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SULFUR TOLERANT ANODE MATERIALS

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ABSTRACT

All electronic conductivity measurements and all electrolyte compatibility tests were completed this quarter bringing to a total of 15 the number of candidate materials that have been tested under this program. Laboratory-scale fuel cell tests were conducted evaluating the sulfur tolerance of two alternative anode materials, cobalt and copper, and a baseline nickel + 10% chromium anode test was also conducted for purposes of comparison. Neither copper nor cobalt proved to be sulfur tolerant to any greater extent than nickel +10% chromium. A sulfur free laboratory-scale fuel cell test was performed using a lithium ferrate (III) anode structure to assess the viability of this material as an alternative anode. A problem developed in that this structure did not partially fill with electrolyte and, as a consequence, the performance was low. However, lithium ferrate (III) still represents the best candidate for a sulfur tolerant anode and work will continue using this material.

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WORK ACCOMPLISHED THIS QUARTER

Task 1. Preparation of a Management Plan

This task was completed in the previous fiscal year.

Task 2. Preparation of a Test Plan

This task was completed in the previous fiscal year.

Task 3. Literature Review

This task was completed in the previous fiscal year.

Task 4. Hydrogen Oxidation Anode Development

Electrical Conductivity Measurements

The d-c electrical conductivity of the last group of candidate materials was determined at 25° and 650°C this quarter using the apparatus described in the previous reports. All samples were heated in a 90% nitrogen/10% hydrogen atmosphere. Results are as follow.

Tantalum Doped Titanium Dioxide

The sample used in this test was a dense cylinder of TiO_2 doped with 3 mole % tantalum.

The initial conductivity of the Ta doped TiO_2 at 20°C was 0.42 mho/cm. The value at 650°C was 8.3 mho/cm. However, a hysteresis in the data developed upon cooling with a higher conductivity, 2.4 mho/cm being observed at 20°C after cooling. This is a six-fold increase in conductivity as the result of thermal cycling. The sample exhibited no change in physical size or weight, but one of the copper, current-carrying, lead wires turned black, suggesting that chemical vapors were given off by the sample during heating.

Lithium Tungstate (Li_2WO_4)

The initial 25°C conductivity of this material was extremely low — too low to be measured with the present apparatus. However, the conductivity appeared to increase with an increase in temperature. Inspection of the sample after the measurement showed that the sample was physically unstable. The material deformed. Initially, the sample was 0.64 cm in diameter and 3.81 cm long and X-ray diffraction of the untested material showed that the major component was hexagonal and hexagonal/rhombic Li_2WO_4 with a minor amount

of Li_2SO_4 . X-ray diffraction of the material recovered from the electrical conductivity apparatus showed the major component to be tungsten metal, a minor-major component to be WO_2 , and that Li_2WO_4 was present only as a minor component. The conclusion is that Li_2WO_4 is unstable at 650°C under a hydrogen/nitrogen atmosphere.

Cobalt Sulfide (Co_9S_8)

Electrical conductivity measurements were made on CoS only at room temperature because the CoS is unstable in the absence of H_2S at elevated temperatures in an H_2/N_2 atmosphere. The van der Pauw method was used and some difficulty was encountered in obtaining highly reproducible results. Twenty measurements gave values that ranged from 4.4×10^3 to 9.6×10^3 mho/cm with an average of 5.9×10^3 mho/cm.

Copper (I) Sulfide (Cu_2S)

Electrical conductivity measurements were made on Cu_2S only at room temperature because the Cu_2S was thought to be unstable at elevated temperatures in an H_2/N_2 atmosphere in the absence of H_2S . The van der Pauw method was used and the conductivity was measured at 3.2 mho/cm.

Lithium Ferrate (III) (LiFe_5O_8)

A dense sample of this material was not available at the time the electrical conductivity experiments were conducted, however, a literature value places the conductivity of this material at approximately 14 mho/cm at 650°C .

Electrolyte Compatibility Tests

The third group of materials was subjected to electrolyte compatibility tests in molten carbonate at 700°C under a simulated coal gasifier fuel stream containing 200 ppm H_2S . The specifics regarding the test procedure has been described in previous reports. In this experiment, the test samples were warmed to temperature under an atmosphere of 10% hydrogen and 90% nitrogen and then the gas supply was switched to the simulated gasifier mixture. The materials tested in this group include Co_9S_8 , NiCuCr (82:10:8), TiN (second test), $\text{TiO}_2 + 3\% \text{Ta}$, Li_2WO_4 , and $\text{LiFe}_5\text{O}_8 + \text{LiFeO}_2$. The electrolyte was not washed from the samples at the completion of the test in order to preserve the surface chemistry for X-ray diffraction analysis. Thus, Li_2CO_3 and K_2CO_3 were

reported as minor constituents in some of the samples. Results are as follows.

