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EFFECTS OF H₂S ON MOLTEN CARBONATE FUEL CELLS

Topical Report

**By
Robert J. Remick
G. L. Anderson**

April 1984

Work Performed Under Contract No.: DE-AC21-83MC20212

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Institute of Gas Technology
Chicago, Illinois**

**Technical Information Center
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FOREWORD

This report summarizes work conducted as part of a multi-phase program being conducted by the Institute of Gas Technology (IGT) for the U. S. Department of Energy (DOE). Work was accomplished under the direction of Robert J. Remick. Mr. Frank Gmeindl of the Morgantown Energy Technology Center is the Contracting Officer's Technical Representative.

SUMMARY

This report summarizes the results of a literature survey conducted by the Institute of Gas Technology (IGT) under Phase I of a multi-phase program to investigate and identify the mechanism(s) responsible for molten carbonate fuel cell (MCFC) performance losses when operating on sulfur-containing gases. The objective of this literature survey was twofold: 1) to review the reported data on the interaction of H_2S with nickel-containing materials, and 2) to review reported investigations on the specific effects of H_2S on the electrochemical oxidation of H_2 in MCFC. The ultimate goal of this literature review is to determine the poisoning mechanism.

Because the anode used in the MCFC is predominately nickel and H_2S is known to poison the activity of many nickel-containing catalysts at low concentrations (<10 ppm), a review of the accumulated knowledge on the interaction of H_2S with nickel-containing materials was considered important. The literature survey on the interaction of H_2S with nickel-containing materials revealed that: 1) the adsorption of H_2S on the surface of nickel-containing materials is dissociative; 2) when the surface coverage by H_2S becomes appreciable, H_2 is liberated from the surface and replaced by additional H_2S ; 3) the degree of surface coverage by H_2S is primarily dependent on the H_2S/H_2 ratio of the gas and the temperature, yet supports and alloying materials can significantly affect the degree of surface coverage; 4) at $650^\circ C$, the literature data suggests that surface coverage by sulfur can exceed 50% with fuel gases with an H_2S/H_2 ratio as low as 1×10^{-9} , assuming negligible competition for nickel surface sites by other fuel gases such as CO , CO_2 , and H_2O and the molten carbonate electrolyte; 5) however, the data also suggests that saturation of the surface coverage by sulfur does not occur at $650^\circ C$ until the H_2S/H_2 ratio of the fuel gas exceeds 1×10^{-4} .

A review of available data on the specific effects of H_2S on the electrochemical oxidation of H_2 in an MCFC suggests that H_2S does not completely poison the H_2 oxidation reaction. The presence of H_2S does, however, affect the voltage-current relationship of the cell significantly. The most notable effect of the presence of H_2S is a decrease in the limiting current of the cell as the P_{H_2S}/P_{H_2} ratio of the fuel gas increases.

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INTRODUCTION

The effect of H_2S on molten carbonate fuel cell performance has been the subject of numerous investigations since 1976. The original justification for this work was the Energy Conversion Alternatives Study (ECAS) commissioned in 1976 by the National Aeronautics and Space Administration (NASA) in cooperation with the Energy Research and Development Administration (ERDA), the National Science Foundation (NSF) and the Office of Management and Budget.¹

In the ECAS, the concept of integrating a molten carbonate fuel cell with a coal gasifier to produce electrical power was considered in detail for perhaps the first time. The study concluded that this combination of technology offered an attractive alternative to conventional coal-fired power plants. The integrated coal gasification/molten carbonate fuel cell had the potential to provide energy conversion efficiencies (i.e., the percentage of the chemical energy content of the coal converted to electrical energy) of slightly less than 50% at a capital investment of about \$590/KW in mid-1975 dollars. Furthermore, the technology was significantly cleaner than conventional coal-fired power plants with stack gas scrubbing.

The assumptions made in the ECAS were 1) that the molten carbonate fuel cell would have a service life of 40,000 hours, 2) the fuel cell would be able to provide 0.85v per cell at 150 amperes per square foot and 85% fuel conversion, and 3) the fuel cell would be able to tolerate 200 parts per million by volume (ppm/v) of H_2S . The final assumption was based on thermodynamic data that suggested that this H_2S level was sufficiently low to preclude conversion of the anode in the fuel cell to an unreactive sulfide.

As the ECAS was being concluded, ERDA and the Electric Power Research Institute initiated technical efforts to verify the assumptions of the study. These early studies were conducted at United Technologies Corporation (UTC) and the Institute of Gas Technology (IGT). From these studies it was quickly realized that the molten carbonate fuel cell could not operate at the desired current flux, voltage, and fuel gas utilization with fuel gases containing 200 ppm/v of H_2S .

Because very stringent fuel gas purity requirements could have a significant impact on the economics of the integrated coal gasification/molten

carbonate fuel cell power plant concept, laboratory- and bench-scale investigations on the effect of H_2S on fuel cell performance have continued.

Whereas the early work sought simply to verify the assumptions of ECAS, the recent investigations sought not only to quantify the effects of H_2S on fuel cell performance, but also to determine the mechanism for fuel cell performance loss.

The only consensus that has arisen from these recent investigations is that H_2S levels as low as 1 ppm/v have a negative effect on cell performance. Voltage losses of tens of millivolts have been observed in various laboratory- and bench-scale fuel cells when using fuel gases containing between 1 and 10 ppm of H_2S . However, the mechanism for the performance loss is still the subject of debate and proposed specifications for the H_2S content of fuel gases used in the molten carbonate fuel cells range from as little as 20 parts per billion by volume (ppb/v) to more than 1 part-per-million by volume (ppm/v).

The overall objective of this program is to develop a predictive model of the effects of H_2S in the MCFC performance. This is to be accomplished through a review of previously published information and additional experimental investigations. With this improved understanding on the effects of sulfur-containing gases on MCFC performance, it is expected that the large range that presently exists, regarding fuel-gas purity requirements, can be narrowed and more definitive plant design studies be undertaken.

BACKGROUND

The Molten Carbonate Fuel Cell

The molten carbonate fuel cell is an electrochemical device that converts the chemical energy of fuel gases into electrical energy. The operating temperature of a molten carbonate fuel cell is between 550° and 700°C. The basic concept of the molten carbonate fuel cell is shown schematically in Figure 1. Fuel gas containing H₂, CO, small amounts of CH₄ and diluents such as CO₂, H₂O, and N₂ are fed to the anode of the fuel cell. At the anode several reactions occur. First, the H₂ contained in the fuel gas is electrochemically converted to H₂O and CO₂ with the generation of electricity. The overall reaction is —

Simultaneously, the water-gas shift reaction utilizes CO contained in the fuel gas to create more H₂; the reaction is —

Finally, methane, if it exists in the fuel gas, may be reformed by steam, to additional H₂ by the overall reaction —

As a result of these simultaneous reactions, the molten carbonate fuel cell is able to convert more of the chemical energy content of the fuel gas into electrical energy than other fuel cells.

The electrical circuit of the molten carbonate fuel cell is completed by feeding oxygen or air and CO₂ to the cathode of the cell. At the cathode, the CO₂ and O₂ combine electrochemically with the returning electrons to produce the carbonate ion consumed at the anode. The overall reaction is —

Materials of Construction

The anode developed for use in the molten carbonate fuel cell is made from porous, reduced nickel with added chromium to reduce sintering at the elevated operating temperatures. The amount of added chromium, however, differs amongst the various developers. The percentage of chromium ranges from as little as 2 wt % to as much as 10 wt %.

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Figure 1. SCHEMATIC OF MOLTEN CARBONATE FUEL CELL

The cathode developed for the molten carbonate fuel cell is also porous, reduced nickel but without chromium. The porous nickel cathode undergoes in situ oxidation to porous NiO which is a ceramic like material that does not sinter at fuel cell operating temperatures.

A eutectic mixture of lithium and potassium carbonates having a composition of 62 mole percent lithium carbonate and 38 mol % potassium carbonate is used almost exclusively as the electrolyte in molten carbonate fuel cells. Although the melting point of this eutectic is 498°C, long term compositional changes brought about by preferential vaporization of one of the components may increase the melting point of the electrolyte. The electrolyte is held between the electrodes of the fuel cell by a ceramic support matrix. Presently, alkali aluminates such as LiAlO_2 are used as the ceramic components.

The Proposed Effects of H_2S on Molten Carbonate Fuel Cell Performance

While the effect of H_2S on molten carbonate fuel cell performance has been the subject of numerous investigations, the results of these investigations have produced only one general consensus — that H_2S has a negative impact on fuel cell performance. The degree of performance loss, the mechanism for the performance loss, and the level to which H_2S must be reduced in the fuel gas so that the molten carbonate fuel cell performance is economically viable remain subjects of debate.

Of the many mechanisms that have been proposed for the observed cell performance loss, the poisoning of the electrochemical hydrogen oxidation reaction by H_2S was, perhaps, the first. It has been known for some time that nickel-based catalysts such as those used for the catalytic conversion of H_2 and CO to methane or for the steam reforming of methane are quite susceptible to poisoning by very small concentrations of H_2S . Poisoning of these catalysts occurs at H_2S levels many orders of magnitude below that required for conversion of nickel into nickel sulfide. The apparent cause of the poisoning is due to the strong adsorption of H_2S on the catalytically active sites. It was reasoned that the same phenomena occurred in the molten carbonate fuel cell.

