these polarizations are not affected by the selection of Z , but only by the time at which they occur.

For time periods above about 100 hours for the 10 ppm case, the polarization increase due to halides increases above the 12 mV associated with the concentration polarization and liquid junction potential. The model indicates that this additional loss is due to a loss of electrolyte. This cell was filled with 11.6 g of electrolyte when the amount in the matrix and fine pore in the wet seals is subtracted from the total initial electrolyte mass. If the cell is assumed to have lost 3 to 6 g due to creepage through the cell seals in the 876 hours before the 10 ppm HCl were introduced, as indicated in [27], about 6 to 9 g of electrolyte were in the cell when the 10 ppm HCl test began. The 60 ppm test is estimated to have resulted in only a 0.08 g loss. The line increasing above the 12 mV increase in polarization from concentration polarization for the 10 ppm case shows the calculated additional increase due to the loss of electrolyte, assuming 7 g of electrolyte were present at the time the 10 ppm HCl were introduced. The increased polarization is readily explained by this mechanism.

Teardown analysis of this cell indicated that it was low in electrolyte.

The total decay in performance due to chloride in the fuel can therefore be explained by the consideration of two loss mechanisms: concentration polarization, liquid junction potential due to electrolyte composition differences between the electrodes and loss of electrolyte from the cell. This result is surprising since in this study chloride in the electrolyte was measured in half-cell tests to have a large effect in increasing cathode polarization. An explanation for this apparent discrepancy is that the cathode in the half-cell tests was held for several days in chloride-containing electrolyte at open circuit prior to being placed on current load. Under such circumstances, the cathode could have reacted with the chloride. In the cell test, the cathode was almost continuously on load, generating carbonate, thereby cleansing itself of chloride and avoiding the reaction with the chloride.

An attempt was made to compare the results predicted by this model with experimental data obtained by General Electric Company on the effects of HCl in the fuel and oxidant [1]. However, comparisons could not be made because of the different cell configuration, the manner in which the tests were performed with short periods of open-circuit operation during the test, and General Electric's use of simulated air-blown gasifier fuel instead of oxygen-blown gasifier fuel.

The data indicates that the effect of hydrogen chloride is much greater when it is introduced in the oxidant stream than when it is introduced in the fuel stream at the same concentration levels. This much more severe effect is predicted by the model to be caused by a greatly increased concentration polarization and liquid junction potential due to the higher rate of hydrogen chloride flow into the cell caused by the higher oxidant volume flow rate. Possibly, an increase in cathode polarization also occurs due to the presence of chloride in the oxidant as indicated by the half-cell data of the present study. Deterioration of the structural integrity of the cathode was apparent on teardown.

TABLE OF NOMENCLATURE

<u>Computer Symbol</u>	<u>Text Symbol</u>	<u>Definition</u>	<u>Units</u>
Amps	I	Current	amps
BA	--	Anion fraction carbonate in anode due to chloride conversion in short times	
BB	--	Anion fraction carbonate in anode due to fluoride conversion in short times	
BC	C_{ACL}	Chloride anion fraction in anode at fuel exit at steady state	
BD	C_{AF}	Fluoride anion fraction in anode at fuel exit at steady state	
CC	η_{conc} Chloride	Concentration polarization due to chloride in short times	Volts
CD	η_{conc}	Concentration polarization at steady state due to chloride	Volts
CE	η_{conc}	Concentration polarization at steady state due to fluoride	Volts
CF	η_{conc} Fluoride	Concentration polarization due to fluoride in short times	Volts
Density	ρ	Electrolyte density	g/cm ³
FF	FF	Multiplier on H adsorption area in short times defined by Equation (39)	
FG	FG	Multiplier on H adsorption area in steady state defined by Equation (37)	
FO	FO	Mole fraction of fluoride in fuel effluent at steady state	
IA	I/A	Current density	amps/cm ²
KHR	K_3	Equilibrium constant for Reaction 3	ATM ⁻¹
--	K_1	Equilibrium constant for Reaction 1	ATM ⁻¹
KTW	K_2	Equilibrium constant for Reaction 2	ATM ⁻¹
LO	LO	Mole fraction of chloride in fuel effluent at steady state	