Cobalt Sulfide (Co_9S_8)

The cobalt sulfide samples shown in Figure 1 was fabricated by CERAC and had a chemical purity of 99.5%. Its color was gray with silver specks and was irregularly shaped but was approximately 2.7 cm long by 0.93 cm wide by 0.32 cm thick. It weighed 2.827 g and was tested along with 1.216 grams of electrolyte. After the test, the sample was removed from the apparatus and examined. In appearance, it was gray, deformed, cracked, and swollen at one end as can be seen in Figure 2. The sample now weighed 3.35 g indicating that some of the electrolyte wicked into the porous material. The end surfaces of the sample were scraped off and analyzed by X-ray diffraction. The results of the X-ray diffraction analysis is presented in Table 1. It is apparent that the Co_9S_8 decomposed and may have done so during the initial warm-up period.

Table 1. RESULTS OF X-RAY DIFFRACTION STUDY OF Co_9S_8 SAMPLE

<u>Relative Intensity</u>	<u>Untested Sample</u>	<u>Expanded End</u>	<u>Square End</u>
Major	Co_9S_8	Co, LiKCO_3 (Eutectic)	Co
Minor-Major	--	$\text{K}_2\text{C}_2\text{O}_6$	--
Minor	Co_4S_3	--	LiKCO_3 (Eutectic)
Trace-Minor	--	Co_4S_3	--

Nickel-Copper-Chromium Alloy

The Ni/Cu/Cr alloy was fabricated into sample by CERAC and had a composition of 82 wt % nickel, 10 wt % copper, and 8 wt % chromium. The sample, shown in Figure 3, has a length of 3.87 cm, a weight of 3.404 grams, and was tested with 0.985 grams of electrolyte. The sample was originally cylindrical with a diameter of 0.63 cm, but was cut lengthwise and smoothed with a file to provide a flat surface for easier X-ray diffraction work. This surface was originally metallic gray in color. The surface shown in the figure is the one cut and smoothed with a file and is metallic in luster but looks dark because

CoS
Before Test

Figure 1. CoS BEFORE CORROSION TEST

CoS
After Test

Figure 2. CoS AFTER CORROSION TEST

NiCuCr
82:10:8 wt%
Before Test

Figure 3. NiCuCr BEFORE CORROSION TEST

NiCuCr
82:10: wt%
After Test

Figure 4. NiCuCr AFTER CORROSION TEST (Caption Should Be 82:10:8 Wt %)

of the angle of illumination. The marks on the right hand side and near the lower left hand corner are saw marks that were not filed away.

After the test, the sample shown in Figure 4 was still gray, but was bent and swollen. The end that was in the electrolyte had developed cracks and protrusions. The sample weighed 4.174 grams, a gain of 0.770 grams, indicating that some electrolyte was picked up by the sample. The X-ray diffraction results are presented in Table 2. It is not clear from these results whether this alloy is chemically stable or not. No corrosion products were detected by the X-ray analysis, although some lithium chromite was expected to be on the surface. The physical deformation noted was probably due to uneven wicking of electrolyte into the sample and subsequent contraction during cooling.

Table 2. RESULTS OF X-RAY DIFFRACTION STUDY OF Ni/Cu/Cr ALLOY

<u>Relative Intensity</u>	<u>Untested Sample</u>	<u>Tested Sample</u>
Major	Ni*	Ni
Minor-Major	--	--
Minor	--	LiKCO ₃ (Eutectic)
Trace-Minor	--	--

* Nickel only analysis indicates that sample is an alloy with no discrete Cu or Cr crystals present.

Titanium Nitride (TiN)

This is the second attempt at a compatibility test with TiN. The first time the sample was washed in dilute acetic acid after the test to remove the electrolyte. However, the sample fell apart during the acid wash and the results were compromised.

The second sample, shown in Figure 5, was prepared by CERAC, weighed 2.134 grams and was yellow-brown in color. It was a cylinder 3.20 cm long and 0.69 cm in diameter. It was cut lengthwise and smoothed with a hand file. The smoothed surface faces the camera in Figure 5. Electrolyte weighing 0.902 grams was added to the sample prior to the compatibility test.

After the test, the color of the sample was brown with some white lines and areas as shown in Figure 6. The length was 3.22 cm which is within

TiN
Before second
Test

Figure 5. TiN BEFORE SECOND CORROSION TEST

TiN
After second
Test

Figure 6. TiN AFTER SECOND CORROSION TEST

measurement error of the original length. The weight was 2.451 g, a gain of 0.318 grams. X-ray diffraction results are presented in Table 3. The production of Li_2TiO_3 has been confirmed, indicating that this material is not stable.

