

Georgia Tech Sponsored Research

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Project director	Winnick Jack
Research unit	Chem Engr
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E-19-46
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Annual Report to the National Science Foundation
on Grant No. CTS-9321968

December 31, 1994

Summary

A novel high temperature solid oxide fuel cell, with electrolytes based on ceria, which uses hydrogen sulfide as the fuel and air as the oxidant is in development. Removing H₂S with a fuel cell more effectively takes advantage of its high chemical potential as opposed to the more conventional method of oxidizing it in the Claus process which releases this energy as heat. Such a device can produce clean electrical energy and simultaneously convert a highly toxic gas into a safe raw material. Three different materials, each with a different ionic conduction mechanism, are being examined as the potential electrolyte.

With an oxide-conducting electrolyte two different reactions, neither of which is favored thermodynamically over the other one, can occur with H₂S. One produces sulfur and water and the other sulfur dioxide and water. The former reaction is more desirable, yielding a non-toxic end product. The oxide conductor samaria-doped ceria has been examined with significant success, giving better results (maximum power density of 5.05 mW/cm² at 686 °C) than seen previously with hydrogen sulfide as the fuel in a solid oxide fuel cell. Furthermore, a reliable fabrication process has been developed for this electrolyte, and this material is apparently stable in a hydrogen sulfide atmosphere. It will now be necessary to characterize the reaction kinetics of this system.

With a proton conducting electrolyte the possibility of producing SO₂ is eliminated since oxygen and sulfur are never in direct contact; instead, steam is emitted into the cathode effluent and elemental sulfur vapor into the anode. Improved results have been acquired with the proton conductor ytterbia-doped strontium cerate; however, the stability of this electrolyte in hydrogen

sulfide is a major concern and further improvements in the fabrication of this membrane need to be developed.

The other electrolyte composition being examined is samaria-doped barium cerate. This electrolyte is actually a mixed-ionic conductor, conducting both protons and oxide ions. This mixed conduction is temperature dependent with it being primarily proton conducting at lower temperatures ($T < 700\text{ }^{\circ}\text{C}$) which is the temperature range of interest here. This electrolyte has shown performance between those of the other two electrolytes. The stability of this electrolyte, though, is somewhat questionable at this time, and more refinement of the fabrication process needs to be made.

Background

The United States alone produces in excess of ten million tons of hydrogen sulfide each year. Most of it is formed as a byproduct from coal gasification/liquefaction and heavy oil desulfurization processes. Because this gas is a toxic pollutant it must be removed before this effluent stream from is released to the atmosphere. Typically this is accomplished by concentrating the H₂S in any of several scrubbing/regeneration schemes, which require a cooling of the process stream. Furthermore, because hydrogen sulfide has no large-scale commercial use, virtually all of it is converted to sulfur in the Claus process, which is an incomplete oxidation of hydrogen sulfide with air:



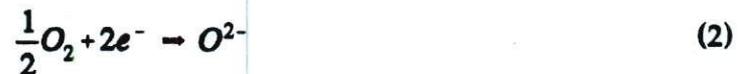
During this exothermic process a large amount of heat is released, much of which is captured in the form of steam. The energy associated with this reaction is over 36 kcal/g mol, and the fuel value of hydrogen sulfide is high, being near that of hydrogen, even when only partially oxidized as above. Removing this toxic gas by using it as the fuel in a fuel cell would utilize its high chemical potential much more effectively than simply oxidizing in the Claus process and would not require the cooling and reheating of the process gas stream. With such a setup this pollutant would be removed while producing a sellable byproduct, sulfur, and simultaneously generating electricity as opposed to heat. Use in this manner would result in a much more effective use of this fuel's energy because of the fuel cell's inherently high efficiency. Such a process would be very marketable.

The potential for using hydrogen sulfide as the fuel in a fuel cell has been known for quite some time; the problem has been the implementation. H₂S is detrimental to molten

carbonate and phosphoric acid fuel cells even in trace amounts [1]. However, with the recent success in the development of fuel cell systems utilizing a solid oxide electrolyte, the technology for this concept may be at hand. Westinghouse has successfully developed a complete, operating fuel cell unit of nominal 25 kW (40 kW max) capacity which is now being demonstrated at user sites [2].

There are two different ionic conduction mechanisms which can occur in the solid electrolytes depending on the ceramic oxide material used and the defect structures present. These are oxide conduction, in which oxide ions are transported through the electrolyte, and proton conduction, in which protons (hydrogen cations) are the conducted species. When using hydrogen sulfide as the fuel, the overall reaction which occurs and, hence, the products formed depend on the ionic conduction mechanism of the electrolyte.