<u>Computer Symbol</u>	<u>Text Symbol</u>	<u>Definition</u>	<u>Units</u>
M	M	Mass of electrolyte in cell/area	gm/cm ²
MA	MA	Mass of electrolyte in anode/area	gm/cm ²
MC	MC	Mass of electrolyte in cathode/area	gm/cm ²
MM	MM	Mass of electrolyte in matrix/area	gm/cm ²
NA	η_A	Anode polarization at 160 ma/cm ²	Volts
NB	η_B	Anode polarization at utilization at 160 ma/cm ²	Volts
NC	η_C	Cathode polarization at 160 ma/cm ²	Volts
NU	η_U	Fuel side utilization loss at 160 ma/cm ²	Volts
PO	P _{H₂out}	Hydrogen pressure at fuel exit	ATM
PR	P _{H₂avg.}	Average hydrogen pressure	ATM
PS	η	Total cell polarization (less oxidant and fuel normal utilization losses)	Volts
PT	PT	Total pressure	ATM
T	T	Time	Hours
Total	-	Total cell polarization	Volts
UCO2C	OUT	Oxidant (CO ₂) utilization	
UH2COA	FUT	Fuel (H ₂ and CO) utilization	
X	Z	Fraction of electrolyte in anode for transient halide storage	
XCLA	CL	Mole fraction of chlorine in fuel	
XCOAIN	XCO	Mole fraction of carbon monoxide in fuel	
XCO2AIN	XC	Mole fraction of carbon dioxide in fuel	
XCO2CIN	XOC	Mole fraction of carbon dioxide in oxidant	
XH2AIN	XH	Mole fraction of hydrogen in fuel	
XH2OCIN	XOH	Mole fraction of water in oxidant	

<u>Computer Symbol</u>	<u>Text Symbol</u>	<u>Definition</u>	<u>Units</u>
XFC	F	Mole fraction of fluorine in oxidant	
XH2OAIN	XHO	Mole fraction of water in fuel	
XN2CIN	XN	Mole fraction of nitrogen in oxidant	
XO2CIN	ZO	Mole fraction of oxygen in oxidant	
--	C	Concentration of halide	g/cm ³
--	$\frac{C_{ACL}}{C_{AF}}$	Anion fraction of halide on anode side	
--	$\frac{C_{CCL}}{C_{CF}}$	Anion fraction of halide on cathode side	
--	$C_{CARB A}$	Carbonate anion fraction at anode	
--	$C_{CARB C}$	Carbonate anion fraction at cathode	
--	D	Diffusion coefficient	cm ² /sec.
--	$\dot{M}$	Mass flux	g/sec cm ²
--	MFC	Mass of chloride in the anode from the fuel per unit anode area	moles/cm ²
--	MFF	Mass of fluoride in the anode from the fuel per unit anode area	moles/cm ²
--	MOC	Moles of chloride in the anode from the oxidant per unit of anode area	moles/cm ²
--	MOF	Moles of fluoride in the anode from the oxidant per unit anode area	moles/cm ²
--	PF	Mole fraction of fluorine in fuel	
--	PCL	Mole fraction of chlorine in fuel	
--	R	Resistance	Ω
--	S	Matrix thickness	cm
--	V	Velocity	cm/sec.
--	W	Positive mobility	cm ² /volts sec
--	x	Distance in direction through matrix measured from the cathode	cm
--	ϕ	Electrolyte potential	volts

CONCLUSIONS AND RECOMMENDATIONS

ESTIMATED CELL TOLERANCE TO HALIDES

The overall objective of this contract was "to develop a model and to determine the probable limits of halides in fuel and oxidant streams to achieve a desired coal-gas-fueled molten carbonate fuel cell life between 25,000 to 40,000 hours". The description of the model and its comparison with existing experimental data are discussed in the previous section. This section describes the application of the model to the prediction of halide tolerance for a typical set of molten carbonate fuel cell operating conditions.

The tolerance of the cell stack to halides was found to depend on the cell design and its electrolyte inventory, the operating conditions of the stack and the system which incorporates the stack. For a stack operating at the conditions shown in Table 7-1 at 10 atm pressure, where none of the halide leaving the stack in the fuel enters the stack in the oxidant gas, the tolerance level to both HCl and HF is shown in this section to be about 0.1 ppm based on a performance loss of 20 mV in 40,000 hours.

The reactant compositions presented in Table 7-1 are the same as those used in the experiments performed under this contract and are representative of operation with an oxygen-blown Texaco gasifier and an oxidant with a reduced carbon dioxide pressure to extend the life of the nickel-oxide cathode. Two pressure levels were selected to demonstrate the effect of this variable.