Table 3. RESULTS OF X-RAY DIFFRACTION STUDY OF TiN

<u>Relative Intensity</u>	<u>Untested Sample</u>	<u>Tested Sample</u>
Major	TiN	TiN
Minor-Major	--	Li_2TiO_3
Minor	$\text{TiO}_2, \text{KHCO}_3$	LiTi_2O_4
Trace-Minor	$\text{K}_2\text{C}_2\text{O}_6$	Ti_2O_3

Titanium Dioxide + 3% Tantalum (TiO_2)

The tantalum doped titanium dioxide, shown in Figure 7, was obtained from CERAC, was gray in color with a few silver specks, and weighed 2.090 grams. It was a right rectangular solid, 0.81 cm by 0.56 cm x 1.58 cm, with round edges. It was tested with 0.557 grams of electrolyte.

After the test, the sample, as shown in Figure 8, was gray with some lighter lines and areas. One end was slightly swollen; dimensions increased about 4% to 6%. The sample also had a crack in it. The sample weighed 2.396 grams, which is an increase of 0.306 grams. The X-ray diffraction results are presented in Table 4. The electrolyte (eutectic LiKCO_3) was present as well as some lithium salts of titanium.

Table 4. RESULTS OF X-RAY DIFFRACTION STUDY OF TiO_2

<u>Relative Intensity</u>	<u>Untested Sample</u>	<u>Tested Sample</u>
Major	TiO_2	TiO_2
Minor-Major	--	Li_2TiO_3
Minor	--	$\text{LiKCO}_3, \text{K}_2\text{C}_2\text{O}_6$
Trace-Minor	--	TiO

$\text{TiO}_2 + 3$
mol % Ta
Before Test

Figure 7. $\text{TiO}_2 + 3$ MOL % Ta BEFORE CORROSION TEST

$\text{TiO}_2 + 3$
mol % Ta
After Test

Figure 8. $\text{TiO}_2 + 3$ MOL % AFTER CORROSION TEST

Lithium Tungstate (Li_2WO_4)

The sample of Li_2WO_4 shown in Figure 9 was prepared by CERAC and had a purity of 99.9%. The sample weighed 3.047 g, and was white and gray in color. The sample and 0.790 g of electrolyte were added to the crucible and placed in the test apparatus. The original dimensions of the sample were 2.44 cm long and 0.63 cm in diameter with a flat surface ground into it on one side parallel to the main axis.

The Li_2WO_4 deteriorated significantly during the compatibility test in a manner that suggested that it dissolved in the electrolyte. A small portion of the original sample, shown in Figure 10, was recovered from the test apparatus and analyzed. The X-ray diffraction results are reported in Table 5. This material has proved to be physically unstable in both the conductivity tests and this compatibility test and has been dropped from further consideration.

Table 5. RESULTS OF X-RAY DIFFRACTION STUDY OF Li_2WO_4

<u>Relative Intensity</u>	<u>Untested Sample</u>	<u>Tested Sample</u>
Major	Li_2WO_4	Li_2WO_4
Minor-Major	--	Li_4WO_5 , $\text{Li}_6\text{W}_2\text{O}_9$
Minor	Li_2SO_4	--
Trace-Minor	--	--

Lithium Ferrate (III) (LiFe_5O_8)

A dense sample of LiFe_5O_8 was not available for testing at the time these compatibility tests were undertaken. However, a powder was available which was a mixture of Fe_2O_3 , LiFeO_2 , and LiFe_5O_8 . This powder is shown in Figure 11 and was the result of an earlier attempt to fabricate the LiFe_5O_8 material by the sol-gel process. Subsequent attempts resulted in a high purity material of the desired formula. All of the high purity LiFe_5O_8 was sent to CERAC to be fabricated into test samples and porous disks for evaluation as anode. The solid samples of LiFe_5O_8 had not been prepared in time for this test sequence so the decision was made to use the above mixture of materials in its place.

Li_2WO_4
Before Test

Figure 9. Li_2WO_4 BEFORE CORROSION TEST

Li_2WO_4
After Test

Figure 10. Li_2WO_4 AFTER CORROSION TEST

$\text{LiFe}_5\text{O}_8/$
 LiFeO_2
Before Test

Figure 11. $\text{LiFe}_5\text{O}_8/\text{LiFeO}_2$ BEFORE CORROSION TEST

$\text{LiFe}_5\text{O}_8/$
 LiFeO_2
After Test

Figure 12. $\text{LiFe}_5\text{O}_8/\text{LiFeO}_2$ AFTER CORROSION TEST

This mixture of materials was placed in an alumina crucible along with approximately 1.0 gram of electrolyte and loaded into the test apparatus. At the completion of the 200 hour test, the sample was retrieved from the apparatus in the form of a solid plug held together by frozen electrolyte. This plug is shown in Figure 12. X-ray diffraction analysis of this plug indicated that LiKCO_3 and LiFeO_2 were the major constituents with trace amounts of KHCO_3 also present. A mixup in the analysis data sheets lead to the mistaken report, in the February monthly, that the material recovered from this test was exclusively LiFe_5O_8 when in fact it was primarily LiFeO_2 .