Another mechanism that has been proposed for fuel cell performance loss is that H_2S changes the electrolyte composition which either changes the wetting characteristics of the melt and reduces the coverage of the electrodes by the electrolyte or reduces the carbonate content to such an extent that the

electron transfer process is hindered. Two possible reactions of the H_2S with the electrolyte have been proposed. In one reaction, H_2S simply reacts with the alkali carbonate to form an alkali sulfide by the reaction —

In the second reaction, H_2S and H_2O react with the alkali carbonate to form an alkali sulfate by the reaction —

The first reaction is expected to predominate at the entrance to the fuel cell where the H_2O and CO_2 content are the lowest. The second reaction is expected to predominate close to the exit of the fuel cell where the H_2O content of the fuel gas is a maximum. A combination of these two reactions is also possible, namely —

Another postulated cause for fuel cell performance loss by H_2S is poisoning of the water gas shift reaction. The mechanism for the poisoning the water gas shift reaction by H_2S is analogous to the mechanism for poisoning of the H_2S -oxidation reaction. The H_2S is strongly adsorbed by the anode material and the adsorbed H_2S blocks the catalytically active sites for the water-gas shift reaction. The reason that poisoning of the water-gas shift reaction can produce significant performance loss is that at high fuel gas conversion, the CO content of the gas must be converted into hydrogen. If the water-gas shift is poisoned, a hydrogen deficiency develops in the cell and the potential of the cell drops off rapidly.

Poisoning of the methane steam reforming reaction by the H_2S has also been postulated. While the effect of H_2S on this reaction has not been seriously investigated because the fuel gases most often considered for use have had very small concentrations of CH_4 , if this effect is operative, it could limit the degree of fuel gas consumption in the fuel cell and also restrict the compositions of fuel gases used in the molten carbonate fuel cell.

In summary, four effects of H_2S on molten carbonate fuel cells have been postulated. These include —

1. Poisoning of the electrochemical hydrogen oxidation reaction
2. Poisoning of the water gas shift reaction
3. Poisoning of the methane-steam reforming reaction
4. Reaction with the electrolyte melt to change its composition or wetting characteristics.

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LITERATURE REVIEW

In this report, we address only two of the issues regarding the effects of H_2S on molten carbonate fuel cell performance — 1) the interaction of H_2S with nickel-containing materials which underlies the hypothesis that H_2S poisons the H_2 -oxidation reaction, the water gas shift reaction, and methane steam-reforming reaction by adsorbing on active catalytic sites; and 2) specific evidence regarding the effect of H_2S on the H_2 -oxidation reaction. In subsequent reports, we will address the other postulated effects of H_2S on fuel cell performance loss, namely, changes in the molten electrolyte composition, poisoning of the water-gas shift reaction, and poisoning of the steam-reforming reaction.

The Interaction of H_2S With Nickel-Containing Materials

Fundamental studies on the interaction of H_2S with nickel-containing materials under conditions where bulk sulfidation of the nickel is not expected have been numerous. The reason for this interest is undoubtedly the fact that nickel-containing catalysts are quite susceptible to poisoning by H_2S and a better understanding of the cause of this poisoning could logically lead to the development of more sulfur resistant catalysts. Several review articles have been published on the subject (e.g., Bartholomew, *et al.*,² Bernard³). For the purpose of this review, only that literature which is considered particularly relevant to the subject of molten carbonate fuel cells will be discussed.

In 1961, Saleh and co-workers⁴ reported one of the earliest studies on the interaction of H_2S with nickel. In this study, small volumes of H_2S were injected into an evacuated glass adsorption vessel in which a thin nickel film had been deposited on the walls. The pressure in the vessel was monitored with respect to time after each addition of H_2S and the gas phase was analyzed semi-quantitatively by condensing H_2S in a cold finger immersed in liquid nitrogen.

The significance of this early study was that it showed, for perhaps the first time, that the adsorption of H_2S on nickel is strong and dissociative. At $-80^\circ C$, it was observed that upon addition of H_2S to the system, the uptake of H_2S by the film was very rapid and nearly quantitative with the system pressure quickly falling to about 10^{-5} mm Hg. Successive doses were similarly

adsorbed until the calculated amount of sulfur adsorbed by the nickel film approached $16 \times 10^{-9} \text{ g/cm}^2$. Upon addition of more H_2S at this level of surface coverage, the evolution of H_2 from the nickel surface was observed. The evolution of H_2 continued with further addition of H_2S until the sulfur content of the nickel surface was approximately $50 \times 10^{-9} \text{ g/cm}^2$ at which point the adsorption of H_2S ceased. A similar behavior was observed when the experiment was repeated at 0°C . After the amount of sulfur adsorbed on the nickel film reached about $16 \times 10^{-9} \text{ g/cm}^2$, the evolution of H_2 was observed. However, in contrast to the work at -80°C , the evolution of H_2 and the adsorption of H_2S did not cease at 0°C until the sulfur content on the nickel surface was more than $60 \times 10^{-9} \text{ g/cm}^2$.

Saleh and co-workers estimated the hydrogen-to-sulfur atom ratio on the nickel surface as a function of coverage based on the analysis of the gas phase. While the precision of these results are not known, it is seen in Figure 2 that the ending H/S ratio on the nickel film significantly decreases with an increase in temperature. At -80°C , the ending H/S ratio on the surface was about 1.25:1. However, at 0°C , the ending ratio was only 0.6:1. This decrease in the H/S ratio on the nickel surface at saturation with an increase in temperature was attributed to the fact that the chemisorbed sulfur is held more strongly than the hydrogen atoms and at higher temperatures the hydrogen atoms are able to move more easily on the surface and recombine to liberate H_2 . As a result, the sulfur was able to displace more hydrogen atoms on the surface at the higher temperature.

Saleh and co-workers also performed a series of experiments in which the nickel film was presaturated with hydrogen at -80°C and then displaced by hydrogen sulfide. Saleh and co-workers concluded from this data, which is shown in Table 1, that one molecule of hydrogen sulfide occupies the same amount of surface as 3 to 3.5 atoms of hydrogen. If one assumes that the hydrogen sulfide is dissociatively adsorbed under these conditions, these results would suggest that one atom of adsorbed sulfur occupies about the same surface area as 1 to 1.5 atoms of hydrogen.

*Nickel surface area estimated
from krypton adsorption data

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Figure 2. H/S RATIO ON NICKEL SURFACE VERSUS COVERAGE AT -80°C

Table 1. DISPLACEMENT AT -80°C BY HYDROGEN SULFIDE OF HYDROGEN
FROM NICKEL FILMS SATURATED WITH HYDROGEN AT 10^{-2}mm Hg

$\frac{\text{H}_2\text{S Adsorbed}}{(\text{mL} \times 10^3)}$	$\frac{\text{H}_2\text{Desorbed}}{(\text{mL} \times 10^3)}$	$\frac{\text{H Atoms Desorbed}}{(\text{H}_2\text{S Adsorbed})}$
21.3	36.7	3.44
14.4	20.7	2.88
19.0	28.4	2.98

At about the same time that Saleh and co-workers were investigating the interaction of H_2S with nickel films, Den Besten and Selwood were initiating studies on the interaction of H_2S with a nickel-Kieselguhr catalyst containing 52.8% Ni.⁵ The catalyst was contained in an evacuated vessel and subjected to successive amounts of H_2S at 25°C . Equilibrium system pressure and catalyst magnetization were measured after each addition. The experiment was terminated after the total system pressure exceeded atmospheric pressure. At the conclusion of the test, the gas space was analyzed by evacuation through a Topley pump to a mass spectrometer.

Den Besten and Selwood found that the gas space at the conclusion of each test was H_2 with no measurable amounts of H_2S . They also found that the slope of the change in catalyst magnetization with the adsorption of H_2S was double that measured during the adsorption of H_2 . Den Besten and Selwood concluded from this data that the adsorption of H_2S on nickel at low surface coverage involved four nickel atoms. The two hydrogen atoms contained in the H_2S occupied two separate nickel adsorption sites and the sulfur atom occupied two adjacent nickel adsorption sites, or —

At high surface coverages, however, the H_2S competed with the hydrogen atoms on the surface resulting in desorption of the additional H_2 .

In subsequent experiments, Den Besten and Selwood attempted to confirm their hypothesis. In one set of experiments, Den Besten and Selwood heated the catalyst to a temperature of about 400°C under a vacuum in an attempt to recover the chemisorbed hydrogen. They found that at low surface coverage, nearly all of the hydrogen could be recovered. However, at high surface coverage less than two-thirds of the hydrogen could be recovered by this

procedure. Similar results were obtained when they tried to exchange the hydrogen on the surface with deuterium.

These results were explained by the following mechanism. At low surface coverage and high temperature, the hydrogen atoms are free to migrate on the surface and can recombine with the evolution of H_2 . However, at high surface coverages, the sulfur atoms greatly restrict the mobility of the hydrogen atoms. Furthermore, unless hydrogen atoms are on adjacent sites they will neither desorb nor exchange with deuterium. Therefore, at high surface coverage, the ability to recover chemisorbed hydrogen is restricted.

The experimental results of Den Besten and Selwood also suggested that the adsorption of sulfur atoms on nickel was very strong. The catalyst, although heated to as high as 400°C , demonstrated no willingness to desorb the sulfur atoms contained on the surface.