The model was used to estimate the decline in performance with time due to the presence of halides for four cases: hydrogen chloride in the fuel and oxidant and hydrogen fluoride in the fuel and oxidant. The performance decay after 40,000 hours of operation is shown as a function of halide content in Figure 7-1. These decay levels are those due only to the presence of halide and do not include any decay due to other sources. Other decay modes include electrolyte loss, nickel-oxide cathode dissolution, current collector corrosion, cathode compaction, and anode creepage all in the absence of halides [29].

TABLE 7-1

Operating Pressure = 10 atm, 1 atm

Operating Temperature = 650°C

Current Density = 172 mA/cm² (160 ASF)

Fuel Composition:

29.4 m% H₂

5.5 m% CO

17.5 m% CO₂

47.6 m% H₂O

Fuel Utilization (H₂ + CO) = 85%

Oxidant Composition:

9.6 m% O₂

7.2 m% CO₂

64.6 m% N₂

18.7 m% H₂O

Oxidant Utilization (CO₂) = 37%

Operating Time = 40,000 hours

FIGURE 7-1. Predicted Performance Decay in 40,000 Hours Due to Halides

The performance loss due to halides shown in Figure 7-1 indicates that the tolerance to halides is very small, tenths of a ppm in the fuel gas and hundreths in the oxidant for a 20 mV performance loss. The reason for the small tolerance can be seen in Table 7-2 which shows the breakdown of the performance loss into its components for the particular case of 0.1 ppm HCl in the fuel gas and 10 atm operating pressure. This table shows the polarization levels of each of the contributors to the total loss as a function of operating time. Those components are the anode polarization, cathode polarization, matrix resistance, and the performance loss due to differences in halide ion concentrations between the electrodes. The total cell polarization and cell electrolyte content are shown in the last two columns. The total cell polarization here contains only those elements of polarization that are affected by halides and, therefore, should not be used to estimate cell performance by subtraction of the total cell polarization from the open circuit voltage.

Almost all of the performance loss can be seen to be caused by electrolyte loss. Most of the performance loss is associated with electrolyte loss from the anode and occurs after 10,000 hours of operation. Only 12 percent of the electrolyte is lost in 40,000 hours. Because electrolyte loss is the major mode of decay, increasing the electrolyte inventory of the cell package, improving its tolerance to electrolyte loss, and adding electrolyte during power plant life would increase tolerance to halides.

The validity of electrolyte loss as a decay mode is increased because this mode of decay is similar to that seen by the in-cell test using 10 ppm HCl in the fuel gas as shown by Table 7-3. There, about 12 mV was lost due to the chloride concentration difference and the rest was due to electrolyte loss, primarily from the anode. Table 7-4 shows that the performance of the in-cell test using 60 ppm HCl in the fuel gas decayed in 10 hours primarily due to the chloride concentration difference and not electrolyte

TABLE 7-2

COMPONENT POLARIZATIONS

P = 10 ATM

I/A = 160 ASF (172 mA/cm²)

0.1 PPM HCl IN FUEL ONLY

----- Polarization results -----							
Time (hours)	Anode (volts)	Cathode (volts)	Matrix (volts)	Cl conc. (volts)	F conc. (volts)	Total (volts)	Elyte (gm/cm ²)
0.0	0.1045	0.0834	0.0349	0.0000	0.0000	0.2229	0.0680
0.1	0.1045	0.0834	0.0349	0.0000	0.0000	0.2229	0.0680
0.4	0.1045	0.0834	0.0349	0.0000	0.0000	0.2229	0.0680
1.0	0.1045	0.0834	0.0349	0.0001	0.0000	0.2229	0.0680
4.0	0.1045	0.0834	0.0349	0.0001	0.0000	0.2230	0.0680
10.0	0.1045	0.0834	0.0349	0.0001	0.0000	0.2230	0.0680
40.0	0.1045	0.0834	0.0349	0.0001	0.0000	0.2230	0.0680
100.0	0.1046	0.0835	0.0349	0.0001	0.0000	0.2231	0.0679
400.0	0.1046	0.0835	0.0349	0.0001	0.0000	0.2232	0.0679
1000.0	0.1048	0.0836	0.0349	0.0001	0.0000	0.2235	0.0678
4000.0	0.1056	0.0841	0.0350	0.0001	0.0000	0.2248	0.0672
10000.0	0.1077	0.0851	0.0352	0.0001	0.0000	0.2281	0.0660
40000.0	0.1267	0.0893	0.0374	0.0001	0.0000	0.2535	0.0600

