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EFFECTS OF H_2S ON MOLTEN CARBONATE FUEL CELLS

Progress Report for the Period January 1—March 31, 1984

By
Robert J. Remick

July 1984

Work Performed Under Contract No. AC21-83MC20212

For
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Institute of Gas Technology
Chicago, Illinois

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Morgantown Energy Technology Center
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FOREWORD

This report summarizes the technical progress achieved during the third quarterly reporting period of a multi-phase program addressing the effects of sulfur contaminants on molten carbonate fuel cells. The program is being conducted by the Institute of Gas Technology (IGT) for the U.S. Department of Energy (DOE). Work is being accomplished under the supervision of Robert J. Remick; assisting in the study are G. L. Anderson, E. H. Camara, L. G. Marianowski, and D. R. Vasil. Mr. Frank Gmeindl of Morgantown Energy Technology Center is the Contracting Officer's Technical Representative.

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SUMMARY

This report summarizes the work accomplished at the Institute of Gas Technology during the third quarterly reporting period from January 1 through March 31, 1984. The overall program objective is to identify the poisoning mechanism(s) responsible for performance losses of molten carbonate fuel cells (MCFC) when operating on sulfur-containing gases. This objective is being addressed by focusing out-of-cell and in-cell experiments on single mechanistic issues, followed by incorporation of the results into a model that correlates cell potential decline to contaminant(s) concentration. When coupled with gas cleanup cost projections, the model can be used to conduct trade-off studies leading to the selection of optimum feed-gas compositions for MCFC power plants. The importance of this program is that the degree to which H₂S and other contaminants must be removed from typical MCFC fuels can have a profound effect on the cost of cleaning the fuel gas, especially if contaminant levels lower than 0.1 ppm are required. The anticipated product from the overall program is a justifiable specification for gas cleanup requirements for MCFC power plants.

During the third quarter, progress was made toward understanding the mechanism by which hydrogen sulfide poisons the hydrogen oxidation reaction, thus increasing anode polarization, in bench-scale molten carbonate fuel cells. The electrochemical oxidation of hydrogen was investigated in half-cell tests employing a nickel wire electrode and a clean carbonate electrolyte using linear scan cyclic voltammetry to obtain a baseline voltammogram of the hydrogen reaction. Hydrogen sulfide was then added to the fuel stream at a 10-ppm level, and cyclic voltammograms were recorded on a daily basis. A reversible peak, tentatively identified as the formation of a nickel sulfide, was observed after 24 hours. This peak was first observed at a position about 200 mV positive of the reversible anode potential and both grew in area and moved in the negative direction with time. The most important aspect of this discovery is the indication that the anode is clean and sulfide free at potentials near open circuit, but develops a sulfide layer under load.

Two bench-scale fuel cell tests were also performed this quarter, one using a 10% hydrogen, 5% carbon dioxide, 10% water vapor, and the balance helium fuel mixture and the other using UTC's Stack A fuel composition, which

is approximately 34% hydrogen, 18% carbon dioxide, 22% water vapor, and 12% carbon monoxide with the balance being nitrogen.

Unexpected results were obtained in both experiments. In the first experiment it was expected, on the basis of work from the last quarter, that the addition of carbon dioxide and water vapor to the fuel would protect the cell somewhat and that the polarization losses for this fuel mixture when contaminated with H_2S would be less than those of previous cells operated on 10% hydrogen and 90% helium. This proved not to be the case. Polarization losses were the same, within experimental error, for this cell as for all previous cells operated on fuel containing 10% hydrogen. It also was expected, on the basis of previous technical reports from UTC, that the cell operated on "Stack A" gases would suffer no significant polarization losses if the cell was operated at only 25% fuel utilization with 5 ppm hydrogen sulfide in the fuel. In fact, some polarization losses were noted, approximately 35 mV at 200 mA/cm².

Phase II work was begun in the third quarter. This work addresses the impact of H_2S contaminants on the shift reaction that must occur within the fuel electrode (anode) in order to achieve high utilizations of fuels containing significant amounts of carbon monoxide. Out-of-cell tests were conducted at 650°C with three powdered catalysts. The three catalysts consisted of powdered nickel, 90% nickel with 10% chromium powder, and the nickel/chromium powder wet with about 3% carbonate electrolyte. Results indicate that a few ppm of hydrogen sulfide completely poisons the dry nickel powder in a few hours. However, although both the wet and dry samples of nickel/chromium do suffer some loss of catalytic activity when exposed to hydrogen sulfide containing fuels, they are not poisoned completely but do retain about half their activity toward the shift reaction.

These results can have a significant impact on the design specifications for MCFC since recent trends have been away from high chromium content anodes.

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INTRODUCTION

There is general agreement^{1,2} that H_2S levels in the range of 1 to 10 ppm in typical molten carbonate fuel cell (MCFC) fuels — for example, coal gasification and hydrocarbon reforming products — cause a decline in cell potential of tens of millivolts. There are conflicting statements, however, regarding 1) the actual cell potential decline per ppm (or fraction) of H_2S in the fuel, 2) the cause of the performance decline, and 3) the reversibility of the poisoning when the cell is returned to clean fuels. There are currently two schools of thought on the problem. One holds that the performance loss is the result of poisoning of the shift reaction, which is vital for cells operating on fuels containing substantial amounts of carbon monoxide. The other holds that the performance loss is caused by the poisoning of the electrochemical reaction occurring at the anode.

The objective of Phase I of the overall effort is to obtain a better understanding of the effect of H_2S on the electrochemical oxidation of H_2 . The tasks required to achieve this objective are —

- Task 1.1 Literature Review and Preliminary Model
- Task 1.2 Fundamental Single-Electrode Cell Studies
- Task 1.3 Bench-Scale Cell Operation
- Task 1.4 Physicochemical Model Development.

Task 1.1 was completed during the second quarter and a Topical Report (DOE/MC/20212-1569) was issued. The remaining tasks were active during this reporting period.