In 1968, Rostrup-Nielsen studied the effect of H_2S/H_2 ratio on the sulfur uptake of nickel-containing catalysts at temperatures ranging from 550°C to 645°C .⁶ In these experiments of Rostrup-Nielsen, a sample of a nickel-containing catalyst was placed in a tubular reactor and reduced at 850°C for one hour with dry hydrogen. Hydrogen containing between 0.1 ppm/v and 30 ppm/v H_2S was then passed through the bed of catalyst until the amount of H_2S admitted to the reactor was at least two times the amount expected to be required to saturate the catalyst. After the test, the sulfur content of the catalyst was determined by driving off H_2S with hydroiodic acid and collecting the H_2S .

The significance of Rostrup-Nielsen's experiments was that they showed that the amount of sulfur adsorbed nickel is controlled by the H_2S/H_2 ratio of the gas. Results of the tests conducted by Rostrup-Nielsen are shown in Figure 3. While a significant amount of scatter exists in the data, the figure clearly shows that the sulfur uptake by the nickel-containing catalyst increases with an increase in the H_2S/H_2 ratio of the gas. Furthermore, a saturation layer apparently develops on the nickel-containing catalysts at these temperatures at a H_2S/H_2 ratio of between 2 to 5×10^{-6} with approximately equal amounts of sulfur per unit area taken up at both temperatures.

Rostrup-Nielsen also correlated the extent of sulfur retained by the catalyst at saturation with the hydrogen chemisorption capacity of the catalyst. The results of sulfur and hydrogen capacity data for four different

Figure 3. SULFUR UPTAKE BY A NICKEL-MAGNESIUM ALUMINATE CATALYST
AT 550°C AND 645°C FROM REFERENCE 6. ESTIMATED LANGMUIR
ISOTHERMS ARE SHOWN

catalysts that Rostrup-Nielsen studied are shown in Figure 4. The slope of the line indicated that about 3 sulfur atoms were accommodated by the same surface as 4 hydrogen atoms. According to the general assumption that one hydrogen atom is chemisorbed per nickel atom on the surface, this correlation suggested that 0.74 atoms of sulfur are chemisorbed per surface nickel atom.

The conclusion of Rostrup-Nielsen that 0.74 atoms of sulfur are chemisorbed per nickel atom differs from the conclusion drawn by Den Besten and Selwood. Den Besten and Selwood concluded that only 0.25 atoms of sulfur were chemisorbed per each surface nickel atom. However, the experiments conducted by Den Besten and Selwood were performed at much lower temperatures than those of Rostrup-Nielsen.

In 1970, Pedereau and Oudar showed that the adsorption of hydrogen sulfide on nickel surfaces could be reversed.⁷ Earlier, Oudar had demonstrated that the sulfur adsorbed on copper by the adsorption of H_2S could be removed by placing the metal in a gas containing H_2 .⁸ In addition, he showed that the amount of sulfur adsorbed on the surface was controlled by the H_2S/H_2 ratio of the gas. At $830^\circ C$, the temperature at which Oudar worked, complete coverage of copper surface by sulfur was observed at H_2S/H_2 ratios greater than 10^{-4} . However, decreasing the H_2S/H_2 ratio to less than 10^{-5} resulted in desorption of sulfur and an equilibrium coverage of about 25%.

With the information gained from the experiments with copper, Pedereau and Oudar proceeded to investigate the adsorption of H_2S on both silver and nickel. The complete determination of the reversible adsorption of sulfur on nickel proved impossible, but at $900^\circ C$, Oudar and co-workers were able to detect the beginning of a reversible adsorption isotherm for the nickel/ H_2S/H_2 system when the H_2S/H_2 ratios fell to less than 10^{-4} .

While Pedereau and Oudar were not able to trace the reversible adsorption isotherm for H_2S on nickel to low surface coverages, they were able to measure the adsorption density of sulfur at apparent surface saturation on various crystal faces of nickel at $600^\circ C$. The results are shown in Table 2. For the Ni(111) and Ni(100) planes the number of sulfur atoms per surface nickel atom at saturation was about 0.5 in agreement with the data of Den Besten and Selwood. However, for the Ni(110) and Ni(210) planes the sulfur to nickel

Figure 4. CORRELATION BETWEEN SULFUR CAPACITY AND HYDROGEN CAPACITY OF SEVERAL REDUCED NICKEL CONTAINING CATALYSTS FROM REFERENCE 6

Table 2. SULFUR ADSORPTION DENSITIES ON VARIOUS CRYSTAL FACES OF NICKEL AT 600°C (ref. 7)

<u>Crystal Face</u>	<u>Sulfur Concentration at Saturation (gS/cm²)</u>	<u>Number of Ni Atoms/cm² (x10¹⁵)</u>	<u>S Atoms per Surface Ni Atoms</u>
(111)	$(47 \pm 1) \times 10^{-9}$	1.8	0.48
(100)	$(43 \pm 1) \times 10^{-9}$	1.6	0.50
(110)	$(44.5 \pm 1) \times 10^{-9}$	1.1	0.74
(210)	$(42 \pm 1) \times 10^{-9}$	0.72	1.09

atom ratio was measured to be 0.74 and 1.09, respectively. More interestingly, the measured sulfur concentration per square centimeter of surface area was apparently independent of the crystal plane at about 0.8×10^{15} atoms/cm².

Bartholomew and co-workers continued the investigation of the interaction of H₂S with nickel containing materials. In 1978, they published results of studies conducted with unsupported nickel, alumina-supported nickel, nickel-platinum, nickel-cobalt, and ruthenium.⁹ In contrast to the work conducted by Rostrup-Nielsen, Bartholomew and co-workers sought to study the desorption of sulfur from the presulfided catalyst using H₂ at 450°C. It was anticipated that this approach would provide more accurate data near the sulfur saturation point of the material than that of Rostrup-Nielsen.

In the study, identical samples of the materials were placed in a packed-bed reactor. The samples were then reduced in flowing hydrogen at 450°C. After reduction, a gas mixture containing 8, 12, or 30 ppm H₂S in H₂ was passed through the bed and the concentration of H₂S in the feed and product were measured with respect to time. When the H₂S concentrations of the entering and exiting streams were identical (usually after 16-24 h), it was assumed that the catalyst was in equilibrium with the entering gas stream. Pure hydrogen was then passed through the bed of material and the H₂S leaving the bed was collected and analyzed periodically so that an dilution curve of H₂S concentration versus time could be made. The concentration of H₂S in the exit stream was then related to the sulfur content of the material normalized to the hydrogen chemisorption capacity of the material

The results of studies with 3% Ni/Al₂O₃, nickel powder, Ni-Pt, Ni-Co, and Ru are shown in Figure 5. One of the most interesting features of the results is that for the two nickel-containing materials, 3% Ni/Al₂O₃, and nickel powder, the measured sulfur uptake by the material, when normalized to the uptake of hydrogen, are both greater than 1. In Rostrup-Nielsen's studies, which were conducted at higher temperatures, the ratio was only 0.74. Another important feature of the desorption results of Bartholomew and co-workers is that the slopes of the desorption isotherms are greater than zero at an H₂S concentration of 30 ppm. This suggests that the material is not totally saturated with sulfur at concentrations of less than 30 ppm in conflict with the data of Rostrup-Nielsen.

Figure 5. H_2S DESORPTION ISOTHERMS AT 450°C NORMALIZED TO H_2 UPTAKE: (♦) 3% Ni; (▽) Ni powder; (Δ) Ni-Pt; (□) Ni-Co; (○) Ru from Reference 9

To examine the discrepancy between their data and the data of Rostrup-Nielsen, Bartholomew and co-workers determined the equilibrium sulfur uptake of the 3% Ni/Al₂O₃ material at 450°C in a manner identical to that used by Rostrup-Nielsen. A sample of the material was exposed to a H₂S/H₂ mixture of a defined composition for a period of time and then the catalyst was analyzed for sulfur by reacting the sulfided material with hydroiodic acid, collecting the H₂S, and determining the amount collected colorimetrically.

The results of these equilibrium sulfur adsorption studies are plotted in Figure 6, along with the desorption isotherms for the 8, 12, and 30 ppm saturation experiments. At a H₂S/H₂ ratio below 10 ppm, where most of the studies of Rostrup-Nielsen were conducted, the sulfur uptake of the material normalized to the hydrogen uptake was less than 0.8 in good agreement with Rostrup-Nielsen's data. However, at higher ratios, the sulfur uptake of the material was larger and at a H₂S/H₂ ratio of about 25 ppm, the sulfur uptake relative to hydrogen uptake for the 3% Ni/Al₂O₃ material was 0.9. No explanation was offered by Bartholomew et al., as to why the sulfur uptake for the sample equilibrated at 8 ppm was higher than the sulfur uptake of the sample equilibrated at 12 ppm.

The data of Bartholomew, et al., shown in Figure 5 also have another significance. The nickel alloy catalysts, Ni-Pt and Ni-Co, show less capacity for H₂S adsorption when measured against the hydrogen chemisorption capacity of the material than either nickel- or nickel-alumina catalyst. Furthermore, the ruthenium catalyst adsorbed only 1/3 as much H₂S as H₂. One explanation may be that the alloying materials platinum, cobalt, and ruthenium which are able to chemisorb hydrogen have less affinity for sulfur than does nickel. Thus, in hydrogen chemisorption measurements all surface sites are available while in hydrogen sulfide adsorption measurements only the nickel sites are active.