Evaluation of Materials in Fuel Cells

Cobalt Anode Experiment

In a literature search conducted in the first year of this program, cobalt was identified as a material which may be more tolerant of sulfur than is nickel.¹

Although contaminant induced performance losses were reported in this literature for cells using cobalt anodes, the magnitude of these losses were less than those reported for cells using nickel anodes. A recent DOE/METC funded study performed at IGT also provided experimental evidence that a threshold exists for the onset of contaminant induced performance losses that is tied to an electrochemical reaction occurring on the anode surface.² Data taken from the EPRI report,¹ when viewed in light of the threshold hypothesis suggests that the threshold for cobalt occurs at higher contaminant levels. In other words, there is reason to believe that cobalt anodes may be able to operate at higher contaminant levels and suffer lower performance losses than nickel. An experiment was devised to investigate this sulfur tolerance in a fuel cell. Since cobalt suffers the same problems with sintering and creep as does nickel when used as an MCFC anode, cobalt must also be stabilized with a sintering inhibitor. Chromium was selected as the stabilizing agent.

A porous metal plaque having a composition of 90% cobalt and 10% chromium was used as an anode in this experiment. This plaque was part of a larger sample fabricated by Gould Metallurgics about 10 years ago. This plaque has a porosity of 62% and a mean pore size of 4.6 μm , and is 0.76 mm (30 mils) thick. These specifications are a close match to those of the nickel/chromium anodes currently under development at IGT. This cobalt/chromium plaque was

placed in a laboratory-scale MCFC (3-cm²) and matched with a porous nickel plaque having a porosity of 79% and a mean pore size of 8.7 μ m. This porous nickel plaque is the cathode of the cell and as the cell is warmed to operating temperature, the nickel metal oxidizes and lithiates in the oxidant stream. A hot pressed tile was used as an electrolyte matrix and contained the usual 62/38 Li/K ratio carbonate eutectic. The tile was 1.79 mm thick and was 55% carbonate eutectic and 45% lithium aluminate support. The fuel gas used was 35% H₂, 32% H₂O, 12% CO, and 20% CO₂; the oxidant was 68% air, 29% CO₂, and 3% H₂O. Flow rates of fuel and oxidant were adjusted so that only 6 and 15% of the fuel and oxidant were used in a single pass through the cell at a current density of 200 mA/cm².

The cell was warmed to operating temperature over a 24 hour period and then operated for a period of one week before cell testing began. This week-long break-in period is required to allow all chemical reactions, such as the oxidation and lithiation of the cathode, to take place and for the cell to reach chemical equilibrium with its chemical environment. This cell was operated for 192 hours on uncontaminated fuels and then 30 ppm H₂S were added to the fuel gas, downstream of the humidifier. The cell was operated on contaminated fuel for 192 hours, returned to uncontaminated fuel for 312 hours, and then recontaminated for 120 hours.

A significant decrease in performance was noted upon the addition of H₂S to the fuel supply. The performance recovered completely when the contaminant was removed from the fuel. A second contamination experiment with the same cell indicated that the performance loss was reproducible in quantitative as well as qualitative terms. Table 6 summarizes the cell voltage at various current densities for the cell on both clean and contaminated fuels. The performance of this cell on contaminated fuel was poor and does not represent a significant improvement over the standard nickel/chromium anode.

Table 6. CURRENT/VOLTAGE CHARACTERISTICS OF Co/Cr ANODE CELL

Current Density	Cell Voltage	
	192 Hours (Clean)	792 Hours (H ₂ S)
0 mA/cm ²	1022 mV	1016 mV
80 mA/cm ²	902 mV	880 mV
160 mA/cm ²	779 mV	727 mV
240 mA/cm ²	658 mV	522 mV

Cobalt + 10% chromium anodes do not appear to possess superior sulfur tolerance when compared to the standard nickel + 10% chromium anodes.

Nickel Anode Experiment

The results of the cobalt/chromium experiment reported above pointed out a gap in the data for 3-cm² cells operating on sulfur contaminated fuels. In the previous work conducted for EPRI,¹ 3-cm² laboratory-scale MCFC tests were utilized to evaluate the sulfur tolerance of a variety of composite materials including cobalt/chromium and nickel/chromium. Medium- and low-Btu fuels were used in those experiments under conditions different from those used here. This pointed out the need to do a baseline sulfur poisoning test on a nickel/chromium anode in a 3-cm² cell. Up to this point in time, this program has been relying on nickel/chromium data taken in 3-cm² cells 10 years ago and more recently in 94-cm² bench-scale cells at high fuel utilizations. The following baseline nickel/chromium experiment was set up and run.

The baseline experiment utilized a porous nickel plus 10% chromium plaque which was 0.76 mm (30 mils) thick, had a porosity of 65% and a mean pore size of 4.6µm. The anode was matched to an electrolyte matrix and a cathode identical to the one used in the cobalt experiment described above. This cell was operated for 336 hours on clean, uncontaminated fuel and then switched to a fuel contaminated with 30 ppm H₂S. Performance of clean and contaminated fuel are summarized in Table 7. All of the decrease in performance observed when H₂S was added to the fuel occurred at the anode in the form of increased polarization. The information in Table 7 can now be used as a basis of comparison for the other metals already tested as sulfur tolerant anodes.