TABLE 7-3

COMPONENT POLARIZATIONS
FOR
10 PPM IN-CELL TEST

----- Input data -----
 Cell temperature 1200 (degF) Cell pressure 1 (atm)
 Current density 172 (mA/cm2)
 Fuel utilization 81(%) Oxidant utilization 30(%)

 Mole fractions of fuel gas at anode inlet
 H2=0.510 CO=0.096 CO2=0.106 H2O=0.288

 Mole fractions of fuel gas at anode exit
 H2=0.053 CO=0.025 CO2=0.440 H2O=0.483

 Mole fractions of oxidant gas at cathode inlet
 O2=0.117 CO2=0.171 N2=0.641 H2O=0.071

 Mole fractions of oxidant gas at cathode exit
 O2=0.099 CO2=0.130 N2=0.694 H2O=0.077

 Halides in fuel inlet
 ppm Cl= 10.0 ppm F= 0.0

 Halides in oxidant inlet
 ppm Cl= 0.0 ppm F= 0.0

----- Polarization results -----

Time (hours)	Anode (volts)	Cathode (volts)	Matrix (volts)	Cl conc. (volts)	F conc. (volts)	Total (volts)
0.0	0.1877	0.0824	0.0349	0.0000	0.0000	0.3050
0.1	0.1877	0.0824	0.0349	0.0004	0.0000	0.3054
0.4	0.1877	0.0824	0.0349	0.0017	0.0000	0.3067
1.0	0.1877	0.0824	0.0349	0.0043	0.0000	0.3093
4.0	0.1878	0.0825	0.0349	0.0117	0.0000	0.3168
10.0	0.1880	0.0825	0.0349	0.0117	0.0000	0.3171
40.0	0.1889	0.0828	0.0350	0.0117	0.0000	0.3183
100.0	0.1907	0.0834	0.0351	0.0117	0.0000	0.3209
400.0	0.2111	0.0863	0.0360	0.0117	0.0000	0.3450
1000.0	0.2366	0.0917	0.0405	0.0117	0.0000	0.3806
4000.0	0.2572	0.1183	0.2352	0.0117	0.0000	0.6225

NOTE: No electrolyte remaining in cell

TABLE 7-4

COMPONENT POLARIZATIONS

FOR

60 PPM IN-CELL TEST

Cell temperature 1200° (degF) Cell pressure 1 (atm)
 Current density 172 (mA/cm²)
 Fuel utilization 81(%) Oxidant utilization 30(%)
 Initial electrolyte mass 7.00 grams

Mole fractions of fuel gas at anode inlet

H₂=0.510 CO=0.096 CO₂=0.106 H₂O=0.288

Mole fractions of fuel gas at anode exit

H₂=0.053 CO=0.025 CO₂=0.440 H₂O=0.483

Mole fractions of oxidant gas at cathode inlet

O₂=0.117 CO₂=0.171 N₂=0.641 H₂O=0.071

Mole fractions of oxidant gas at cathode exit

O₂=0.099 CO₂=0.130 N₂=0.694 H₂O=0.077

Halides in fuel inlet

ppm Cl= 60.0 ppm F= 0.0

Halides in oxidant inlet

ppm Cl= 0.0 ppm F= 0.0

----- Polarization results -----							
Time (hours)	Anode (volts)	Cathode (volts)	Matrix (volts)	Cl conc. (volts)	F conc. (volts)	Total (volts)	Elyte (gm/cm ²)
0.0	0.1877	0.0824	0.0349	0.0000	0.0000	0.3050	0.0680
0.1	0.1877	0.0824	0.0349	0.0026	0.0000	0.3076	0.0680
0.4	0.1877	0.0824	0.0349	0.0110	0.0000	0.3160	0.0679
1.0	0.1878	0.0825	0.0349	0.0324	0.0000	0.3376	0.0679
4.0	0.1884	0.0826	0.0349	0.0632	0.0000	0.3692	0.0677
10.0	0.1895	0.0830	0.0350	0.0632	0.0000	0.3707	0.0672
40.0	0.2010	0.0846	0.0354	0.0632	0.0000	0.3842	0.0651
100.0	0.2262	0.0878	0.0370	0.0632	0.0000	0.4142	0.0608
400.0	0.2462	0.0997	0.0812	0.0632	0.0000	0.4902	0.0391

NOTE: No electrolyte remaining in cell

loss.