In 1980, McCarty and Wise¹⁰ published results on the adsorption of H₂S on nickel-containing materials that greatly expanded the range of available information. McCarty and Wise investigated the equilibrium H₂S adsorption on nickel sponge and alumina-supported nickel at H₂S/H₂ ratios in the range of 1 ppb to 1 ppm and temperatures in the range of 150° and 650°C. The data of McCarty and Wise also showed that the composition of the nickel-containing

Figure 6. EFFECT OF HYDROGEN SULFIDE CONCENTRATION ON HYDROGEN SULFIDE ADSORPTION ON 3% Ni/Al₂O₃. (□) DESORPTION ISOTHERM DATA AFTER SATURATION AT 30 PPM; (○) AFTER SATURATION AT 12 PPM; (Δ) AFTER SATURATION AT 8 PPM; (▼) SINGLE EQUILIBRIUM ADSORPTION POINTS

material can significantly effect the sulfur coverage at a given P_{H_2S}/P_{H_2} ratio.

In the study by McCarty and Wise, a specially designed closed-loop gas-recirculation system was constructed for measuring the reversible sulfur chemisorption on various materials. The material under investigation was contained in an electrically heated quartz microreactor. Either hydrogen or an H_2S/H_2 mixture could be admitted to the reactor using teflon rotary valves and the gas contained in the system could be recirculated through the reactor using a teflon diaphragm pump.

To measure the equilibrium sulfur chemisorption on the materials, McCarty and Wise injected small volumes of an H_2S mixture into the reactor and recirculated the gas. Periodically, a sample of the recirculating gas was analyzed by gas chromatography. When no further change in the gas composition was evident, equilibrium was assumed to exist and the amount of sulfur adsorbed on the material was determined by a material balance.

Once a uniform sulfur coverage was attained, the temperature of the microreactor was raised or lowered and resulting equilibrium gas composition redetermined. Normally, this procedure did not appreciably effect the amount of sulfur adsorbed on the material under investigation and was a very convenient method of studying the reversible adsorption of H_2S .

Because the amount of sulfur adsorbed by the material was determined by a material balance, the use of quartz and teflon was necessary to avoid errors due to adsorption of H_2S on the materials of construction. A blank run performed with a 1 ppm H_2S in H_2 mixture indicated that less than 3% of the H_2S was adsorbed by the materials of construction at room temperature, suggesting that the results of the investigation were reasonably precise.

The sulfur chemisorption isosteres measured by McCarty and Wise for a 5% Ni/ α - Al_2O_3 catalyst are shown in Figure 7. In contrast to the studies of Rostrop-Nielsen and Bartholomew and co-workers, McCarty and Wise normalized their sulfur uptake data to the CO adsorption capacity of the material. On well defined nickel planes, CO adsorption studies¹¹ indicate a nearly constant saturation coverage regardless of crystal orientation of 11×10^{14} CO molecules/cm². The data of Pannell, et al.,¹² indicates that a typical H_2 saturation coverage on nickel surfaces is about 12.1×10^{14} H atoms/cm².

Figure 7. SULFUR CHEMISORPTION ISOTHERES ON $Ni/\alpha-Al_2O_3$
COVERAGE NORMALIZED TO CO UPTAKE AT
300 K FROM REFERENCE 10

Therefore, to convert the data of McCarty and Wise to a hydrogen adsorption basis a conversion factor of roughly 0.9 must be applied.

The data of McCarty and Wise show that even for very small concentrations of H_2S the surface coverage by sulfur is appreciable. As can be seen by the extrapolation of the 0.98 coverage isostere to $650^\circ C$ ($1000 K/T = 1.08$), the anticipated coverage by sulfur is less than unity at P_{H_2S}/P_{H_2} ratios of less than 4×10^{-6} . However, the magnitude by which the equilibrium sulfur coverage decreases with a decrease in P_{H_2S}/P_{H_2} is very slow.

Another significant observation from the investigations of McCarty and Wise is that the equilibrium sulfur coverage of nickel-containing materials can be dependent upon the support. The equilibrium P_{H_2S}/P_{H_2} ratio measured by McCarty and Wise for three different nickel-containing materials is shown in Figure 8. The equilibrium P_{H_2S}/P_{H_2} ratio for a 5% Ni/ γ - Al_2O_3 with a surface coverage of about 64% of the CO uptake of the material is slightly greater than that of nickel sponge at 50%, but the equilibrium ratio of both is approximately an order of magnitude higher than that for the 5% Ni/ α - Al_2O_3 with 75% coverage. If there were no support interaction, the curve for the 5% Ni/ α - Al_2O_3 should be above the curves for nickel sponge and Ni/ γ - Al_2O_3 . Bartholomew and co-workers observed a similar trend between nickel powder and a 3% Ni/ γ - Al_2O_3 . At high surface coverages, the equilibrium P_{H_2S}/P_{H_2} ratio for the 3% Ni/ γ - Al_2O_3 was about 5 times that for the nickel powder at equivalent S/Ni_g ratios. Unfortunately, there is a problem with the practice used by McCarty and Wise of normalizing data to CO adsorption capacity. Bartholomew and Pannell¹³ have shown that the CO adsorption stoichiometry on nickel varies from 0.5 to 3.0 molecules of CO per surface nickel atom while the hydrogen adsorption stoichiometry is clearly one hydrogen atom per nickel surface atom. The difference in the equilibrium surface coverage reported by McCarty and Wise for unsupported and supported nickel could be artificial due to differences in CO adsorption stoichiometry.

More recently, Bartholomew and Uken have also demonstrated that certain additives can greatly affect the sulfur uptake of a nickel-containing material.¹⁴ Bartholomew and Uken compared the H_2 and H_2S uptake of several metal boride catalysts, a Raney nickel catalyst and a 20% Ni/ γ - Al_2O_3 catalyst. The results are shown in Table 3. The H_2S uptake of the boride catalysts and the Raney nickel catalyst were an order of magnitude higher than the measured H_2

Figure 8. THERMODYNAMIC ACTIVITY OF SULFUR CHEMISORBED ON SUPPORTED NICKEL. (o) 5 wt % Ni/ γ -Al₂O₃, $\xi = 0.75$; 5 wt% Ni/ γ -Al₂O₃, $\xi = 0.64$; (Δ) Ni SPONGE, $\xi = 0.5$ WHERE ξ IS THE COVERAGE NORMALIZED TO CO UPTAKE

Table 3. COMPARISON OF H₂ AND SULFUR UPTAKE OF NICKEL POWDER, RANEY NICKEL, AND SEVERAL NICKEL-BORIDE CATALYSTS

Catalyst	H ₂ uptake ^a /μmol ⁻¹	S _O ^b /μmol g ⁻¹	S/M _S ^c
Ni (INCO)	5	6.2	0.62
Raney Ni	267	2150	4.02
Ni-B-102	103	2660	12.9
Ni-Ru-B-101	188	3745	9.96
201 Ni/Al ₂ O ₃	213	230	0.54
Ni-B-A-102	164	519	1.58
Ni-B-A-105	325	2699	4.15
Ni-Co-B-A-101	128	208	0.81
Ni-Ru-B-A-101	178	1022	2.87

^a Total H₂ uptake at 298K.^b Total Sulfur adsorption in a flowing stream of 91% H₂, 8% N₂, 1% CO, and 10 ppm H₂S at 525K and 130 kPa^c Atoms of sulfur adsorbed relative to total hydrogen atom uptake at 298K.

uptake. Bartholomew and Uken concluded that the increased sulfur uptake of the boride and Raney nickel catalysts were due to selective adsorption of the H_2S by boron and aluminum promoters. This conclusion is probably valid, since the experiments by Bartholomew and Uken were made with H_2/CO mixtures. Under these conditions the boron and aluminum remained in a reduced state and are able to react with H_2S .

Finally, Rostrup-Nielsen and co-workers recently expanded their previously reported investigation on the chemisorption of H_2S on a $Ni/MgAl_2O_4$ catalyst.¹⁵ In the recent investigation, they extended the temperature range down to $500^\circ C$ and up to $750^\circ C$ and extended the P_{H_2S}/P_{H_2} ratio from about 7 to 50×10^{-6} .

The H_2S uptake by the $Ni/MgAl_2O_4$ catalyst was determined in a manner different from their previous investigation. A single catalyst pellet was suspended on a thin platinum wire from one arm of an electronic microbalance. An H_2S/H_2 mixture was prepared by flowing H_2 through a cell containing an H_2S permeation tube and passed over the catalyst pellet. The flow of gas continued until the mass increase of the pellet ceased.

The results of these studies, which were conducted with a 13% $Ni/MgAl_2O_4$ catalyst are shown in Figure 9. In this figure, the surface coverage by sulfur has been normalized to the measured saturation coverage by sulfur at $500^\circ C$.

The significance of the recent investigation by Rostrup-Nielsen and co-workers is that the results differed significantly from their earlier work. In the previous investigation, Rostrup-Nielsen concluded that a P_{H_2S}/P_{H_2} ratio of between 2 and 5×10^{-6} resulted in complete coverage of the nickel-containing catalyst at a temperature of either $550^\circ C$ or $645^\circ C$. In the present investigation, the results indicate that at a temperature of $650^\circ C$ ($924K$) saturation of the surface by sulfur is not attained even at a P_{H_2S}/P_{H_2} ratio of 46×10^{-6} . Furthermore, it appears that at $650^\circ C$ saturation coverage comparable to that measured at $500^\circ C$ may not be attained until the P_{H_2S}/P_{H_2} value is much greater. However, the change in the fractional surface coverage in going from a P_{H_2S}/P_{H_2} ratio of 15×10^{-6} to a P_{H_2S}/P_{H_2} ratio of 46×10^{-6} is only 0.006 at $650^\circ C$.