The objective of Phase II of this program is to obtain an understanding of the impact of H_2S contaminants upon the shift reaction in the MCFC environment. The tasks required to achieve this objective are —

- Task 2.1 A Brief Literature Review of the Shift Reaction
- Task 2.2 Out-of-Cell Tests to Determine the Catalytic Activity of Individual Cell Components and the Impact of H_2S on That Catalytic Activity

Task 2.3 Bench-Scale Fuel Cell Tests to Monitor the Change in the Shift Related Gas Composition as H_2S Is Introduced into the Gas Stream

Task 2.4 Physicochemical Model Development

Tasks 2.1 and 2.2 were active during this quarter.

PHASE I POISONING OF HYDROGEN OXIDATION

Task 1.2 Fundamental Half-Cell Studies

The objective of this task is to investigate the poisoning of the electrochemical oxidation of hydrogen in molten carbonate fuel cells using nickel electrodes in controlled half-cell experiments.

Work this quarter was directed toward a continued investigation of the unusual results observed in the cyclic voltammetry experiments reported on in the previous quarterly report, DOE/MC/20212-1570. The half-cell apparatus used in this study consists of a 50-ml nickel crucible filled with molten carbonate eutectic having the nominal composition of 62 mole % Li_2CO_3 and 38 mole % K_2CO_3 and maintained at 650°C . This nickel crucible serves as a counter electrode for the half-cell. A high purity (99.9+%) nickel wire is suspended in this melt with the upper part of the electrode masked by an alumina sleeve such that the only exposed portion of the wire is that which is completely submerged in the melt. This nickel wire serves as the working electrode. An alumina tube with a small hole drilled in the bottom is used to contain a reference electrode. Both the hole and the bottom 3-mm of this tube are packed with lithium aluminate to create a porous plug which, when wet with carbonate, serves as a salt bridge to keep the carbonate melt within the reference from mixing with the melt contained in the crucible. The alumina tube contains carbonate melt to a depth of approximately 3-cm above the lithium aluminate plug. A gold wire is suspended in this melt to serve as the reference electrode. This reference electrode assembly is supplied with a dry gas having the composition of 33% oxygen and 67% carbon dioxide.

The entire half-cell assembly is suspended from a 316 stainless steel head and fitted into an airtight alumina chamber heated by a three-zone furnace. The chamber is continually purged with fuel gas and provisions are made to raise or lower the inlet tube so as to admit the gas either directly above the melt or by bubbling through the melt.

A nickel crucible was chosen for these experiments for several reasons. First, the half-cell experiments are conducted only under a reducing atmosphere so oxidation of the nickel is not a problem. Second, the high surface area of the crucible, $>80\text{ cm}^2$, as compared to the low surface area of the working electrode, $<1\text{ cm}^2$, allows large polarization to be achieved at the

working electrode by applying only a small reverse polarization to the crucible. Third, the nickel crucible does not complicate the chemistry of the melt by introducing unrepresentative impurities into the melt. Fourth, there is reason to believe that gold, which is the usual choice for a crucible material, is not stable in the presence of H_2S . As a result, it is necessary to have a lithium aluminate plug at the tip of the reference electrode to drastically reduce diffusion of H_2S into the reference electrode compartment.

A half-cell having the specifications and geometry described above was assembled and purged with dry nitrogen. The cell was then heated under nitrogen purge to 650°C over a 40-hour period. Preliminary cyclic voltammograms were made under this inert atmosphere to detect the presence of impurities that might interfere with later tests. The cyclic voltammogram was relatively smooth and free of oxidation or reduction waves, which would be indicative of impurities. The shape of the voltammogram and the relationship between scanning speed and measured electrode current indicated that the main source of that current was capacitance charging of the double layer as would be expected in the absence of a redox species.

The gas feed into the cell was then changed from nitrogen to an experimental fuel gas composition of 10% hydrogen, 5% carbon dioxide, 10% water vapor, and 75% helium. This fuel gas mixture was purged through the cell for 48-hours with the inlet tube above the melt. Figure 1 is a representative cyclic voltammogram of a series taken at this point in time. Since the fuel gas was not being sparged through the solution, the melt was not saturated with hydrogen and was unstirred during the time data were being collected. The potential of the working electrode was -1.0539 volts from the reference when the cell was on open circuit. The sharp rise in current, which occurs about 200 mV positive of the open circuit, is assumed to be the oxidation of nickel according to Equation 1.

It should be noted that upon reversing direction of the scan, only a small reduction wave is noted at the position (+150 mV from O.C.) expected for the reverse of Equation 1. One possible explanation for this is the lack of CO_2 in the melt and the fact that nickel oxide can be reduced chemically by way of Equation 2.

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Figure 1. CYCLIC VOLTAMMOGRAM OF NICKEL WIRE ELECTRODE IN
UNSTIRRED CARBONATE MELT

After 48 hours of purging the vessel, the inlet tube was lowered into the melt and the fuel gas bubbled through the electrolyte for 24 hours. During this period, the half-cell was allowed to remain on open circuit. At the completion of the 24 hours, a series of cyclic voltammograms was made at various scan rates and over various potential ranges. The open circuit voltage of the working electrode was now -1.084 volts versus the oxygen reference and the onset of nickel oxidation via Equation 1 was observed to move to a new position beyond +250 mV from the open circuit potential. Both of these results were expected and are the result of the increase in activity (concentration) of the hydrogen dissolved in the melt as a result of the bubbling action. Figure 2 is a representative voltammogram from this series.

A hydrogen sulfide permeation tube (KIN-TEK Laboratories) was then added to the inlet gas stream and a water bath was used to adjust the temperature of the assembly so as to add 10 ppm H_2S to the fuel gas mixture. A series of cyclic voltammograms made 1 hour after the addition of the H_2S was identical to a series made 1 hour earlier. Therefore, it can be assumed that the addition of H_2S has no immediate impact upon the electrochemistry. However, the series of voltammograms recorded 72 hours after the start of H_2S contamination showed considerable change. Figure 3 is a reproduction of the voltammograms recorded at 5 mV/sec and 50 mV/sec scan rates. A substantial oxidation wave is noted starting at about 100 mV position of the open circuit potential, which after 72 hours was at -1.103 volts versus the reference electrode. This oxidation wave had a corresponding reduction wave on the reverse scan the beginning of which was closely aligned with the start of the oxidation wave on the forward scan, thus indicating a reversible reaction. The shape of the voltammogram recorded at 5 mV/sec gives an indication of a limiting current such as would be expected were one of the reacting species present in low concentrations in the electrolyte. The shape of the reduction wave, however, is sharp with a precipitous edge such as would be expected for the reduction of a surface layer or adsorbed species. Equation 3, for the formation of a solid nickel sulfide layer from a dissolved sulfide species,

fits well with the shape of the voltammogram depicted in Figure 3.