The reason for the small performance loss due to a small chloride concentration difference at low HCl levels in the fuel is caused by the fact that only a small chloride concentration is needed on the anode side of a cell to result in the halide evaporation rate from the anode balancing the influx in the fuel gas. This analysis calculates the flux of a specie leaving a cell from the vapor pressure of that specie and the assumption that the specie saturates the reactant gas. This assumption may not be valid.

Electrolyte loss from molten carbonate fuel cells is a major decay mode in the absence of halides. This loss is due primarily to creepage of the electrolyte from the cell package through the edge seals [29]. The mechanism for this creepage has been described [30]. In experiments in which the exhaust gases of a cell were scrubbed to trap the components of the evaporating electrolyte, less electrolyte was found than was anticipated based on measured vapor pressures [29]. This electrolyte loss was minor compared to that due to creepage. The evaporating components are thought to be KOH, LiOH, and $(\text{LiOH})_2$. Measured vapor pressures are in the range of ppm's [31].

This disparity between the amount found in the reactant effluents and the anticipated values based on measured vapor pressures, makes the assumptions of the saturation of the exhaust gas with halides and complete reaction of incoming halides with the electrolyte questionable, particularly at the very low predicted tolerance levels. The 12 percent electrolyte loss in 40,000 hours, due to 0.1 ppm HCl in the fuel gas is insignificant compared to the 27 percent lost from the central cells in a 20 cell stack in 650 hours [30]. This electrolyte loss rate from stacks has been greatly reduced by stack design changes [32].

The actual electrolyte loss caused by halides is also dependent upon the molten carbonate fuel cell power plant system design. Hydrogen chloride present in gasified coal can be removed to a large extent using hot-gas cleanup. The residual HCl may partially react to form alkali metal chlorides in the cell stack and partially pass through the stack unreacted. The fuel exhaust gas is burned to provide carbon dioxide to the oxidant gas. Therefore, chlorides will enter the stack with the oxidant. Since some systems under consideration involve diverting some of the fuel gas for other uses such as recirculation or to provide for H₂S removal, all of the chloride leaving the stack in the fuel exhaust may not enter the stack with the oxidant. The chloride that does enter with the oxidant will be partially scrubbed by the electrolyte and partially leave with the oxidant exhaust. Most of the chloride is expected to be scrubbed and be transported to the anode, thereby trapping the chloride in the system, much as sulfur is anticipated to be trapped [33]. The importance of the difference in chloride concentration in the electrolyte as a performance decay mode then increases and the effect of electrolyte loss perhaps reduced. The tracing of the halide flows in system components and the resulting effect on the steady-state halide flows that reach the stack in the fuel and oxidant streams were not considered in the model. The model was developed for comparison with bench-scale, single-cell data. To predict the decay rate due to halides, a system configuration must be selected and the decay phenomena used in the model must be applied to the stack for the resulting rate of halide flows.

Figure 7-2 shows that operating pressure also affects the performance decay due to halides. This pressure effect is caused by the increase in anode polarization as pressure is reduced. Therefore, loss of electrolyte from the anode has a larger effect at a lower pressure.

A final difference between the model predictions and the performance decay that may occur in an actual stack could result due to long term stack

FIGURE 7-2. Effect of Operating Pressure
on Performance Loss

operation. The model does not include decay due to the increase in corrosion of cell components. The corrosion experiments performed in this program did not show large increases in corrosion rate on the cathode current collector with 1 ppm halide in the oxidant in 1000 hours. However, some changes in the protective oxide scale were found such that temperature cycling over longer periods of operation might result in performance decay due to an increasing contact resistance. The likelihood of this occurring is reduced by the small tolerance level of the cell due to other decay modes.

RECOMMENDATIONS

Although the experimental data and the model developed in this Contract increased the understanding of the effects of halides on molten carbonate fuel cells, the effects halides may have over longer time periods in actual power plants are still uncertain for reasons mentioned above. Long-term endurance tests of single cells using simulated power plant reactants containing low levels of halides are still needed. These tests should include shutdown-restart cycles. Further development of hot-gas cleanup systems should be performed for the removal of halides and other impurities. Molten carbonate power plant system studies should be conducted to evaluate approaches to handle all harmful impurities because the best manner to handle halides may depend on the techniques for handling other impurities. This information should be used to determine the best approach for achieving the desired life of 25,000 to 40,000 hours.

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APPENDIX A

ELECTROLYTE THERMODYNAMIC ANALYSIS

Halides in the form of either HCl or HF are anticipated to react with the molten carbonate electrolyte by:

where M represents either lithium (Li) or potassium (K).