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Figure 9. ISOBARS FOR SULFUR CHEMISORPTION ON
 $Ni/MgAl_2O_4$ CATALYST. Δ , CONTINUOUS
 MEASUREMENT AND O, INTERMITTENT
 MEASUREMENT OF H_2S IN
 THE EXIT GAS

While the results of the investigations cited above, provide a wealth of information on the adsorption of H_2S on nickel-containing materials in the presence of H_2 , very little is known about the possible influence of other gases such as CO , CO_2 , and H_2O on the adsorption of H_2S . Furthermore, no information is available on the possible influence of the molten carbonate electrolyte which generally coats a significant portion of the fuel cell anode.

Pannell, et al., have studied the influence that H_2S adsorption on unsupported nickel has on the subsequent chemisorption of CO .¹² Although their data suggest that preadsorption of H_2S significantly decreases the amount of CO that will chemisorb on the nickel, their studies were conducted at $-83^\circ C$ and $25^\circ C$. After treating the nickel with H_2 containing 5 ppm of H_2S for 6 hours at $25^\circ C$, the amount of CO chemisorbed by the nickel dropped from about $2.5 \mu \text{ moles/g}$ to about $1.7 \mu \text{ moles/g}$ at $-83^\circ C$ and from about $5.8 \mu \text{ moles/g}$ to about $3.5 \mu \text{ moles/g}$ at $25^\circ C$. However, insufficient data is presented to determine the amount of preadsorbed H_2S on the nickel samples. On the other hand, Gardner and Bartholomew¹⁶ have investigated the effects of sulfur poisoning on methanation catalyst at $300^\circ C$. They have determined that even on a completely sulfur poisoned catalyst the amount of CO adsorbed dissociatively is lowered by only 50%.

In 1971, Rostrup-Nielsen reported results of attempts to regenerate sulfur-poisoned nickel-containing catalysts with steam.¹⁷ Rostrup-Nielsen concluded from his studies that steam has no apparent influence on the H_2S adsorption equilibrium on nickel-containing catalysts. This conclusion was based on two series of tests. In one series, several samples of a nickel-containing catalyst were subjected to various hydrogen/steam/ H_2S mixtures. The amount of sulfur retained on the catalyst was determined by reaction of the adsorbed sulfur with hydriodic acid followed by quantification of the amount of H_2S liberated. In the second series of tests, the catalyst samples were first subjected to a hydrogen/steam mixture without H_2S for the same period of time as in the first series. The catalyst was then subjected to a H_2S/H_2 gas mixture to determine the sulfur capacity of the catalyst. In both series of the tests nearly identical sulfur uptakes by the catalyst were observed. The only significant observation made, other than the fact that steam did not influence the amount of H_2S adsorption, was that the amount of

catalyst sintering was aggravated by an increase in the H_2O/H_2 ratios of the gas.

Rostrup-Nielsen showed that steam could remove adsorbed sulfur from the surface of the nickel but only under conditions where the bulk nickel would transform to NiO. Typical conditions required were temperatures above $500^\circ C$ and H_2O/H_2 ratios exceeding 100.

Two obstacles prevent a quantitative assessment of the amount of H_2S expected to be adsorbed on the surface of a molten carbonate fuel cell anode. First, the different concentrations of chromium used in the anodes may alter the equilibrium sulfur adsorption and second, the molten carbonate electrolyte may also effect the amount of sulfur adsorption.

If the data of McCarty and Wise are combined with the recent data of Rostrup-Nielsen, however, a qualitative picture of the degree of nickel surface coverage by H_2S can be made. This combination of data is shown in Figure 10. As can be seen, at $650^\circ C$, the typical operating temperature of a molten carbonate fuel cell, the degree of surface coverage by H_2S that may be expected is appreciable. At a P_{H_2S}/P_{H_2} ratio of 0.01×10^{-6} , the degree of coverage by sulfur may be as high as 60% of saturation. Furthermore, at a P_{H_2S}/P_{H_2} ratio of 10×10^{-6} , the degree of coverage by sulfur may be as high about 92%. At $700^\circ C$, the degree of surface coverage by H_2S at each P_{H_2S}/P_{H_2} ratio is expected to be less than at $650^\circ C$. Similarly, at $600^\circ C$, the degree of surface coverage by H_2S at an equivalent P_{H_2S}/P_{H_2} ratio is expected to be greater than at $650^\circ C$. At a given partial pressure of H_2S , a $50^\circ C$ increase in temperature lowers the surface coverage by about 3 to 4%.

Conclusions

The literature data on the interaction of H_2S with nickel-containing materials suggest the following:

1. The adsorption of H_2S on the surfaces of nickel-containing materials, such as the fuel cell anode, is dissociative and very strong.
2. At temperatures above $600^\circ C$ and H_2S concentrations below 10 ppm, the adsorption is partially reversible.
3. The degree of surface coverage by sulfur will depend, to a large extent, on the H_2S/H_2 ratio of the fuel gas in contact with the anode and the temperature of operation.

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Figure 10. EFFECT OF TEMPERATURE AND P_{H_2S}/P_{H_2} ON SURFACE COVERAGE BY SULFUR.

4. At 650°C and H₂S concentrations below 10 ppm in pure hydrogen, 10 to 20% of the surface will not be covered by sulfur.
5. The degree of surface coverage by sulfur is not influenced by steam and is probably not influenced by the CO, although sulfur clearly influences the adsorption of CO and H₂ albeit less at 650°C than at room temperature.
6. Support or alloying material, when added to nickel can significantly effect the amount of H₂S surface adsorption.
7. The possible influence of molten carbonate on the degree of sulfur coverage is not known.

The Effect of H₂S on the Electrochemical H₂-Oxidation Reaction

One of the possible influences of H₂S adsorbed on the nickel anode of a molten carbonate fuel cell is poisoning of the electrochemical H₂-oxidation reaction —

As discussed in the previous section, the degree of anode surface coverage by H₂S at 650°C is expected to range from about 50% at a P_{H₂S}/P_{H₂} ratio of 1 x 10⁻⁹ to more than 90% at a P_{H₂S}/P_{H₂} ratio greater than 1 x 10⁻⁶.

The amount of data on the direct impact of H₂S on the electrochemical oxidation of H₂ in a molten carbonate fuel cell is very limited. Part of the reason is that most of the investigations on the influence of H₂S on molten carbonate fuel cell performance have been conducted at high fuel gas utilizations. Under these conditions, performance losses may be due not only to poisoning of the electrochemical reaction but also poisoning of the water-gas shift reaction which must proceed for high fuel gas utilization.

The limited data that is available, however, suggests that H₂S does not completely poison the electrochemical H₂ oxidation reaction in the fuel cell but does hinder the reaction. The major effect of H₂S on the electrochemical reaction appears to be a decrease in the limiting current of the fuel cell (i.e., the maximum current achievable from the cell). Data that support this claim can be found in the studies of Claar, et al.,¹⁸ Tang, et al.,¹⁹ Vogel and Smith,²⁰ and recent data from United Technologies Corporation.²⁰

In 1979, Claar, et al.,¹⁸ reported laboratory-scale studies conducted on numerous anode materials including nickel, cobalt, and a 50% nickel-50% cobalt, alloy. The objective of this study was to identify anode materials that are

more sulfur tolerant than nickel. Polarization curves for the various anodes were determined in a small laboratory apparatus with clean fuel gas and fuel gas containing 50 ppm H_2S . The anodes were immersed in a 62 mol % Li_2CO_3 - 38 mol % K_2CO_3 eutectic melt at 650°C and the fuel gases were bubbled through the molten carbonate. An 80% Au-20% Pd electrode was used as the cathode because of its high sulfur tolerance. The fuel gas had the composition of 34.1% N_2 , 22.4% H_2 , 17.7% CO , 11% CH_4 , and 5.6% H_2O .

The data from this study are relevant to the issue of poisoning of the electrochemical H_2 -oxidation reaction because the amount of fuel gas conversion was small (<10%). Consequently, the product fuel gas composition remained relatively unchanged from the feed gas composition and the possible influence of other factors such as poisoning of the water-gas shift reaction were minimal.

In Table 4, the measured current flux for the various anodes at 50 mV from the open circuit potential of the anode is shown for a clean low-Btu fuel gas and a low-Btu fuel gas containing 50 ppm H_2S . For the nickel electrode, the current flux with clean low-Btu fuel gas at 50 mV was 0.25 mA/cm^2 , while the current flux with the low-Btu fuel gas containing 50 ppm H_2S was 0.193 mA/cm^2 .

More definitive evidence that the presence of 50 ppm H_2S in the fuel gas did not poison the electrochemical H_2 -oxidation reaction over nickel is shown in Figure 11. Claar and co-workers determined the current flux for the nickel electrode with clean and contaminated low-Btu fuel gas at voltages ranging from 1030 mV to 1300 mV. They found that the change in current flux with a change in voltage was nearly identical for both fuel gases about the rest potential of the cell. However, at low voltages, the current flux with the nickel anode appeared to be reaching a limiting current condition sooner with the contaminated fuel gas containing 50 ppm H_2S . This is shown in Figure 11 in the upper right portion of the two curves.