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Figure 2. CYCLIC VOLTAMMOGRAM OF NICKEL WIRE ELECTRODE IN CARBONATE MELT SPARGED WITH CLEAN FUEL GASES

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Figure 3. CYCLIC VOLTAMMOGRAM OF NICKEL WIRE ELECTRODE IN CARBONATE MELT SPARGED WITH HYDROGEN SULFIDE CONTAMINATED FUELS

Task 1.3 Bench-Scale Cell Operation

To obtain a better understanding of the effects of H_2S on the electrochemical oxidation of hydrogen and the importance and interrelationship of the various operating parameters, it is necessary to collect data using bench-scale (100 cm^2) molten carbonate fuel cells. Because it is more difficult to accurately characterize all of the operating parameters of such cells, it is also necessary that a series of nearly identical experiments be conducted in which only one major parameter is investigated at a time.

In the two previous quarters, cell tests (see DOE/MC/20212-1507 and -1570) were conducted using 10% hydrogen and 90% helium fuel contaminated with 1 to 5 ppm H_2S and a fuel flow velocity consistent with only 25% fuel utilization at 200 mA/cm^2 current density. Severe poisoning in the form of increased anode polarization was noted with these cells when H_2S was added to the fuel stream. The effects of the poisoning were not reversed when the H_2S contamination was removed. In the second quarter, a bench-scale cell was also operated on a high hydrogen fuel having the approximate composition: 48% hydrogen, 32% carbon dioxide, and 20% water vapor. This fuel cell, designated 5AC, exhibited no excess polarization when 5 ppm H_2S were added to the fuel. This led to the speculation that the polarization losses may be due to the reaction of sulfide contained in the electrolyte rather than from sulfide adsorbed from the gas phase. Equation 4 was proposed as the mechanism by which the sulfide was taken up by the electrolyte;

where M is potassium or lithium. Equation 4 suggests that fuels high in carbon dioxide and water vapor should protect the cell from the effects of hydrogen sulfide. Such a suggestion is different from previous conclusions^{2,3} that high hydrogen partial pressure is required to mitigate the effect of hydrogen sulfide on fuel cell performance. To test this hypothesis, suggested by Equation 4, two bench-scale fuel cells were operated this quarter using fuels with compositions intermediate between the extremes used in 4AC and 5AC.

Cell 6AC

A bench-scale molten carbonate fuel cell having an anode with a frontal area of 94 cm^2 was assembled using a nickel plus 10% chromium anode, a nickel anode current collector, an electrolyte matrix of $LiAlO_2$ (60% porous) filled

with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ eutectic (62 mole % lithium carbonate), a nickel cathode, a Type 316 stainless steel cathode current collector and 316 SS boiler plate housing. This cell was operated for 144 hours at a load of 200 mA/cm^2 on clean fuel having the composition: 10% hydrogen, 5% carbon dioxide, 10% water vapor, and 75% helium. This is the same fuel composition as used in the half-cell experiments described in Task 1.2 above. Fuel flow velocity was adjusted such that only 25% of the fuel content of the incoming fuel gas is required to maintain 200 mA/cm^2 current density.

After 144 hours, the fuel flow was rerouted over H_2S permeation tubes. These permeation tubes were maintained at a constant temperature in a bath adjusted to a temperature such that the fuel was contaminated with approximately 5 ppm H_2S . The decline in fuel cell performance under constant load was continuously monitored using a strip chart recorder. The cell was operated for 196 hours on contaminated fuel and then returned to clean gas for 140 hours. Unlike cells operated on 10% hydrogen and 90% helium only, this cell, which included carbon dioxide and water vapor in the fuel, recovered fully when the H_2S contamination was removed. At 480 hours into the test, the cell was again returned to contaminated fuel operation and the performance of the cell rapidly decayed to previous levels observed with contaminated fuel. After an additional 100 hours of operation on contaminated fuel, the cell was again placed on clean fuel gas for 72 hours over a weekend. This time, however, only partial recovery of the initial levels of performance was achieved. Once every 24 hours during the course of this 650-hour test, the cell was placed on open circuit until a stable open circuit voltage was achieved. The cell was then placed under a load at a current density of 40 mA/cm^2 ; when a stable cell voltage was noted, the load was increased to 60 mA/cm^2 . This process was continued in increments of 20 mA/cm^2 until either 240 mA/cm^2 was reached or the cell voltage fell below 500 mV. This incrementally determined voltage versus current density relationship was used as a measure of cell performance. Figure 4 summarizes the results of this fuel cell test through 650 hours. This cell was maintained at a load consistent with a current density of 200 mA/cm^2 at all other times. The solid lines tying together points of equal current density in Figure 4 are drawn for purposes of clarity.

A gas chromatograph (GC) was used to monitor the hydrogen sulfide concentration at both the inlet and outlet of the anode compartment. The H_2S level

Figure 4. PERFORMANCE OF CELL 6AC OPERATING ON 10% HYDROGEN, 5% CARBON DIOXIDE, 10% WATER VAPOR, AND 75% HELIUM AT A FUEL FLOW RATE CONSISTENT WITH 25% HYDROGEN UTILIZATION

in the outlet gases slowly rose from near zero at the start of contaminated gas operation to between 3 and 4 ppm after 48 hours while the cell was under load. However, when the cell was placed on open circuit, the quantity of H_2S in the outlet gases increased drastically. Figure 5 is a graph of the quantity of H_2S in the outlet gas as a function of time and is constructed on the basis of GC measurements taken every 3 minutes. This phenomenon proved to be reproducible and was observed every time the cell was first placed on open circuit after 24 hours under load, but only when contaminated fuel was being used. The phenomenon was not observed after 48 hours of operation on clean gas but reappeared when the cell was returned to contaminated fuel operation. It should be noted that this behavior is the reverse of that observed with the 10% hydrogen-90% helium fuel in cells 1AC, 2AC, 3AC, and 4AC. In those cells, the H_2S concentration in the outlet gases fell to near zero when the cell was placed on open circuit. In those experiments, the only source of carbon dioxide and water vapor was the electrochemical reaction. Since these two gases are required to maintain the equilibrium in Equation 4 when these cells were placed on open circuit, the CO_2 and H_2O concentrations fell to near zero and Equation 4 shifted to the right. Thus, any H_2S that might have been released by the electrodes when first going to the open circuit condition dissolved in the electrolyte instead.