The ideal activity of an ionized salt C_mA_n is [34]:

$$(\text{C}_m\text{A}_n) = \{C\}^m \{A\}^n \quad (\text{C} = \text{Cation}, \text{A} = \text{Anion})$$

where $\{C\} = \frac{N_c}{\sum N_{\text{CATIONS}}}$ and $\{A\} = \frac{N_a}{\sum N_{\text{ANIONS}}}$

N_i = moles of ion i

The equilibrium constants for Equations (A-1) and (A-2) are represented by:

$$K_1 = \frac{\{Cl^-\}^2 P_{H_2O} P_{CO_2}}{P_{HCl}^2 \{CO_3^{2-}\}}$$

$$K_2 = \frac{\{F^-\}^2 P_{H_2O} P_{CO_2}}{P_{HF}^2 \{CO_3^{2-}\}}$$

K_1 and K_2 can be calculated by using free energy data from JANAF [6]. In cases where M in Equations (A-1) and (A-2) is both lithium and potassium, a molar-weighted average is used:

$$K_1 = \exp \left[\frac{1}{RT} \left(2\mu_{HCl}^{o, GAS} + W(\mu_{K_2CO_3}^{o, LIA} - 2\mu_{KCl}^{o, LIA}) + (1-W)(\mu_{Li_2CO_3}^{o, LIA} - 2\mu_{LiCl}^{o, LIA}) - \mu_{H_2O}^{o, GAS} - \mu_{CO_2}^{o, GAS} \right) \right]$$

$$K_2 = \exp \left[\frac{1}{RT} \left(2\mu_{HF}^{o, GAS} + W(\mu_{K_2CO_3}^{o, LIA} - 2\mu_{KF}^{o, LIA}) + (1-W)(\mu_{Li_2CO_3}^{o, LIA} - 2\mu_{LiF}^{o, LIA}) - \mu_{H_2O}^{o, GAS} - \mu_{CO_2}^{o, GAS} \right) \right]$$

where $W = \{K^+\}$
 R = gas constant
 T = temperature
 μ^o = standard Gibbs free energy of formation of specie i

K_1 and K_2 are plotted as a function of temperature in Figures A-1 and A-2, respectively.

EQUILIBRIUM CONSTANT

FIGURE A-1. Equilibrium Constant for Reaction A-1

FIGURE A-2. Equilibrium Constant for Reaction A-2

The vaporization of the alkali-metal halide is also important:

Equilibrium constants for Equations (A-3) - (A-6) can also be calculated from JANAF data [6]:

$$\begin{aligned} K_3 &= \frac{P_{\text{KCl}}}{\{K^+\}\{Cl^-\}} = \exp \left[\frac{1}{RT} (\mu_{\text{KCl}}^{0, \text{LQ}} - \mu_{\text{KCl}}^{0, \text{GAS}}) \right] \\ K_4 &= \frac{P_{\text{LiCl}}}{\{Li^+\}\{Cl^-\}} = \exp \left[\frac{1}{RT} (\mu_{\text{LiCl}}^{0, \text{LQ}} - \mu_{\text{LiCl}}^{0, \text{GAS}}) \right] \\ K_5 &= \frac{P_{\text{KF}}}{\{K^+\}\{F^-\}} = \exp \left[\frac{1}{RT} (\mu_{\text{KF}}^{0, \text{LQ}} - \mu_{\text{KF}}^{0, \text{GAS}}) \right] \\ K_6 &= \frac{P_{\text{LiF}}}{\{Li^+\}\{F^-\}} = \exp \left[\frac{1}{RT} (\mu_{\text{LiF}}^{0, \text{LQ}} - \mu_{\text{LiF}}^{0, \text{GAS}}) \right] \end{aligned}$$

K_3 , K_4 , K_5 and K_6 are plotted as a function of temperature in Figures A-3 - A-6, respectively. Each of the gaseous species in Equations (A-3) - (A-6) polymerize. The dimerisation equations are:

FIGURE A-3. Equilibrium Constant for Reaction A-3

EQUILIBRIUM CONSTANT

FIGURE A-4. Equilibrium Constant for Reaction A-4

FIGURE A-5. Equilibrium Constant for Reaction A-5

FIGURE A-6. Equilibrium Constant for Reaction A-6

Equilibrium constants for Equations (A-7) - (A-10) are calculated from JANAF data [6]:

$$\begin{aligned} K_7 &= \frac{P_{\text{K}_2\text{Cl}_2}}{P_{\text{KCl}}^2} = \exp \left[\frac{1}{RT} (2\mu_{\text{KCl}}^{0,\text{GAS}} - \mu_{\text{K}_2\text{Cl}_2}^{0,\text{GAS}}) \right] \\ K_8 &= \frac{P_{\text{Li}_2\text{Cl}_2}}{P_{\text{LiCl}}^2} = \exp \left[\frac{1}{RT} (2\mu_{\text{LiCl}}^{0,\text{GAS}} - \mu_{\text{Li}_2\text{Cl}_2}^{0,\text{GAS}}) \right] \\ K_9 &= \frac{P_{\text{K}_2\text{F}_2}}{P_{\text{KF}}^2} = \exp \left[\frac{1}{RT} (2\mu_{\text{KF}}^{0,\text{GAS}} - \mu_{\text{K}_2\text{F}_2}^{0,\text{GAS}}) \right] \\ K_{10} &= \frac{P_{\text{Li}_2\text{F}_2}}{P_{\text{LiF}}^2} = \exp \left[\frac{1}{RT} (2\mu_{\text{LiF}}^{0,\text{GAS}} - \mu_{\text{Li}_2\text{F}_2}^{0,\text{GAS}}) \right] \end{aligned}$$

K_7 , K_8 , K_9 , and K_{10} are plotted as a function of temperature in Figures A-7 - A10, respectively. Free energy data for potassium chloride and potassium fluoride trimers were not available, but data were used to calculate the lithium chloride and lithium fluoride trimerization equilibrium constants [6]. The equations for the trimerization of the monomer in the molten state are:

Equilibrium constants for Equations (A-11) and (A-12) are calculated from JANAF data [6]:

$$\begin{aligned} K_{11} &= \frac{P_{\text{Li}_3\text{Cl}_3}}{\{\text{Li}^+\}^3 \{\text{Cl}^-\}^3} = \exp \left[\frac{1}{RT} (3\mu_{\text{LiCl}}^{0,\text{LQ}} - \mu_{\text{Li}_3\text{Cl}_3}^{0,\text{GAS}}) \right] \\ K_{12} &= \frac{P_{\text{Li}_3\text{F}_3}}{\{\text{Li}^+\}^3 \{\text{F}^-\}^3} = \exp \left[\frac{1}{RT} (3\mu_{\text{LiF}}^{0,\text{LQ}} - \mu_{\text{Li}_3\text{F}_3}^{0,\text{GAS}}) \right] \end{aligned}$$

EQUILIBRIUM CONSTANT

FIGURE A-7. Equilibrium Constant for Reaction A-7

FIGURE A-8. Equilibrium Constant for Reaction A-8

FIGURE A-9. Equilibrium Constant for Reaction A-9

EQUILIBRIUM CONSTANT

FIGURE A-10. Equilibrium Constant for Reaction A-10

K_{11} and K_{12} are plotted as a function of temperature in Figures A-11 and A-12, respectively.

FIGURE A-11. Equilibrium Constant vs. Temperature
 $3\text{LiCl}(l) = \text{Li}_3\text{Cl}_3(g)$

FIGURE A-12. Equilibrium Constant vs. Temperature
 $3\text{LiF(l)} = \text{Li}_3\text{F}_3\text{(g)}$

APPENDIX B

TASK 2 TEST PLAN

DESCRIPTION OF EXPERIMENTS

TASK 3 OUT-OF-CELL INVESTIGATION

Three types of out-of-cell experiments will be performed: corrosion tests, anode-side half-cell tests, and cathode-side half-cell tests.

Corrosion Tests

Objective - To determine influence of chlorides and fluorides on the corrosion of cathode-side alloys in molten carbonate electrolyte.

Success Criteria - The thickness and stability of protective oxide layers on the alloys is determined as a function of time in halide-containing carbonate electrolyte.

Operating Conditions - Pressure = 1 atm
Temperature = 700°C
Time = 1000 Hrs

Number of Tests - One electrolyte composition (72 m % Li_2CO_3 , 28 m % K_2CO_3 converted to contain 3.1 anion percent halide) for both chloride and fluoride with three materials (AISI 316 stainless steel, AISI 310 stainless steel, and Incoloy 825) making six tests.