In 1982, Vogel and Smith²⁰ reported results which also indicated that H_2S does not poison but severely hinders the electrochemical H_2 -oxidation reaction. Steady-state polarization curves were determined for a 0.1 cm diameter by 1.8 cm long Ni 201 wire at 650°C in a 62 mol % Li_2CO_3 -38 mol % K_2CO_3 melt, using a gas mixture containing 53.4% H_2 , 11.0% CO_2 , 10.3% CO , and 25.3% H_2O with H_2S added at concentrations ranging from <1 ppm to about 300 ppm.

Table 4. POTENTIOSTATIC EVALUATION OF ANODE MATERIALS USING LOW-Btu
FUEL GAS IN BINARY CARBONATE MELT AT 650°C

Composition (%)	Clean Fuel		Fuel with 50 ppm H ₂ S	
	Open Circuit Potential (mV)	Current, i, at 50 mV From Rest Potential (mA/cm ²)	Open Circuit Potential (mV)	Current, i, at 50 mV from Rest Potential (mA/cm ²)
Nickel-50; Cobalt-50	-1138	0.383	-1102	0.202
Mg ₀₀₅ La ₀₉₅ CrO	-1130	0.040	-1132	0.041
Nickel	-1154	0.250	-1141	0.193
Cobalt	-1158	0.304	-1163	0.304

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Figure 11. STEADY-STATE POLARIZATION CURVES FOR NICKEL
USING LOW-Btu FUEL WITH AND WITHOUT 50 PPM
H₂S ADDED (Li/K ELECTROLYTE, 650°)

The steady-state polarization curves for the nickel wire electrode were determined at various rotational speeds between 300 ppm and 2000 ppm. By extrapolating the results to infinite rotational speeds, the mass transfer and reaction limiting effects of the electrochemical reaction were separated. Figure 12 shows the steady-state current vs polarization curve for the H_2 oxidation reaction in the absence of H_2S .

In Figure 13, the current vs polarization for the H_2 -oxidation reaction for fuel gases containing P_{H_2S}/P_{H_2} ratios of between $<2.4 \times 10^{-6}$ to 86×10^{-6} is shown. The effects of the H_2S content of the fuel gas on the limiting current of the nickel wire electrode are clearly shown. At a P_{H_2S}/P_{H_2} ratio of $<2.4 \times 10^{-6}$, the limiting current was approximately 1.9 mA. At a P_{H_2S}/P_{H_2} ratio of 86×10^{-6} , the limiting current dropped to about 0.5 mA.

By extrapolating the current vs polarization data at various P_{H_2S}/P_{H_2} ratios to infinite rotational speeds, Vogel and Smith found a trend in the limiting current with P_{H_2S}/P_{H_2} ratio of the fuel gas. The correlation is shown in Figure 14. The interesting feature of the correlation is that for P_{H_2S}/P_{H_2} ratios greater than about 1×10^{-4} , the limiting current of the nickel anode is still greater than zero and remains unchanged with a further increase in P_{H_2S}/P_{H_2} . Vogel and Smith suggested that this behavior was due to the fact that at a P_{H_2S}/P_{H_2} ratio of more than 1×10^{-4} the nickel surface was saturated with sulfur and further increases in the P_{H_2S}/P_{H_2} had no further effect on the H_2 -oxidation reaction. The conclusion seems plausible in light of the data on sulfur coverage of nickel surfaces described in the previous section.

Figure 12. STEADY-STATE POLARIZATION CURVES FOR H_2 OXIDATION
IN THE ESSENTIAL ABSENCE OF SULFUR. ROTATING NI WIRE
ELECTRODE OF 0.56 cm^2 GEOMETRIC SURFACE AREA

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Figure 13. EFFECT OF H_2S ON H_2 OXIDATION REACTION USING A ROTATING WIRE ELECTRODE AT 1600 RPM

A83121626H

Figure 14. EFFECT OF H₂S ON THE H₂ OXIDATION REACTION
USING A NICKEL WIRE ELECTRODE.

Further evidence that H_2S hinders but does not poison the H_2 -oxidation reaction by changing the limiting current of the anode was published by Tang, et al., in 1981. In their studies, the effect of H_2S at concentrations between 1.2 and 10 ppm on 3-cm^2 laboratory-scale cells was determined. A low-Btu fuel gas having a composition of 21.7% H_2 , 7.7% H_2O , 15.5% CO , 10.8% CO_2 , 1.1% CH_4 , and 43.2% N_2 was used in most of the experiments; however, the degree of fuel gas conversion was less than 10%. Therefore, the possible contributions to performance loss by poisoning of the water-gas shift reaction are minimized.

The anode used by Tang, et al., was nickel with 10% by weight chromium. The cathode was nickel that was oxidized in-situ and the electrolyte melt was a lithium-potassium mixture with a lithium/potassium ratio of 1.63.

While most of the experiments were conducted at 650°C , some experiments were also performed at temperatures as high as 700°C . In addition, a few experiments were conducted with a low H_2 -containing gas having the composition 4% H_2 , 39.9% CO_2 , 4.7% CO , 17.6% H_2O , and balance N_2 .

In Figure 15, the effects of 10 ppm H_2S on the performance of a 3-cm^2 cell using the low-Btu fuel gas at 650°C are shown. The anode potential decreases with the 10 ppm H_2S containing fuel gas. In addition, the deviation of anode potential in the presence of H_2S with respect to the anode potential in the absence of H_2S increases significantly with an increase in current density.

Figure 16 shows the effects of 2.5 ppm H_2S on a 3-cm^2 cell at 650°C . The curvature of the potential vs current density is more clearly observable in these results. The same trends are shown in Figure 17, where the effects of 1.5, 3, and 6.5 ppm of H_2S on the anode potential are shown.

We have analyzed the results of Tang, et al., by reducing the measured performance by the expression:

$$i = \frac{\eta}{\alpha + \beta\eta} \quad (10)$$

where i is the cell current in ma, η is the difference between the open circuit potential, E° , and the operating potential, E in mv and α and β are constants that may depend on $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ and temperature. This equation is useful because the limiting current of the cell is simply $1/\beta$. Furthermore, α is the reaction resistance at low values of η .

Figure 15. THE EFFECTS ON IR-FREE ELECTRODE POLARIZATION OF 10 PPM H₂S IN LOW-Btu FUEL

Figure 16. THE EFFECTS ON IR-FREE ELECTRODE POLARIZATION OF 2.5 PPM H₂S IN LOW-Btu FUEL

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Figure 17. COMPARISON OF IR-FREE POLARIZATION CURVES ON CLEAN OR CONTAMINATED LOW-Btu FUEL (650°C) 3cm² CELL

The values of α and β deduced from the experimental data of Tang, et al., are shown in Table 5. Because the data was obtained with two different cells and at various times during the life of the cell, an attempt was made to normalize the values of α and β . The values of α and β were normalized by dividing by value of a β determined from the cell performance with clean fuels. This is considered appropriate because the anode undergoes self-decay during the course of the experiments due to sintering. As the anode sinters, the number of active electrochemical sites decreases and the value of α increases. Therefore, the value of α with clean gases is a useful measure of the number of active sites remaining on the anode.

The normalized values of α and β in Table 5 show an interesting trend. The value of β increases much more rapidly than the value of α with an increase in the H_2S concentration of the gas. An increase in the concentration of H_2S from 1.5 ppm to 10 ppm increases the value of α by about 500% whereas it increases the value of β by less than 200%. This indicates an increase in H_2S decreases the limiting current, $1/\beta$, of the cell to a larger extent than it increases the resistance, α , of the electrochemical reaction.

If we compare the ratio of the normalized limiting current, α^0/β , obtained by Tang, et al., with fuel gases containing 1.5 ppm H_2S ($P_{H_2S}/P_{H_2} = 6.9 \times 10^{-6}$) and 10 ppm H_2S ($P_{H_2S}/P_{H_2} = 46.08 \times 10^{-6}$) with the ratio of the anodic reaction limiting currents obtained by Vogel and Smith at identical P_{H_2S}/P_{H_2} ratios we find that the ratios are nearly identical. Vogel and Smith deduced from their rotating wire data the following empirical relationship between the anodic reaction limiting current and the P_{H_2S}/P_{H_2} ratio of the fuel gas —

$$i_{lim} \approx 1.6 + 24.4 \exp(-52,000 P_{H_2S}/P_{H_2}) \quad (11)$$

Using this equation the ratio of i_{lim} at $P_{H_2S}/P_{H_2} = 46.08 \times 10^{-6}$ is 4.765.

The value of the limiting current deduced from the data of Tang, et al., $P_{H_2S}/P_{H_2} = 6.912 \times 10^{-6}$ divided by the limiting current deduced from the data at $P_{H_2S}/P_{H_2} = 46.08 \times 10^{-6}$, normalized to the condition of the anode with clean gases is given by:

$$\frac{i_{lim} (P_{H_2S}/P_{H_2} = 6.912 \times 10^{-6})}{i_{lim} (P_{H_2S}/P_{H_2} = 46.08 \times 10^{-6})} = \frac{\alpha^0/\beta (1.5 \text{ ppm})}{\alpha^0/\beta (10 \text{ ppm})} = 4.624 \quad (12)$$

Table 5. ANALYSIS OF THE DATA OF TANG, et al.