Table 7. CURRENT/VOLTAGE CHARACTERISTICS OF
Ni/Cr ANODE CELL

<u>Current Density</u>	<u>Cell Voltage</u>	
	<u>336 Hours (Clean)</u>	<u>529 Hours (Contaminated)</u>
0 mA/cm ²	1029 mV	1016 mV
80 mA/cm ²	927 mV	900 mV
160 mA/cm ²	824 mV	735 mV
240 mA/cm ²	718 mV	570 mV

Copper Anode Experiment

It has been theorized for some time, by those skilled in the art of MCFC development, that copper represents a viable candidate for a sulfur tolerant anode. It is known that copper is a good catalyst for the electrochemical hydrogen oxidation reaction. Although the exchange current density for this reaction on copper is less than on nickel, the activation polarization for the reaction is sufficiently low on both metals that little increase in total polarization would be experienced if copper were substituted for nickel in the MCFC anode. The logic behind the theory that copper should be more sulfur tolerant than nickel is as follows.

Both the free energy of formation, ΔG , and the heat of formation, ΔH , for the two most common nickel sulfides, NiS and Ni_3S_2 , are higher than those of the stable stoichiometric copper sulfides, CuS and Cu_2S , at 25°C. Hence, higher $\text{H}_2\text{S}/\text{H}_2$ ratios are required to form bulk copper sulfides and the copper sulfides formed are expected to be less stable at higher temperatures than the corresponding nickel sulfides. Support for this contention, however, is not easy to obtain since none of the standard references contain a complete set of thermodynamic data for all compounds at MCFC temperatures. Table 8 is a list of selected values from NBS sources for these compounds at 25°C. Unfortunately, values for the free energy of formation of these compounds at 650°C are unreliable and vary widely from one source to another.

Table 8. THERMOCHEMICAL TABLES FOR COPPER AND NICKEL SULFIDES
IN Kcal/mole AT 25°C

<u>Sulfide</u>	<u>Heat of Formation</u>	<u>Free Energy of Formation</u>	<u>Ref.</u>
CuS	-11.6	-11.7	4
Cu_2S	-19.0	-20.6	4
NiS	-17.6	---	4
	-21.0	-20.4	5
Ni_3S_2	-43.4	---	4
	-51.8	-50.3	5

Although the logic which dictates that copper ought to be more sulfur tolerant than nickel applies directly to the formation of bulk sulfides, it does not directly address the problem of contaminant induced performance loss in the MCFC. Hydrogen sulfide contaminants in fuels supplied to MCFC devices cause significant performance losses at H_2S/H_2 ratios about two orders-of-magnitude lower than those required to produce even the most stable bulk sulfide, Ni_3S_2 . However, from catalyst research, it is known that metallic nickel surfaces are poisoned by chemisorption of sulfur at very low H_2S/H_2 ratios. Bartholomew et. al.³ have written a review of the literature on this poisoning process and have published a compilation of data on the free energy for the formation of chemisorbed sulfur on a variety of metal surfaces at various temperatures. For example, the ΔG of formation of surface sulfides on nickel at 650°C is about 25 Kcal/mole while the ΔG of formation for bulk Ni_3S_2 at this temperature is placed at about 12 Kcal/mole. Information for copper is not available at this temperature, but data taken at 830°C indicates a ΔG for surface sulfides of 17 Kcal/mole.

The problem, of course, is still not resolved since neither the thermodynamics for the surface sulfide formation nor for bulk sulfide formation matches up exactly with the contaminant induced performance loss phenomenon observed in the MCFC. The best way to resolve the question of sulfur tolerance of copper is by experiment.

As far as can be determined, no MCFC developer has succeeded in producing a viable copper anode with performance characteristics equal to that of stabilized nickel. However, to determine if copper has superior sulfur tolerance to nickel, it is not necessary that the copper anodes tested have superior performance. A porous plaque of sintered copper powder reinforced by a copper screen was selected as a candidate anode material. The mean pore size of this plaque was 12.0 μ m which is beyond the range necessary for partial filling with electrolyte. Partial filling of the anode with electrolyte is required to achieve a high electrochemically active surface area in the anode. To achieve partial filling, it is necessary to fill the oversized pores of the copper anode plaque with lithium chromite. When in operation, the lithium chromite wets with electrolyte and acts to wick the electrolyte into the anode interior insuring a high active surface area. Lithium chromite can be added to the anode structure by soaking the plaque in a saturated

solution of lithium chromate in water and then evaporating the water and drying in an oven overnight at 150° to 200°C. The lithium chromate which chrystallizes within the pore structure during evaporation is reduced to lithium chromite when the cell is first heated to operating temperatures with fuel gases flowing.