Oxidant Composition - 9.5 m % O_2 , 7.2 m % CO_2 , 64.6 m % N_2 , 18.7 m % H_2O

Electrolyte Halide Concentration - 1 ppm gas-phase equivalent for chloride (3.1 anion percent halide).

Parameters to be measured - Initial thickness
Final thickness
Initial weight
Final weight
Metallographic analysis of oxide layer
X-ray diffraction analysis of oxide layer
Chemical analysis of oxide layer

Material of Construction - AISI 316 stainless steel
AISI 310 stainless steel
Inconel 825

Configuration - Rectangular Coupon - 1-inch by 0.5-inch by 0.060-inch

Anode-Side Half-Cell Tests

Objective - To determine the short-term effects of chlorides and fluorides on the performance of anode-side components.

Success Criteria - Short-term steady-state performance data are obtained as a function of chloride and fluoride content in the carbonate electrolyte.

Operating Conditions - Pressure = 1 atm
Temperature = 650°C

Number of Tests - Three electrolyte compositions (72 m % Li_2CO_3 , 28 m % K_2CO_3 containing no halide, 23 anion percent chlorides and 23 anion

percent fluoride) resulting in three tests.

Fuel Composition - 29.4 m % H_2 , 5.5 m % CO, 17.5 m % CO_2 , 47.6 m % H_2O

Gas Phase Halide Concentration - 10 ppm for chloride, 0.3 ppm for fluoride.

Parameters to be Measured - Half-cell voltage, current, temperature, halide content in fuel gas, pretest component thicknesses, post-test analyses (see Task 5).

Materials of Construction - Anode - nickel containing 2% chromium
Bubble barrier - nickel containing 2% chromium
Matrix - lithium aluminate
Anode current collector plate - nickel

Electrolyte - 72 m % Li_2CO_3 , 28 m % K_2CO_3
partially converted to contain 23 anion percent halide. This halide concentration is calculated to be in equilibrium with 10 ppm in the gas phase for chloride and 0.3 ppm in the gas phase for fluoride.

Configuration of Cell - Anode - 0.060 inches thick - ribbed
Components Bubble Barrier - 0.004 inches thick

See Figure B-1 for rig configuration.

FIGURE B-1 Half-Cell Apparatus

Cathode-Side Half-Cell Tests

Objective - To determine the short-term effects of chlorides and fluorides on the performance of cathode-side components.

Success Criteria - Short-term steady-state performance data are obtained as a function of chloride and fluoride content in the carbonate electrolyte.

Operating Conditions - Pressure = 1 atm
Temperature = 650°C

Number of Tests - Two electrolyte compositions (72 m % Li_2CO_3 , 28 m % K_2CO_3 converted to contain 3.1 and 23 anion percent halide) for chloride, one electrolyte composition (23 anion percent halide) for fluoride, and halide-free electrolyte resulting in four tests.

Oxidant Composition - 9.5% O_2 , 7.2 m% CO_2 , 64.6 m % N_2 , 18.7 m % H_2O

Gas-Phase Halide Concentration - 1 ppm and 10 ppm for chloride
- 0.3 ppm for fluoride

Parameters to be Measured - Half-Cell Voltage, current, temperature, halide content in the oxidant gas, pretest component thicknesses, post-test analyses (see Task 5).

Materials of Construction - Cathode - in-situ lithiated nickel oxide

Cathode current collector - AISI 310 stainless steel

Matrix - lithium aluminate

Electrolyte - 72 m % Li_2CO_3 , 28 m % K_2CO_3
partially converted to contain 3.1 or 23 anion
percent halide. These halide concentrations
are the steady state values when 1 ppm or 10 ppm
chloride, respectively, are present in the gas
phase. For fluoride, 23 anion percent in the
electrolyte corresponds to 0.3 ppm in the gas
phase.

Configuration of Cell Components - Cathode - 0.040 inches thick

- Current Collector - 0.058 inches thick
shielded slot

TASK 5

POST-TEST ANALYSIS

The post-test analyses depend on the particular experiment.

Task 3

Corrosion Tests

Post-test samples will be weighed and their thicknesses determined. They will be sectioned and the thicknesses, conditions and compositions of the corrosion layers determined.

Anode-Side Half-Cell Tests

The components will be visually inspected and component thicknesses measured.

Cathode-Side Half-Cell Tests

The components will be visually inspected and component thicknesses measured..

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THE EFFECTS OF HALIDES ON THE PERFORMANCE OF COAL GAS-____ED
MOLTEN CARBONATE FUEL CELLS

DOE