<u>Cell</u>	<u>ppm H₂S</u>	<u>Constants From EQ.</u>		<u>Clean Fuel Gas α</u>	<u>Normalized Values of Constants</u>	
		<u>α</u>	<u>β</u>	<u>α°</u>	<u>α/α°</u>	<u>β/α°</u>
EPRI-20	1.5	0.135	0.00038	0.153	0.88	0.0024
EPRI-20	2.5	0.118	0.00048	0.100	1.18	0.0048
EPRI-20	3.0	0.153	0.00084	0.153	1.00	0.0055
EPRI-20	6.5	0.198	0.00096	0.153	1.29	0.0063
EPRI-18	10.0	0.186	0.00110	0.100	1.86	0.0110

The similarity in the results between the two sets of data is quite good, considering that one set was taken with a nonporous wire electrode and the other set was taken with a 3-cm² porous nickel anode with 10 wt % chromium. The similarity suggests that we may be able to develop an empirical model for predicting the effect of H₂S on the H₂-oxidation reaction in the fuel cell by correlating the values of α and β in equation (10) with the P_{H_2S}/P_{H_2} ratio of the fuel.

One of the most interesting set of results obtained by Tang, et al., is shown in Figure 18. Tang, et al., studied the effects of temperature on cell performance in the presence of H₂S. At 700°C, the fuel cell performance with a fuel gas containing 3 ppm H₂S was essentially the same performance with a fuel gas without any H₂S, and the similarity in performance was evident even at current densities as high as 160 mA/cm². This change in effect of H₂S with an increase in temperature cannot be attributed to a change in the surface coverage of the anode by sulfur. In the previous section, it was shown that at the same P_{H_2S}/P_{H_2} ratio an increase in temperature of 50°C will likely reduce the surface coverage by 3-4%. This suggests that the reaction resistance and the limiting current of the cell are strongly affected by temperature and that H₂S has much less effect on the H₂-oxidation reaction with an increase in temperature.

Two sets of data suggest that the partial pressure of H₂ in the fuel gas has an effect on the limiting current independent of the P_{H_2S}/P_{H_2} ratio of fuel. As mentioned previously, Tang, et al., conducted one set of experiments using a fuel gas containing only 4% H₂. The results of this set of experiments is shown in Figure 19. If we fit this data to the empirical equation, $i = n/(\alpha + \beta n)$, we find a value for α of 0.27101 and a value for β of 0.001753. The P_{H_2S}/P_{H_2} ratio in this set of experiments was 25×10^{-6} which is similar to that in the low-Btu fuel gas tests with 6.5 ppm H₂S. In those tests, the values of α and β deduced from the experiments were 0.198 and 0.00096, respectively.

Recently, data from United Technologies Corporation²¹ indicated the same cell performance behavior with a decrease in the partial pressure of H₂. In

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Figure 18. EFFECTS OF TEMPERATURE ON H₂S TOLERANCE
OF NICKEL-BASED ANODE, CELL EPRI-22

Figure 19. COMPARISON OF IR-FREE POLARIZATION CURVES
OF CELL EPRI-21 AT 650°C

their tests, a cell was run at small conversions with three different gas mixtures and P_{H_2S}/P_{H_2} ratios ranging from 1.2×10^{-6} to 24.5×10^{-6} . A summary of the data is shown in Table 6.

As with the data reported by Tang et. al., the UTC data indicates higher polarization losses for fuels with lower partial pressure of hydrogen at the same P_{H_2S}/P_{H_2} ratio.

Conclusions

Review of the experimental data on the effect of H_2S on the electrochemical H_2 -oxidation reaction in a molten carbonate fuel cell indicates that H_2S does not totally poison the H_2 -oxidation reaction but does dramatically effect the limiting current of the cell and to a lesser extent the reaction resistance of the cell. An increase in the P_{H_2S}/P_{H_2} ratio of a fuel gas containing about 20% H_2 from 7×10^{-6} to 46×10^{-6} decreases the limiting current of the cell by a factor of 5, while increasing the resistance by less than 200%. The literature also suggests that by increasing the operating temperature of the fuel cell by $50^\circ C$, the effect of H_2S is significantly reduced.

Another important effect on fuel cell performance that was discovered from this review but is not related to the effect of H_2S is that the partial pressure of H_2 in the fuel gas also appears to have an appreciable effect on the limiting current of the fuel cell and warrants further study.

Table 6. SUMMARY OF CELL PERFORMANCE AS FUNCTIONS OF
GAS COMPOSITION AND HYDROGEN SULFIDE LEVEL

Stack "A" Inlet Fuel: 33.9% H₂, 13.7% CO, 17.6% CO₂, 22.8% H₂O, 12% N₂
10% Util. at 100 ASF

<u>Inlet PPM H₂S</u>	<u>P° H₂S/P° H₂</u>	<u>Performance Loss</u>
0.77	2.3×10^{-6}	5 MV at 100 ASF
1.8	5.3×10^{-6}	15 ± 5 MV at 100 ASF
3.4	10.0×10^{-6}	50 ± 5 MV at 100 ASF
5.4	15.9×10^{-6}	110 ± 5 MV at 100 ASF
8.3	24.5×10^{-6}	No steady state; 52 MV in 25 hours

Stack "B" Inlet Fuel: 10.9% H₂, 6.1% CO, 41.3% CO₂, 37.5% H₂O, 4.2% N₂
10% Util. at 100 ASF

<u>Inlet PPM H₂S</u>	<u>P° H₂S/P° H₂</u>	<u>Performance Loss</u>
0.27	2.5×10^{-6}	4 MV at 100 ASF
0.61	5.6×10^{-6}	25 ± 5 MV at 100 ASF
0.8	7.8×10^{-6}	No steady state; > 140 MV in 6 hours
1.1	10.1×10^{-6}	No steady state; > 140 MV in 7 hours

Stack "B" Exit Fuel: 3.4% H₂, 2.2% CO, 51.0% CO₂, 40.5% H₂O, 2.9% N₂
10% Util. at 50 ASF

<u>Inlet PPM H₂S</u>	<u>P° H₂S/P° H₂</u>	<u>Performance Loss</u> [*]
0.16	4.7×10^{-6}	22 ± 2 MV at 50 ASF
0.37	10.9×10^{-6}	No steady state; > 140 MV in 20 hours
0.56	16.5×10^{-6}	No steady state; > 140 MV in 5 hours.

* Fuel does not contain sufficient hydrogen to sustain 100 ASF even in the absence of H₂S.

DISCUSSION OF RESULTS

The results of this literature review fall short of expectations and leave many questions unanswered, particularly with regard to H_2S adsorption on nickel in a MCFC environment. Most of the research has been performed under conditions far removed from those of a MCFC. Saleh and co-workers⁴ performed research under a partial vacuum at temperatures of $0^\circ C$ and $-80^\circ C$. Den Besten and Selwood⁵ investigated a prepoisoned catalyst at $400^\circ C$ using pure hydrogen in a partial vacuum. Pedereau and Oudar⁷ worked at temperatures well above $650^\circ C$ but used hydrogen atmospheres contaminated with H_2S having H_2S/H_2 ratios on the order of 10^{-4} or higher. Bartholomew and co-workers⁹ worked at atmospheric pressure and $450^\circ C$ using nickel samples prepoisoned with H_2S and then removed the adsorbed sulfur with pure hydrogen. McCarty and Wise¹⁰ worked in the appropriate temperature range, up to $650^\circ C$, but used pure hydrogen at atmospheric pressure which was contaminated with less than 1 ppm H_2S .

Of all the work reviewed, none was found which combined all of the MCFC conditions: 600° to $700^\circ C$, sintered nickel catalyst, H_2S/H_2 ratio of 10^{-4} to 10^{-6} hydrogen partial pressures of 4 to 40 mole percent and total system pressures of 1 to 10 atm. It is these last two parameters which are most significant to MCFC operation. Fuels fed to MCFC will contain about 40% hydrogen while fuel gases exiting the fuel cell anode compartment could contain as little as 4% hydrogen. Also, while most laboratory experiments with MCFC have been performed at atmospheric pressure, full scale production equipment will operate at 10 atmospheres. Therefore, it is of the utmost importance to know how the poisoning phenomenon varies with hydrogen partial pressure and total system pressure.