Another unusual phenomenon was observed to occur in concert with the sudden release of H_2S from the anode when the cell was placed on open circuit. Usually, when a cell is placed on zero load (open circuit), the cell potential quickly rises to a stable open circuit potential. However, since some finite amount of time is required to purge the reaction products from the cell, a stable open circuit voltage, which is representative of the unreactive fuel gas composition, is not achieved immediately. The period of time required usually ranges from 5 to 15 minutes depending on the fuel gas velocity. In Cell 6AC, at the 192-hour mark when the cell was placed on open circuit, the cell potential did not return to the expected 1.060 volts but rather exhibited an open circuit cell potential of only 0.880 volts after the usual 10-minute wait. This potential was moderately stable for about 40 minutes and then slowly rose to reach the expected 1.060 volts only after 2 hours had passed. Such behavior suggests that an electrochemical reaction with a half-cell voltage position of the hydrogen oxidation reaction was initially responsible for the cell potential.

Figure 5. HYDROGEN SULFIDE CONCENTRATION MEASURED AT THE
OUTLET OF CELL 6AC WHEN CELL WAS PLACED ON OPEN
CIRCUIT AFTER 24 HOURS OF OPERATION ON CONTAMINATED GAS

This cell was terminated after 650 hours of operation and cell components were stored for later analysis.

Cell 7AC

This bench-scale fuel cell was identical in construction to Cell 6AC described above. It was also operated in a similar manner with the exception that the fuel gas used was richer in hydrogen, carbon dioxide, and water vapor. The approximate composition of the fuel gas used with this cell is as follows: 36% hydrogen, 16% carbon dioxide, 14% carbon monoxide, 22% water vapor, and the balance nitrogen. This fuel gas composition approximates that designated as "Stack A" gas by UTC. The fuel flow rate was adjusted to be consistent with a 25% fuel utilization rate at 200 mA/cm^2 current density. It should be noted that this fuel gas contains two oxidizable components, hydrogen and carbon monoxide. A 25% fuel utilization rate is calculated on the basis of a gas composition that is considered to be 50% fuel. If only hydrogen is used as a basis for calculation and the carbon monoxide is considered to be inert, then the fuel flow rate used with this cell is consistent with utilization of 34% of the hydrogen at 200 mA/cm^2 .

This cell was started on 5 ppm H_2S at 149 hours into the test and was run on contaminated fuel for 163 hours, returned to clean fuel for 48 hours and returned to contaminated fuel for the remaining 144 hours of the 504-hour test. Figure 6 graphically portrays the results of the incremental performance analysis measurements taken approximately every 24 hours. The fuel flow rate used to obtain this data was 1060 cm^3 per minute on a wet basis. A second series of incremental performance analysis measurements were made each day at a reduced fuel flow rate. After determining cell performance at $1060 \text{ cm}^3/\text{min}$, the fuel flow rate was reduced to $370 \text{ cm}^3/\text{min}$ and the incremental procedure was repeated. This lower fuel rate is consistent with about 64% fuel utilization or 85% hydrogen utilization at 200 mA/cm^2 current density and in excess of 100% hydrogen utilization at 240 mA/cm^2 current density. After completion of this incremental test, the fuel flow rate was returned to the higher rate. Figure 7 presents the results of this low flow rate test. The fact that 240 mA/cm^2 current densities could be achieved at the low flow rate even after 163 hours on contaminated fuel indicates that some shifting of carbon monoxide to carbon dioxide and hydrogen does occur. However, further investigation of the shift reaction will be undertaken in the next quarter.

Figure 6. PERFORMANCE OF CELL 7AC OPERATING ON 34% HYDROGEN, 18% CARBON DIOXIDE, 13% CARBON MONOXIDE, 22% WATER VAPOR, AND THE BALANCE NITROGEN AT 25% FUEL UTILIZATION

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Figure 7. PERFORMANCE OF CELL 7AC AT 75% FUEL UTILIZATION

Discussion

The results from bench-scale tests 6AC and 7AC are in qualitative agreement with the results of the half-cell tests. As can be seen from Figure 3, the onset of electrochemical sulfide formation in the linear scan cyclic voltammetric experiments was about 100 mV positive of the open circuit potential on the 10% H₂, 5% CO₂, 10% H₂O, 75% He fuel. Figure 4, which depicted the long-term results with the bench-scale cell (6AC) operating on the same gas mixture, suggested that some polarization losses due to poisoning are experienced at cell potentials only 50 mV from open circuit at 40 mA/cm² current density. Of course, it is very difficult to equate data derived from bench-scale fuel cell tests using porous gas diffusion electrodes with data from half-cell tests using submerged (flooded) wire electrodes. One important difference is the quantity of electrolyte used. In the half-cell tests, the crucible or pot contains about 50 ml of molten carbonate, all of which is exposed to the fuel stream. In the bench-scale cell, on the other hand, only the small portion of the electrolyte wetting the anode surfaces is directly exposed to the fuel. As a consequence, it is reasonable to interpret the initial rapid decline in performance to a stable plateau, which is observed in the bench-scale cells in terms of the saturation of the electrolyte film contained in the anode with sulfide from the fuel gas. To obtain an equivalent degree of electrolyte saturation in the half-cell tests would require several hundred hours. Thus, it is likely that the half-cell results reported in Figure 3 are for an electrolyte that is not saturated with sulfide.