A laboratory-scale MCFC was assembled using the lithium chromate impregnated porous copper plaque as an anode, a sintered nickel plaque as a cathode, and a hot pressed electrolyte matrix approximately 1.8 mm thick. The mean pore size of the cathode was 6.5 μm .

This cell was operated for 1 week, 168 hours, on clean, uncontaminated fuel and the performance characteristics of the cell were determined every 24 hours. Unlike the standard nickel + 10% chromium anode cells, which usually requires 150 hours to stabilize, this cell exhibited stable performance characteristics after only 48 hours of operation and the performance neither improved nor degraded over the next 120 hours. At Hour 168, approximately 30 ppm hydrogen sulfide were added to the fuel supply. The performance began to deteriorate immediately. In a standard MCFC fuel cell incorporating a nickel + 10% chromium anode, the performance is observed to decrease when H_2S is added to the fuel for the first 24 to 48 hours after the addition. However, the rate of decrease in performance falls to zero after 48 hours and stable, albeit lower, performance is observed for hundreds of hours thereafter, or until the source of contamination is removed. In this copper + lithium chromite experiment, the decrease in performance was continuous. No stable plateau was reached. This is best illustrated in Table 9 which summarized the performance changes with time.

Table 9. PERFORMANCE OF COPPER ANODE MCFC

Current Density, mA/cm^2	----- Cell Voltage in mV -----				
	Clean Fuel, Hour 168	----- Contaminated Fuel -----			Clean Fuel Hour 480
		Hour 192	Hour 216	Hour 288	
0	1025	1017	1020	1020	1020
80	870	851	832	792	853
160	708	649	594	499	655
240	532	400	313	--	428

This cell was operated for 168 hours on clean, uncontaminated fuel and for 120 hours (from Hour 168 to Hour 288) on fuel contaminated with 30 ppm H_2S and then returned to clean fuel operation until termination at Hour 504. Some improvement in performance was noted when the H_2S was removed from the fuel supply. The cell, however, did not recover completely. It is possible that a slow deterioration in performance with time occurred in this cell as the result of changes in anode morphology unrelated to the presence of a contaminant in the fuel. And further, that this change in morphology was the reason the cell did not fully recover when the contaminant was removed. Separate from this issue is the fact that a significant drop in performance was observed when the contaminant was first introduced and a substantial improvement in performance occurred when the contaminant was removed from the fuel. Such behavior is unequivocal evidence that copper is not sulfur tolerant under these conditions.

Lithium Ferrate (III) Anode Experiment

As a candidate sulfur tolerant anode material, lithium ferrate (III) has ideal characteristics. It is an oxide which is more stable than any of the possible sulfides of iron that could form in a reducing atmosphere containing H_2S . It has an electronic conductivity well within the useful range for an MCFC anode and it is known to catalyze the electrochemical oxidation of hydrogen. Sintered porous disks of lithium ferrate (III) were prepared by CERAC from powder prepared by IGT. X-ray diffraction analysis of the powder indicated that it was nearly pure $LiFe_5O_8$. The porous disks were prepared by milling a powder, previously synthesized by a sol-gel process, pressing the powder into a compact, and then sintering the compact in an air atmosphere. Six identical disks were fabricated in this manner.

Mercury intrusion porosimetry was used to determine the pore size distribution of one of the disks. A mean pore size of $8.9 \mu m$ was indicated by the data. A plot of the cumulative pore volume in % versus pore diameter in μm , however, indicated that there are no pores smaller than about $1.8 \mu m$, as shown in Figure 13. Experience teaches that some submicron porosity is necessary for an MCFC electrode, whether anode or cathode, to deliver optimum performance. It is thought that the submicron cavities fill with electrolyte and provide a low resistance ionic pathway from the electrolyte matrix to the electroactive surfaces which are present in the larger open pores. An

Figure 13. CUMULATIVE PORE VOLUME VERSUS PORE SIZE FOR LITHIUM FERRATE (III) ANODE

electrode that has no submicron porosity, holds little electrolyte, and will not perform well despite the fact that its inner surfaces may be wet with electrolyte. Partial filling of the smaller pores is required for optimum performance.

The decision was made to use one of these disks in a laboratory-scale fuel cell test, in spite of the lack of submicron pores. The lithium ferrate (III) anode was matched with a porous nickel plaque having a mean pore size of 11.2 μm . This large mean pore size plaque was selected to prevent flooding of the cathode structure with electrolyte under operating conditions. Of course, as the cell is heated to operating temperature, the nickel in the cathode oxidizes and the pores decrease in size, so the effective mean pore size in the fuel cell may be less than 8 μm .