In an oxide conducting electrolyte, the half-cell reaction which occurs at the cathode is:



The oxide ion produced is then transported through the electrolyte to the anode where it can react with H_2S in one of two ways, as shown below:

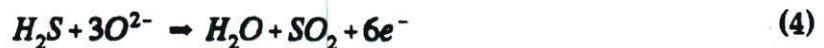


Figure 1A shows a schematic of the operation of this fuel cell. The former reaction is the desired one since no sulfur dioxide is produced; however, thermodynamics does not clearly favor one of the reactions over the other. At 800 °C the full cell potential of reactions 2 & 3 is

0.783 V while that of equations 2 & 4 is 0.750 V. The theoretical voltage for the two reaction schemes is similar enough that, when Nernstian effects are accounted for, discrimination between them is difficult. As a result, kinetics studies are underway in order to determine the extent of the reactions and what factors, if any, affect the resulting product distribution.

On the other hand, the reactions occurring with a proton-conducting electrolyte are much more straight forward. In this case hydrogen ions migrate across the electrolyte from the anode to the cathode. With such an arrangement the possibility of producing sulfur dioxide is eliminated since there is no opportunity for sulfur and oxygen to come into contact with one another. The anode and cathode half-cell reactions respectively are given below and also displayed in figure 1B.



State of the art solid oxide fuel cell systems use a yttria-stabilized zirconia electrolyte and typically operate at temperatures of 800-1000 °C. Recent developments, though, have shown that doped-ceria can also be used as an electrolyte material. The advantage of doped-ceria over stabilized-zirconia is that it has an inherently better ionic conductivity allowing for the operating temperature of the fuel cell to be about 200 °C lower than that for yttria-stabilized zirconia based fuel cell systems.

This project is examining three different ceria-based electrolytes. The first one is ceria doped with 20 mole percent samaria. This oxide conductor, and composition, was chosen since it exhibits the highest ionic conductivity of the doped-ceria family, as is shown in figure 2, and

because it is the least expensive. Both of these factors result in better fuel cell performance (i.e. higher power density). The proton conductor strontium cerate doped with 5 mole percent ytterbia also has been examined. Much of the literature on proton conducting electrolytes in solid oxide fuel cells uses this material; however, its ionic conductivity is more than one order of magnitude lower than that of samaria-doped ceria with a value similar to that of yttria-stabilized zirconia. Finally, the use of barium cerate doped with 10 mole percent samaria as an electrolyte has been investigated. This material is actually a mixed-ionic conductor, meaning that it conducts both protons and oxide ions. This mixed conduction has been found to be temperature dependent. At lower temperatures ($T < 750\text{ }^{\circ}\text{C}$) the conduction is primarily protonic in nature, at higher temperatures ($T > 850\text{ }^{\circ}\text{C}$) oxide ions are the dominant conducting species, and at temperatures in between both forms of ionic conduction are present [4]. Furthermore, this conductivity is higher than that seen in other protonic or mixed conducting electrolytes. Because the ideal operating temperature for this fuel cell system in power plant applications is in the lower range mentioned above, this material is a candidate for the electrolyte.

Another important part of a solid oxide fuel cell are the electrodes. The material from which these are fabricated must have high electronic conductivity in order to allow for the flow of electrons to and from the reaction sites and, preferably, should have some ionic conductivity as well. It must also be suitably thin and porous in order to produce an extensive gas/electrode/electrolyte interfacial region for electrochemical reaction and must have appropriate reactivity for catalyzing the reactions. In addition, the electrode material must be stable to the gases to which it is exposed. Because different half-cell reactions occur at the two electrodes, which are physically separated, it is possible to optimize each electrode individually.

Because determining an appropriate electrolyte material has been the focus of this research to this point, platinum has been used for both electrodes; however, for economic reasons it will need to be replaced. Most of the effort will concentrate on evaluating anode candidate materials since these have to be both thermodynamically and electrochemically stable in a hydrogen sulfide environment. Furthermore, it is believed that certain materials may favor one of the oxide-conducting electrolyte anodic reactions (reactions 3 and 4) over the other one. The cathode material, on the other hand, only needs to be stable in air at high temperatures.

State of Research

The research carried out up to this point for this project can be divided into two distinct areas: 1) fabrication of the various electrolytes and the platinum electrodes and 2) fuel cell experiments using the electrolytes produced. Both of these topics play important roles in the overall success of this project.