In Cell Test 7AC, which utilized a fuel richer in hydrogen than 6AC, polarization losses due to H₂S poisoning do not become measurable until the cell potential is about 100 mV from the open circuit potential (80 mA/cm²). It is noteworthy that this is true at both the high and low fuel flow rates (low and high fuel utilizations, respectively). However, the magnitude of the polarization losses are different for the different fuel flow rates. At high fuel flow rate (low fuel utilization), the polarization losses due to 5 ppm H₂S in the fuel is about 35 mV at 200 mA/cm²; while at the low fuel flow rate, the losses increase to 100 mV at 200 mA/cm². This result suggests a unique relationship between the magnitude of the polarization losses and the hydrogen partial pressure at a fixed current density. For example, although Cells IAC (10% H₂, 90% He) and 6AC (10% H₂, 5% CO₂, 10% H₂O, 75% He) differed appreciably

in gas composition to the extent that 1AC did not recover after poisoning and 6AC did recover, nevertheless, both cells experienced about 200 mV polarization losses due to poisoning at a current density of 200 mA/cm² and a fuel utilization of 25%. Fuel Cell 7AC, operating on fuel gas containing 34% hydrogen, experienced only 30 mV loss under similar operating conditions and Fuel Cell 5AC, operating on fuel containing 48% hydrogen (unshifted composition), experienced less than 10 mV of losses under these conditions.

From the above observations, it appears that a definite relationship exists between the magnitude of the polarization losses on contaminated gas and the partial pressure of hydrogen in the fuel.

The unusual phenomenon observed at 192, 216, and 240 hours, which accompanies placing Cell 6AC on open circuit after 24 hours of operation under load on contaminated gas, can be explained if it is assumed that a nickel sulfide layer does in fact form on the electrode. As can be seen in Figure 3, the supposed sulfide layer is not stable at open circuit potentials but is reversibly reduced during the cyclic voltammometric experiments. Operating a bench-scale cell under high load on contaminated gas would build up a substantial layer of nickel sulfide. When this cell is placed on open circuit, the sulfide layer is no longer stable. But, because of the thickness of the sulfide layer, the anode potential does not return to the reversible potential for hydrogen oxidation but to the more positive reversible potential for the sulfidation reaction (Equation 3).

However, unlike the half-cell tests, the bench-scale cell on open circuit does not permit the electrochemical reduction of the sulfide layer since the anode and cathode are no longer in electrical communication with one another. This cell would have remained at this potential (0.88 V) except for the chemical stripping action of hydrogen.

Because substantial amounts of carbon dioxide and water vapor were present in the fuel gas in Cell 6AC, the H₂S produced in the porous anode could not be taken up by reaction with the electrolyte as occurred in Cell 1AC with 10% H₂ and 90% He. In Cell 6AC, this H₂S was exhausted into the outlet stream and was responsible for the increase in H₂S observed immediately after placing the

cell on open circuit. After this reaction (Equation 5) had succeeded in stripping all the sulfide from the electrode surface, the anode potential rose to the redox potential for hydrogen oxidation resulting in the expected cell potential of 1.06 volts.

These qualitative observations lend strong support for a nickel sulfide layer on the nickel anode and suggest that this layer is the cause of the polarization losses experienced with contaminated gases.

PHASE II SHIFT REACTION POISONING

Background

Production-scale molten carbonate fuel cell power plants, fueled from coal gasifiers, must be able to handle fuel feeds containing substantial amounts of carbon monoxide. The UTC Stack A gas mixture, 34% H₂, 22% H₂O, 13% CO, 18% CO₂, and 12% N₂, is typical of the gas compositions that would be supplied to such a power plant. Here, nearly 25% of the heating value of the fuel is tied up as carbon monoxide. Unfortunately, the electrochemical oxidation of carbon monoxide is slow compared to that of hydrogen. Thus, fuel residence times consistent with 80% hydrogen utilization are insufficient to allow much of the carbon monoxide to react electrochemically. Fortunately, nickel is a good shift reaction catalyst. As hydrogen is consumed and water vapor produced by the fuel cell electrochemistry, gas mixtures, such as the Stack A mixture which are at full shift equilibrium at the inlet to the anode, are out of shift equilibrium as they near the outlet. Therefore, the shift reaction can serve to produce more hydrogen by consuming the carbon monoxide.

The driving force for Equation 6 is the depletion of hydrogen because both CO₂ and H₂O are produced in equal quantities by the electrochemistry. Since the shift reaction is fast at 650°C, it is possible to operate bench-scale MCFC on Stack A gas mixtures at 80% fuel utilization even though this would require 10% more hydrogen than is available in the original fuel (110% hydrogen utilization). If, however, the shift reaction is poisoned, then the only hydrogen available for use is the 34% supplied at the inlet. Since it is inadvisable to operate a production cell at greater than 90% utilization because of Nernstian-type voltage losses and because a reducing atmosphere must be maintained to prevent damage to the electrode, the electrical energy produced from this gas mixture in the absence of the shift reaction is only 78% that available if shift equilibrium can be maintained across the entire face of the fuel cell anode.

Assuming that all of the problems associated with H₂S poisoning of the hydrogen electrochemistry can be overcome, the poisoning of the shift reaction still represents an obstacle to fuel cell development because the 22% decrease

in performance caused by the loss of the shift reaction rivals the worst decrease in performance (24%) observed with Stack A gases due to poisoning of the electrochemistry. The purpose of Phase II work is to investigate the poisoning of the shift reaction in the MCFC environment.

Task 2.1 Literature Review of the Shift Reaction

A review of the literature addressing the poisoning of shift reaction catalysts was undertaken this quarter. This review is not yet complete and an analysis of the literature as it impacts upon the operation of the molten carbonate fuel cell has not yet been started. However, this review and analysis will be completed during the fourth quarter, and a separate topical report will be issued.

Task 2.2 Out-of-Cell Tests

The purpose of these out-of-cell tests is to obtain a semi-quantitative understanding of the impact of H_2S upon the ability of fuel cell components to catalyze the shift reaction, specifically, the nickel current collector and the 90% nickel-10% chromium porous anode plaque.