A hot-pressed electrolyte tile 1.8 mm thick composed of 40% LiAlO_2 and 60% LiKCO_3 (62/38 mole ratio) was used as the electrolyte matrix. The cell was heated to operating temperature with fuel and oxidant gases passing through the cell. The oxidant used was 30% carbon dioxide in air and the fuel used had a composition of 36% hydrogen, 32% water vapor, 20% carbon dioxide, and 12% carbon monoxide. The nominal open circuit voltage (OCV) expected for this fuel and oxidant combination is about 1.0 volts. However, the measured OCV for this cell was only 970 mV at 650°C. The reason for the low OCV is not known. The OCV actually decreased during the next 150 hours of testing to a low value of 950 mV in the last hour before termination of the experiment. Measurement of the anode to reference and cathode to reference voltages indicated that the cathode was operating correctly and that the anode voltage was low. Post-test analysis of the electrolyte matrix gave no indication of a mechanical failure, such as a crack, which would have allowed fuel and oxidant gases to mix. Such cracks are the usual cause of low OCV, although in most cases the cathode suffers the greatest voltage change.

Attempts to load the cell and draw a current met with only limited success. Although a current was initially observed when a resistance load was placed across the cell, the cell voltage under load was not stable but slowly decayed at a rate of about 100 mV/min. Thus, a load of 10 mA/cm^2 caused an initial polarization of about 80 mV, that is, the cell voltage dropped from an OCV value of 950 mV to 870 mV when the load was first added. However, the cell voltage was not stable and slowly decreased to below 600 mV during the

next 3 minutes. This cell was operated for 150 hours but exhibited no substantial improvement in performance.

Post-test analysis of the anode indicated that it had been essentially dry during the test. In other words, it had not filled, partially or otherwise, with electrolyte. A more surprising result came from the X-ray diffraction (X-rd) analysis of the anode. The pre-test analysis by X-rd indicated nearly pure LiFe_5O_8 whereas the post-test analysis gave LiFeO_2 as a result. This change in composition can be represented by Equation 1.

Since lithium oxide is available via decomposition of the electrolyte

A summary reaction can be written as:

Therefore, it is not inconceivable that such a conversion could take place. The problems which arise as a consequence of this supposed change in composition are as follow. Substantial differences exist between the two forms of lithium ferrate (III). LiFeO_2 is red in color while the samples of LiFe_5O_8 prepared by IGT and sintered by CERAC are blue-black. The electronic conductivity of LiFe_5O_8 is superior to LiFeO_2 by at least one order of magnitude. The sintered disks of LiFe_5O_8 prepared by CERAC were blue-black and had good structural rigidity. The post-test anode still maintained the original blue-black color and did not appear to have structurally weakened during the experiment. The anode was recovered from the cell as a hard sintered disk that appeared unchanged. The fact that it was easily separated from the electrolyte matrix as a single piece was an additional indication that it had not filled with electrolyte.

However, since the X-rd analysis reported a change from LiFe_5O_8 to LiFeO_2 , electrolyte must have penetrated and wet the anode structure, even if partial filling did not occur. Otherwise, there could be no source of Li_2O for forming LiFeO_2 . Additional support for electrolyte wetting can be seen in the current produced under load. This is interpreted as evidence that the electrolyte penetrated and wet a portion of the anode and that the anode material is an active electrocatalyst for the oxidation of hydrogen.

A post-test chemical analysis was performed on the electrolyte matrix using atomic absorption spectrophotometry. Analysis indicated the presence of 0.07% chromium, 0.33% iron, and 0.23% nickel by weight in the matrix. The question arose as to the origin of the chromium in the matrix. The laboratory-scale fuel cells use ceramic hardware to make the wet seal with the electrolyte matrix and the only source of chromium in these cells is the 316-SS cathode current collector. If chromium was found in the electrolyte, then it is possible that part of the iron in the electrolyte also came from the cathode side of the cell. It was decided that an X-ray fluorescence analysis of the electrolyte matrix where it interfaced with the anode would be of value in interpreting the chemical analysis. A portion of the electrolyte matrix was scraped clean of all materials at the anode/matrix interface and an X-ray fluorescence analysis was performed on this isolated area. The results indicated major peaks for potassium and aluminum, as expected. Minor peaks were recorded for iron, nickel, and chromium and trace amounts of copper, calcium, and chlorine. It should be remembered that elements with atomic numbers less than 13 cannot be detected by X-ray fluorescence. This includes lithium, carbon, and oxygen. The presence of minor amounts of chromium at the anode/matrix interface suggests that partially soluble transition metal components such as iron and chromium can spread throughout the electrolyte matrix and that the cathode current collector represents a possible source for some of the iron detected in the matrix. There is nothing unusual about this result. Virtually all fuel cells employing nickel cathodes and stainless steel current collectors show varying amounts of iron, nickel, and chromium in the post-test analysis of their electrolyte matrices. The analysis of this cell is out of the ordinary only in that the iron levels are an order of magnitude higher than those found in cells incorporating nickel-10% chromium anodes. This fact is being interpreted at the present time as indicating that a substantial portion of the iron found in this cell matrix is coming from the lithium ferrate (III) anode.

The conclusions drawn from this cell test suggest that lithium ferrate (III) is still a viable candidate as an alternative anode. Further experimentation is warranted using test anodes which have some submicron porosity.