It appears to be a foregone conclusion in the current literature that H_2S adsorption on nickel is sensitive to hydrogen partial pressure only as it impacts upon the H_2S/H_2 ratio. Only one set of experimental data uncovered in the literature argues to the contrary and that data is compromised by the fact that the author ignores what could be the most significant aspects of the data. The data in question was presented by Rostrup-Nielsen in Reference 6. Table 7 is a compilation of the experimental conditions and results. Rostrup-Nielsen conducted 8 experiments at $550^\circ C$ and 7 experiments at $645^\circ C$ using pure hydrogen contaminated with varying amounts of H_2S . He then plotted the weight of sulfur adsorbed on the nickel versus the H_2S/H_2 ratio. He also conducted

Table 7. SULFUR UPTAKE BY A NICKEL-MAGNESIUM ALUMINATE
CATALYST AT 550°C AND 645°C

<u>mg of Sulfur per hour</u>	<u>Mole of H₂/hr</u>	<u>Mole of Argon/hr</u>	<u>H₂S/H₂ x 10⁶</u>	<u>H₂S/H₂ x 10⁶</u>
Isotherm at 550°C				
0.067	4.0	0	0.42	310
0.110	4.1	0	0.84	520
0.016	4.3	0	0.12	150
0.100	2.0	0	1.56	515
0.004	4.5	0	0.03	96
0.016	1.2	1.9	0.43	395
0.011	2.5	1.9	0.14	222
0.374	3.8	0	3.08	543
0.045	2.2	0	0.64	515
0.034	2.0	0	0.53	470
Isotherm at 645°C				
0.144	3.9	0	1.16	440
0.100	2.0	0.9	1.56	455
0.104	1.9	2.4	1.73	520
0.110	1.5	1.9	2.34	559
0.078	1.4	0	1.74	492
0.20	4.9	0	0.13	140
0.311	1.3	0	7.84	545
0.120	2.0	1.9	2.02	545
0.044	2.0	1.9	0.69	437
0.028	4.5	0	0.20	227
0.061	4.2	0	0.45	420
0.054	3.9	0	0.48	420

two experiments at 550°C and 5 experiments at 645°C in which substantial amounts of the inert gas argon, from 30 to 56 mole percent, was mixed with the hydrogen. Rostrup-Nielsen included these experiments in his plot of sulfur adsorbed versus H_2S/H_2 ratio assuming that the presence of argon had no effect on the amount of sulfur adsorbed. His raw data, however, argues for an inert gas effect or a dilution effect. For example, the weight of sulfur adsorbed at a H_2S/H_2 ratio of 1.74 ppm using pure hydrogen is 492 wt-ppm while the weight adsorbed at a H_2S/H_2 ratio of 1.13 ppm from a gas which is 56% argon and 44% hydrogen is 520 wt-ppm. In addition, after drawing isotherms (see Figure 3) which indicated a higher sulfur coverage at the lower temperature, 550°C, for H_2S/H_2 ratios less than those required for saturation the two highest sulfur coverages reported are for two argon containing samples at the higher temperature, 645°C. Unfortunately, the experimental procedure used included too many variables and too little data to allow an accurate determination of the experimental error. Thus it is not possible to determine, from this data, if the inert gas effect is real or simply an artifact resulting from coincidence.

The question of the sensitivity of the poisoning mechanism to the partial pressure of hydrogen is a critical issue in this program. This is best illustrated by the UTC data in Table 6. Contamination of fuel gases with H_2S at H_2S/H_2 ratios of 10×10^{-6} results in a 50 millivolt loss in performance at 100 ASF using a fuel gas containing 33.9% hydrogen, greater than 140 mv loss in performance at 100 ASF using a fuel gas containing 10.9% hydrogen, and more than 140 mv loss in performance at 50 ASF using a fuel with only 3.4% hydrogen. Conventional wisdom suggests that since all three fuel gases have the same H_2S/H_2 ratio than all three nickel anodes should be poisoned to the same degree. If this is true then the relationship between performance loss and hydrogen partial pressure at constant H_2S/H_2 ratio must be linked either chemically or electrochemically to the presence of the carbonate and must be more complex than would be expected from a simple adsorption model based of surface coverage. Therefore, before the development of a predictive model of the effects of H_2S on MCFC performance can be executed it is necessary to have an understanding of how changes in the partial pressure of hydrogen, the H_2S/H_2 ratio and the total system pressure affect this performance loss.

This understanding can best be achieved by elucidating the mechanism by which H_2S poisons the anode reaction. Failing that, a predictive model can be constructed empirically by measuring the actual performance loss experienced by bench-scale cells operated under the full range of conditions expected to be encountered in production equipment.

Experimental Program

The effect on MCFC performance of hydrogen sulfide contamination at ppm levels is being investigated in a series of test tube scale and bench-scale experiments. Phase I of this investigation is concentrating on the impact of H_2S upon the hydrogen oxidation reaction. Half cell experiments are underway using potentiometric and linear scan cyclic voltammetric techniques to identify adsorbed species, on a solid wire electrode, which may undergo oxidation/reduction reactions in the fuel gas/MCFC environment. Bench-scale 10 cm x 10 cm MCFC are being operated on fuel gases containing from 10 to 50 mole percent hydrogen and 0 to 5 ppm H_2S . These bench-scale cells are operated at fuel utilizations of 30% or less to eliminate the need to shift carbon monoxide to hydrogen to sustain operation.

Phase II work will address the impact of H_2S contaminants upon the shift reaction. Out-of-cell experiments will be conducted with nickel and nickel/chromium powders such as are used to fabricate MCFC electrodes. The impact of H_2S at 1 to 5 ppm levels upon the catalytic activity of these powders toward the shift reaction will be determined at 650°C. Bench-scale fuel cells will be operated on fuel mixtures representative of those coming from a coal gasifier. These gases will be contaminated with 1 to 5 ppm H_2S . These cells will be operated at fuel utilizations of 70% to 80% where shift reaction is required to sustain reaction, and the performance loss due to shift reaction poisoning will be investigated.

The results of these experimental investigations will be used to develop a predictive model of the effects of H_2S on MCFC performance.

REFERENCES

1. King, J.M., "Energy Conversion Alternatives Study — United Technologies Phase II Final Report." Report prepared for National Aeronautics and Space Administration Under NASA Lewis Research Center Contract NAS3-19586 (1976).
2. Bartholomew, C.H., Agrawal, P.K., and Katzer, J.R., "Sulfur Poisoning of Metals" Advances in Catalysis 31, 135-242 (1982.)
3. Benard, J., "The Chemical Adsorption of Sulfur on Metals: Thermodynamics and Structure," Catalysis Reviews, 3 (1), 93-109 (1969).
4. Saleh, J.MN., Kemball, C., and Roberts, M.W. "Interaction of Hydrogen Sulfide with Nickel, Tungsten and Silver Films," Trans. Faraday Soc., 57, 1771-1780 (1961).
5. Den Besten, I.E., and Selwood, P.W. "The Chemisorption of Hydrogen Sulfide, Methyl Sulfide and Cyclohexane on Supported Nickel Catalysts," J. Catal. 1, 93-102 (1962).
6. Rostrup-Nielsen, J.F., "Chemisorption of Hydrogen Sulfide on a Supported Nickel Catalyst," J. Catal. 11, 220-237 (1968).
7. Pedereau, M., and Oudar, J., Surf. Sci 20, 80 (1970).
8. Oudar, J., Compt. Rend., 249, 91 (1959).
9. Oliphant, J.L., Fowler, R.W., Pannell, R.B., and Bartholomew, C.H., "Chemisorption of Hydrogen Sulfide on Nickel and Ruthenium Catalysts I. Desorption Isotherms," J. Catal. 51, 229-242 (1978).
10. McCarty, J.G., and Wise, H., "Thermodynamics of Sulfur Chemisorption on Metals I. Alumina-Supported Nickel," J. Chem. Phys. 7 (12) 6332-6337 (1980).
11. Klier, K., Zettlemoyer, A.C., and Leidheiser, J., J. Chem Phys 52, 589 (1970).
12. Pannell, R.B., Chung, K.S., and Bartholomew, C.H., "The Stoichiometry and Poisoning by Sulfur of Hydrogen, Oxygen and Carbon Monoxide Chemisorption on Unsupported Nickel," J. Catal. 46, 340-347 (1977).
13. Bartholomew, C. H. and Pannell, R. B., "The Stoichiometry of Hydrogen and Carbon Monoxide Chemisorption on Alumina- and Silica-Supported Nickel," J. Catal., 65, 390 (1980).
14. Bartholomew, C.H. and Uken, A.H., "Metal Boride Catalysts in Methanation of Carbon Monoxide. III Sulfur Resistance of Nickel Boride Catalysts Compared to Nickel and Raney Nickel," Appl. Catalysis 4, 19-19 (1982).
15. Alstrup, I., Rostrup-Nielsen, J.R., and Ryen, S., "High Temperature Hydrogen Sulfide Chemisorption on Nickel Catalyst," Appl. Catal. 1, 303-314 (1981).

16. Gardner, D. C. and Bartholomew, C. H., "Gravimetric Study of Adsorbed Intermediates in Methanation of Carbon Monoxide." I&E.C. Fundamentals, 20, 229 (1981).
17. Rostrup-Nielsen, J.R., "Some Principles Relating to the Regeneration of Sulfur-Poisoned Nickel Catalyst," J. Catal. 21, 171-178 (1971.)
18. Claar, T.D., Marianowski, L.G., and Sammells, A.F., "Development of Sulfur-Tolerant Components for Second-Generation Molten Carbonate Fuel Cells," Interim report prepared for Electric Power Research Institute under Project 1085-2. Report No. EPRI EM-1114, July 1979.
19. Tank, T.E., Claar, T.D., and Marianowski, L.G., "Effects of Sulfur-Containing Gases on the Performance of Molten Carbonate Fuel Cells," Interim report prepared for Electric Power Research Institute under Project 1085-2. Report No. EPRI EM-1699, February 1981.
20. Vogel, W.M., and Smith, S.W., "The Effect of Sulfur on the Anodic H_2 (Ni) Electrode in Fused Li_2CO_3 - K_2CO_3 at $650^\circ C$," J. Electrochem. Soc. 129 (7), 1441-1445, (1982).
21. United Technologies Corporation, "Development of Molten Carbonate Fuel Cell Power Plant Technology," Quarterly Technical Progress Report No. 8 for Period July 1, 1981 to September 30, 1981. Prepared for Department of Energy Under Contract DE-AC01-79ET15440. Report No. DOE/ET/15440-8, February 1983.