In the initial series of experiments, 1 gram of nickel powder or 1 gram of 90% nickel-10% chromium powder, produced by abrading a porous metal plaque, was dispersed on quartz wool and placed in a 1-inch-diameter quartz tube. This assembly was placed in a tube furnace and heated to $650^{\circ}C$ under ultra pure nitrogen. Experimental gas mixtures were then passed through the tube at gas flow rates of from 35 to $200\text{ cm}^3/\text{min}$. The outlet of the tube was passed through a cold trap at $0^{\circ}C$ and a drying tube loaded with anhydrous calcium sulfate. The dry gas stream was then split in two with one stream passing through a gas sampling tube of an automated Varian Model 3700 Gas Chromatograph and the other stream passing into a bubbler, which maintained a positive pressure on the system, with respect to the atmosphere, of about 2 inches of water. Gas chromatograms were taken at regular intervals and the results recorded on both a Varian Model 9176 strip chart recorder and a Varian CDS 111 integrator. The experiments performed this quarter are as follows:

Shift Experiment No. 1

Since the desired shift reaction in the molten carbonate fuel cell is the conversion of carbon monoxide and water vapor to hydrogen and carbon dioxide, it was decided that the shift reaction should be investigated by starting with

gas mixtures containing only carbon monoxide and water vapor and monitoring the progress of the reaction by measuring the production of carbon dioxide. However, it was suspected that carbon deposition by way of the disproportionation of carbon monoxide —

may be a problem with this approach so a preliminary experiment was undertaken to identify technical obstacles.

A mixture of 11% carbon monoxide and 89% nitrogen gases was passed through a humidifier adjusted to 45°C. The resulting wet gas stream contained 10% carbon monoxide, 10% water vapor, and 80% nitrogen (10-10-80). The catalyst consisted of about 2 grams of metal chunks produced by the breakup of a 90% nickel-10% chromium porous metal plaque of the kind used as fuel cell anodes in the bench-scale tests. These chunks were supported on quartz wool in a quartz tube and heated to 650°C under ultra pure nitrogen. The 10-10-80 gas mixture was then passed through the 1-inch-diameter quartz tube at a flow rate of 105 cm³/min on a wet basis (96 cm³/min dry). The composition of the product gases were determined using the automated gas chromatograph. The carbon monoxide and carbon dioxide content of the gaseous product stream are listed on a wet basis in Table 1.

Table 1. COMPOSITION OF EFFLUENT GAS IN EXPERIMENT NO. 1

<u>Time</u>	<u>% CO</u>	<u>% CO₂</u>
0 hours	3.7	6.1
1 hour	6.6	3.4
2 hours	7.4	2.6
3 hours	8.0	2.0
4 hours	8.1	1.9

As can be seen from these results, the catalyst rapidly lost activity over the course of the 4-hour experiment. Comparison of the weight of the catalyst before and after the experiment indicated an increase in weight of about 1%. The weight increase, however, could be caused either by the deposition of carbon or by the oxidation of the chromium to chromia —

which is known to occur under these conditions. Therefore, it was decided to repeat the experiment using a powdered sample that could later be analyzed for carbon.

Shift Experiment No. 2

A section of 90% nickel-10% chromium porous metal plaque of the type used for anodes in bench-scale fuel cells was abraded using a tungsten-carbide file. The powder produced was supported on quartz wool in the same manner used above. As with Experiment No. 1, the catalyst was heated under nitrogen and then exposed to the experimental 10-10-80 gas mixture. In this experiment, however, measurements were taken at three gaseous flow rates, 35, 75, and 150 cm³/min, on a wet basis. If the 10% CO, 10% H₂O, and 80% N₂ gas mixture were allowed to come to shift equilibrium at 650°C, we would expect a gas composition of 5.9% H₂, 5.9% CO₂, 4.1% CO, 4.1% H₂O, and 80% N₂. The actual CO and CO₂ content of the effluent gases at the three flow rates as measured after approximately 1 hour and 24 hours are listed in Table 2. During the intervening 24 hours, the flow rate was maintained at the highest value, 150 cm³/min.

Table 2. COMPOSITION OF EFFLUENT GAS IN EXPERIMENT NO. 2

Results:	<u>% CO</u>	<u>% CO₂</u>
After 1 Hour:		
35 cm ³ /min	5.9	4.1
75 cm ³ /min	7.0	3.0
150 cm ³ /min	8.1	1.9
After 24 Hours:		
35 cm ³ /min	7.2	2.8
75 cm ³ /min	9.5	Trace
150 cm ³ /min	9.8	Trace

At the completion of the 24-hour experiment, the catalyst was removed and analyzed for carbon by combusting the sample in pure oxygen and collecting the carbon dioxide produced on Ascarite. Results indicated that 0.6 weight percent of the sample was carbon. From these results, it was concluded that the carbon monoxide plus water vapor approach to studying the shift reaction was not technically feasible.

Shift Experiment No. 3

In light of the problems encountered with carbon deposition in the first two experiments, it was decided to approach the shift reaction from the opposite direction by using hydrogen and carbon dioxide. In this experiment, 1 gram of nickel powder, -325 mesh, was supported on quartz wool in a quartz tube and heated under nitrogen as before. An experimental gas mixture of 60% hydrogen and 40% carbon dioxide (60-40) was then passed through the tube at a flow rate of $185 \text{ cm}^3/\text{min}$. The presence of carbon monoxide in the product was used as evidence of the reverse shift reaction. The gas composition at shift equilibrium at 650°C for the 60-40 mixture is 40.1% H_2 , 20.1% CO_2 , 19.9% CO , and 19.9% H_2O . After 1 hour on the 60-40 gas mixture, the gas chromatograph indicated 20.8% carbon monoxide and 19.1% carbon dioxide on a wet basis. After 24 hours, the product gases contained 18.8% CO and 21.1% CO_2 indicating a slight loss in catalytic activity. At the completion of the experiment, the catalyst was recovered and analyzed for the presence of carbon. None was found within the limits of detection, 0.1% by weight.