Task 5. Water-Gas-Shift Reaction and Methane Reforming Catalyst Development

This section is reproduced from the January technical report. Although work is proceeding on this task, no technical results are available yet describing the outcome of the latest experimental series.

During the month of January, experimental evaluation of United Catalyst's G3B and Shell 538 catalysts for promoting the reverse water-gas-shift reaction was continued. All the tests were performed with a gas having the same nominal composition with the exception that the gas used for the G3B catalyst tests was spiked with 100 ppm of H_2S . The nominal experimental conditions were as follows:

Inlet Gas:	25% H_2 , 20% CO_2 , 55% H_2O
Space Velocity, hr^{-1}	5000
Temperature, $^{\circ}\text{C}$:	600, 650, 700
Pressure:	Atmospheric

The results of the tests are presented in Table 10. Figure 14 is a comparison of the experimental product ratio ($[\text{CO}][\text{H}_2]/([\text{CO}_2](\text{H}_2))$), and the equilibrium constant for the reverse shift reaction. The results from previous tests made with G3B using a clean gas feed are also included for comparison purposes. These results show that equilibrium conversion is essentially achieved with the G3B in both the clean gas and sulfur spiked gas tests.

The performance of the Shell catalyst resulted in CO_2 conversions that were substantially below equilibrium. Part of this poor performance may be attributed to the high space velocity of 5000 hr^{-1} used in the tests. These tests will be run at a nominal space velocity of 3000 hr^{-1} so that a fair evaluation of the catalyst can be made. It should be pointed out that the G3B tests were also made at the higher space velocity but this did not effect the extent of conversion of the catalyst as indicated by the achievement of equilibrium.

Table 10.
REVERSE WATER-GAS-SHIFT REACTION CATALYSIS STUDY

Catalyst	G3B	G3B	G3B	Shell 538
Feed Gas, l/hr	30.42	42.64	30.96	33.66
Feed H ₂ O, g/hr	31.92	25.44	29.52	30.90
H ₂ O/C Ratio	--	--	--	--
Feed Composition, mol %				
CO ₂	18.41	24.32	21.67	19.21
CO	--	--	--	--
H ₂	24.95	26.21	23.86	27.22
CH ₄	--	--	--	--
C ₂ H ₆	--	0.21	0.20	0.24
H ₂ O	56.64	49.26	54.27	53.33
H ₂ S	100 ppm	100 ppm	100 ppm	--
Total	100.00	100.00	100.00	100.00
Avg. Reactor Temperature, °C	603	656	704	591
Reactor Pressure, psig	<2	<2	<2	<2
Avg. Product Gas, l/hr	28.50	30.12	27.84	32.70
Product H ₂ O, g/hr	33.99	28.14	32.10	30.90
Product Composition, mol %				
CO ₂	17.64	19.22	16.85	18.79
CO	3.40	4.55	4.16	0.30
H ₂	26.22	21.70	19.44	26.08
CH ₄	0.60	0.62	0.49	0.55
C ₂ H ₆	0.22	0.18	0.18	0.23
H ₂ O	51.87	53.73	58.88	54.05
H ₂ S	50 ppm	22 ppm	12 ppm	--
Total	100.00	100.00	100.00	100.00
CO ₂ Conversion, %	19.1	19.8	22.01	3.50
Space Velocity, hr ⁻¹	4764	4367	4598	4898

Table 10. (CONTINUED)
REVERSE WATER-GAS-SHIFT REACTION CATALYSIS STUDY

Catalyst	Shell 538	Shell 538
Feed Gas, L/hr	34.62	35.22
Feed H ₂ O, g/hr	27.24	31.74
H ₂ O/C Ratio	--	--
Feed Composition, mol %		
CO ₂	20.79	19.90
CO	--	--
H ₂	29.49	27.00
CH ₄	--	--
C ₂ H ₆	0.26	0.22
H ₂ O	49.46	52.88
H ₂ S	--	--
Total	100.00	100.00
Avg. Reactor Temperature, °C	644	692
Reactor Pressure, psig	<2	<2
Avg. Product Gas, L/hr	33.84	34.44
Product H ₂ O, g/hr	30.06	31.74
Product Composition, mol %		
CO ₂	18.94	18.32
CO	0.58	1.15
H ₂	27.20	26.32
CH ₄	0.54	0.55
C ₂ H ₆	0.24	0.24
H ₂ O	52.00	53.42
H ₂ S	--	--
Total	100.00	100.00
CO ₂ Conversion, %	4.34	8.87
Space Velocity, hr ⁻¹	4654	5075

Figure 14. PRODUCT RATIO VERSUS TEMPERATURE

WORK FOR NEXT QUARTER

Work during the next quarter will concentrate on studying the properties of the lithium ferrate (III) material. Included will be continuing work addressing improving the performance of anodes constructed from this material. The catalytic properties of this material will also be surveyed to determine if it is active for the shift reaction.

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