Shift Experiment No. 4

The catalyst bed in this experiment also consisted of 1 gram of powdered nickel, -325 mesh, supported on quartz wool and was about 0.5-cm thick and 2.5-cm in diameter. The bed was contained in a quartz tube and was heated under nitrogen and then switched to the 60-40 gas mixture. The flow rate of the gas was $196 \text{ cm}^3/\text{min}$ on a dry basis (60-40 feed gas contains no water vapor) giving a residence time of the gas in the bed of less than 1 second. After 2 hours, the GC indicated a product gas composition containing 19% carbon monoxide and 21% carbon dioxide, which is very close to predicted equilibrium concentrations of 19.9% CO and 20.1% CO_2 . After 2 hours, a hydrogen sulfide permeation tube was added to the system at the entrance to the quartz reactor. Addition of the H_2S at this point eliminates the need for special hardware upstream of the reactor. Standard gas regulators and flow meters can be used without fear of H_2S adsorption. Weight lost by the permeation tube indicated that 3 ppm of H_2S were added to the gas stream on a continuous basis during the course of the 24-hour experiment. The gas chromatograph was placed in the automatic sampling mode and set to sample the product gases every 15 minutes. Over the course of the next 10 hours, the

concentration of the carbon monoxide decreased to near zero. After about 18 hours, the integrator ceased to recognize a carbon monoxide peak. The signal to noise ratio was set to disregard a signal below about 0.1% of the total. After 24 hours, there was no evidence of a carbon monoxide peak on the strip chart. Figure 8 is a graph of the carbon monoxide concentration as a function of time for the first 12 hours of this experiment.

The conclusion drawn here is that the 3 ppm of H_2S totally poisoned the reverse shift reaction on the nickel powder at 650°C . At the $196\text{ cm}^3/\text{min}$ gas flow rate, the residence time of the gas in the bed was slightly less than 1 second. The residence time of this same gas mixture used in a bench-scale fuel cell adjusted to utilize 80% of the fuel on a single pass is about 2 seconds in the region of the electrode. Thus, results obtained here should be predictive of those expected for the fuel cell if we assume that the reverse shift reaction proceeds at the same rate as the shift reaction.

Shift Experiment No. 5

In this experiment, a catalyst was prepared by abrading a porous 90% nickel-10% chromium plaque of the kind used for fuel cell anodes. This abraded material was supported on quartz wool and loaded in a quartz tube in the manner described above for Experiment No. 4. After heating under nitrogen, the 60-40 gas mixture was passed through the quartz tube reactor, and the concentration of carbon dioxide in the product gases was determined. Because of the granular nature of this catalyst, the bed was more compact than with the nickel powder used in Experiment No. 4. Here, the 1-gram sample of nickel/chromium produced a bed thickness of only about 1 mm. As a consequence, gas flow rates on the order of $38\text{ cm}^3/\text{min}$ were required to provide a 1-second residence time.

After 2 hours of operation on the clean 60-40 mixture, the carbon monoxide concentration in the product gases was measured at three separator flow rates. At $186\text{ cm}^3/\text{min}$ (1/5 second residence time), the concentration of carbon monoxide in the product gases was 4.5% on a wet basis. At $110\text{ cm}^3/\text{min}$ (1/3 second residence time), the carbon monoxide concentration was 6.0%, and at $38\text{ cm}^3/\text{min}$, the carbon monoxide concentration rose to 9.7%. A comparison of the carbon monoxide concentrations in the product gases from Experiment No. 3 (20%) with those in Experiment No. 5 (10%) at equal residence times (1 second) indicate that the granules of nickel/chromium electrode are less active as a

Figure 8. EFFECTS OF 3 PPM H_2S ON THE CONCENTRATION OF
CARBON MONOXIDE IN PRODUCT GASES
AS A FUNCTION OF TIME FOR SHIFT EXPERIMENT NO. 4

catalyst for the reverse shift reaction than the -325 mesh nickel powder. A hydrogen sulfide permeation tube was then placed in the system upstream of the catalyst. This permeation tube added H_2S to the fuel stream at the same constant rate as in Experiment No. 4. However, as the flow rate of the fuel changed, so did the concentration of H_2S in the gas. At $38 \text{ cm}^3/\text{min}$, the H_2S concentration in the fuel was about 15 ppm; while at $186 \text{ cm}^3/\text{min}$, the concentration was only about 3 ppm. After addition of the permeation tube to the system, the flow rate was maintained at $38 \text{ cm}^3/\text{min}$ for 48 hours and the composition of the product gases was determined automatically. Table 3 lists the results.

Table 3. RESULTS OF 48-HOUR EXPERIMENT WITH Ni/Cr CATALYST
AND $38 \text{ cm}^3/\text{min}$ FUEL WITH 15 ppm H_2S

<u>Time</u>	<u>% CO</u>
0 hours	9.7
12 hours	8.4
24 hours	7.8
36 hours	6.1
48 hours	6.0

Despite the higher concentration of H_2S in this fuel mixture, this catalyst bed did not poison completely. After 48 hours of operation on 15 ppm H_2S contaminated gas, the carbon monoxide concentration in the product gases was again determined at three different flow rates. At $180 \text{ cm}^3/\text{min}$, the CO content was 2.1% on a wet basis. At $110 \text{ cm}^3/\text{min}$, it was 3.0% and at $38 \text{ cm}^3/\text{min}$ it was 6.0%. The experiment was then terminated and the reactor cooled under nitrogen. The catalyst was recovered and analyzed using x-ray diffraction. The x-ray pattern indicated nickel, chromium, and minor amounts of chromia, Cr_2O_3 , but no evidence of other oxides or sulfides.

Since it is known that chromia can act as a shift catalyst, the tentative conclusion drawn here is that the H_2S poisons the nickel with respect to its ability to catalyze the shift reaction but not the chromium/chromia, which is formed by the reaction between chromium and water vapor in the fuel mixture.

Shift Experiment No. 6

This experiment was set up in the identical manner as Experiment No. 5 with one exception; 1 weight percent lithium carbonate/potassium carbonate

eutectic was mixed in with the nickel/chromium catalyst. The purpose of this carbonate was to provide a "wet" catalyst similar to the "wet" electrode in fuel cells that have operated for several thousand hours. As in the previous experiment, the catalyst bed was warmed under nitrogen and then allowed to stabilize for several hours on 60-40 fuel at a high flow rate. However, because of the presence of the carbonate, this stabilization period was lengthened to 24 hours to allow any liquid-solid reactions that might occur to take place. After 24 hours on clean gas, the catalytic activity of this wetted material was determined by measuring the carbon monoxide concentration in the product gases at three different flow rates. The results are as follows:

0 to 24 hours:	Flow rate 190 cm ³ /min, CO content 3.9%
24 to 28 hours:	Flow rate 36 cm ³ /min, CO content initially 9.8% but fell to 6.2%
28 to 30 hours:	Flow rate 110 cm ³ /min, CO content initially 2.7% but rose to 3.6%
30 to 45 hours:	Flow rate 190 cm ³ /min, CO content initially 2.4% but slowly rose to 4.8%

These results suggest that some chemical change is taking place that changes catalytic activity. Thus, while the 9.8% CO at 36 cm³/min in this test is similar to the 9.7% CO measured at 38 cm³/min in Experiment No. 5, the dry catalysts in Experiment No. 5 could maintain this activity indefinitely while the activity of the wet catalyst slowly decreased. Upon increasing the flow rate, the catalytic activity returned and the 4.8% CO finally measured at 190 cm³/min on the wet catalyst compares favorably with the 4.5% CO measured at 186 cm³/min in Experiment No. 5 on a clean dry catalyst.

A hydrogen sulfide permeation tube was added to this experiment after 45 hours, while the flow rate of the gas was maintained at the high flow rate. The CO content of the product gases immediately began to fall. Within 60 minutes it reached 1.6%. However, it remained at this level for the next 24 hours. At this point, the experiment was terminated.

Although the results of this experiment are qualitatively similar to the results observed in Experiment No. 5, the lack of stability of the catalysts on clean gases casts suspicion on any quantitative interpretation.

Anode Reactor Experiment

The tentative conclusions drawn in Experiment No. 5 and qualitatively supported by Experiment No. 6 can have a significant impact on future fuel cell development. If, as suggested, pure nickel electrodes are poisoned relative to the shift reaction by ppm levels of H_2S but nickel/chromium electrodes are only partially affected, then the extra cost of adding chromium to the anode might be offset by savings in the gas cleanup system. In order to obtain additional information of a useful nature in time for inclusion in this quarterly report, the original experimental schedule, which called for six additional tube furnace experiments, was temporarily suspended and the anode reactor, which was to be the final experiment of this task, was moved forward to this quarter.

In this experiment, one half of a 4-in. x 4-in. bench-scale fuel cell was used as a shift reactor. Figure 9 is a cross-sectional diagram of the reactor. It consists of a stainless steel boilerplate housing, a perforated nickel plate (current collector), a 90% nickel-10% chromium porous metal plaque 30 mils thick, and an electrolyte tile. The cathode side of the cell was replaced by a stainless steel plate. The volume of the gas channels in the anode housing and the perforations in the current collector totals 5.5 cm^3 exclusive of the pore volume in the electrode itself. The experimental gas composition consisted of 58% H_2 , 39% CO_2 , and 3% H_2O produced by humidifying the 60-40 mixture at room temperature. During the course of an experiment, this gas was passed through the reactor at flow rates of 340, 530, and $1130 \text{ cm}^3/\text{min}$ giving residence times of 1, 0.6, and 0.3 seconds respectively. The extent of the reverse shift reaction was determined by monitoring the concentration of carbon monoxide leaving the reactor. The reactor temperature was maintained at 650°C throughout the 340 hours of experimentation. The reactor was operated for 200 hours on clean fuel to stabilize the system, assure uniform wetting of the parts, and to allow all liquid-solid reactions to come to equilibrium. Hydrogen sulfide was then added to the gas stream using a permeation tube at a rate which produced 5 ppm of contamination at $1130 \text{ cm}^3/\text{min}$, 11 ppm at $530 \text{ cm}^3/\text{min}$, and 17 ppm at $340 \text{ cm}^3/\text{min}$. The results of the experiment are summarized in Table 4.

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Figure 9. CROSS-SECTION OF ANODE REACTOR USED IN SHIFT
EXPERIMENTS SIMULATING ANODE COMPARTMENT OF MOLTEN
CARBONATE FUEL CELL

Table 4. RESULTS OF ANODE REACTOR EXPERIMENTS

<u>----- cm³/min -----</u>	<u>ppm H₂S</u>	<u>% CO₂</u>	<u>% CO</u>
<u>Clean Gas After 200 Hours</u>			
340	0	21.3	18.7
530	0	21.4	18.6
1130	0	24.2	15.8
<u>After 16 Hours on H₂S</u>			
340	17	23.4	16.6
530	11	25.0	15.0
1130	5	29.5	10.5
<u>After 40 Hours on H₂S</u>			
340	17	23.6	16.3
530	11	25.6	14.4
1130	5	29.9	10.1
<u>After 64 Hours on H₂S</u>			
340	17	23.5	16.5
530	11	25.4	14.6
1130	5	29.6	10.4
<u>After 136 Hours on H₂S</u>			
340	17	23.3	16.7
530	11	25.2	14.8
1130	5	29.4	10.6

All flow rates and percent compositions are reported on a wet basis.

Discussion

The results of Shift Experiment Nos. 5 and 6, when combined with the results of the anode reactor experiments, make a strong argument for the conclusion that the shift reaction is only partially poisoned by H_2S when nickel/chromium composite materials are used. Although verification of this in operating fuel cells still remains to be accomplished, it is important to note that most MCFC developers are moving away from the use of chromium as a sintering inhibitor in fuel cell anodes.

WORK FOR NEXT QUARTER

Task 1.3

The final in-cell test of Phase I research will be conducted. This test will utilize the Stack A gas mixture containing 5 ppm of hydrogen sulfide and will be carried out at 1, 3, 7, and 10 atmospheres pressure. The purpose of this test is to determine the relationship between pressure and the poisoning reaction.

Task 1.4

The physicochemical model for predicting fuel cell performance loss as a function of hydrogen sulfide contamination will be completed.

Task 2.1

A brief literature review of the shift reaction including the mechanism, catalysts, and catalysts poisoning will be completed and a topical report written.

Task 2.2

The out-of-cell testing program addressing shift reaction and its poisoning on fuel cell hardware will be completed.

Task 2.3

An in-cell testing program will be initiated to ascertain the importance of and methods for controlling shift reaction poisoning in molten carbonate fuel cells.

Task 2.4

The physicochemical model developed in Task 1.4 will be extended to include shift reaction poisoning. This task will be initiated in this quarter.

Task 3.1

A literature review will be undertaken to address the impact of sulfur dioxide in the cathode gases upon fuel cell performance. This review will be used to design the specific experiments in Task 3.2 and 3.3 work.

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