Electrolyte Fabrication

Recently, most of the effort has been concentrated on the fabrication of suitable electrolyte membranes. In order to be used successfully as the electrolyte in a fuel cell, the ceramic oxide membranes formed are required to be thin, homogeneous, dense, and stable in the presence of hydrogen sulfide. Because the electrolyte is the main resistance to ion transfer in the fuel cell, decreasing the electrolyte thickness will improve the fuel cell performance by lowering the IR drop across the cell. Furthermore, the density needs to be as close to the theoretical density as possible. This will insure that the gas streams do not mix chemically, as opposed to electrochemically, and decrease the number of physical defects resulting in a substantial

improvement in the ionic conductivity of the electrolyte. Having a completely homogeneous electrolyte will also improve conductivity. Finally, and most important, for a ceramic oxide material to be under consideration as the electrolyte, it must not react in any way with the gases to which it is exposed. In this case, these are hydrogen sulfide and air.

A successful fabrication technique for samaria-doped ceria has been developed[5]. Briefly, it involves the formation of the powder by coprecipitation of the nitrate forms of cerium and samarium followed by a series of acetone-toluene-acetone washes, calcination of this powder, uniaxial dry pressing of the calcined powder, and finally sintering of the resulting membrane at a temperature of 1600 °C. This procedure has produced membranes that are thin (< 0.7 mm) and dense. Also, samaria-doped ceria is apparently stable in a hydrogen sulfide environment. Of the three electrolytes, this oxide conductor shows the most promise.

Problems have been encountered in obtaining dense membranes of ytterbia-doped strontium cerate that remain in sintered form. It was initially believed that what was occurring is that the all of the strontium was not present in the form of strontium cerate; instead, some of it was present in the form of the very reactive strontium oxide (SrO). Over time it could react with water or carbon dioxide in air to form strontium hydroxide (Sr(OH)₂) or strontium carbonate (SrCO₃). The resulting volume change could then cause the sintered electrolyte to slowly "desinter" to a powder. Because of this problem a spray drying apparatus was employed in hope of obtaining a more uniform, homogeneous powder with a smaller particle size. This piece of equipment operates by pumping a slurry of 50 w/o of the precursor powders in correct stoichiometric amounts through an atomizer, forming a fine mist of uniform droplets, and into a heated chamber where it is rapidly dried and then recovered. However, membranes formed

from this powder also "desintered" in some cases. A more recent hypothesis is that strontium cerate itself is taking on water forming a hydrate $\text{SrCeO}_3 \cdot x\text{H}_2\text{O}$ with a resulting volume change. If so then this electrolyte is not stable in air, though that would not necessarily be true at the temperature of fuel cell operation. Placement of a disintegrating Yb-doped SrCeO_3 membrane in a desiccator apparently inhibited this process. This tends to support the idea that water is responsible for the "desintering."

In fuel cell experiments the surface of this protonic electrolyte exposed to H_2S apparently converts to strontium sulfate (SrSO_4). It was believed that the increased homogeneity of the powder prepared by the spray dryer would alleviate this problem. A stability test was run on a membrane formed from the spray dried powder by running hydrogen sulfide over one side of it at 700°C for almost three days. After cooling it down and performing x-ray diffraction on it (see figure 3), a pattern for strontium sulfate (celestine) was observed and no match with strontium cerate remained. However, this one stability test is far from definitive though it does appear, for reasons discussed above, that this candidate for the electrolyte may not be practical.

There is some question as to the stability of the mixed-ionic conductor samaria-doped barium cerate as well. After use in a fuel cell run sometimes a match between the experimental x-ray diffraction pattern and the reference pattern for barium sulfate (BaSO_4), among other reference patterns, was seen. Similar to Yb-doped strontium cerate this is believed to be formed due to excess barium in the electrolyte not present as barium cerate. Again, spray drying was attempted to alleviate this problem. A stability test like that mentioned above was run with a membrane formed from spray dried powder and the results were inconclusive. As can be seen from figure 4 there is no apparent pattern for barium sulfate (barite) in the experimental

diffraction pattern, but there also is no match with barium cerate. It is possible that sulfur condensed on the surface of the electrolyte and can account for any number of the diffraction peaks.

As with the proton conductor another problem encountered was in obtaining a sufficiently dense specimen with any consistency. The powder with a smaller particle size produced by spray drying should result in a higher green density after uniaxial pressing and, hence, a higher sintered density. However, no significant difference was observed. In order to obtain densities of greater than 95% of the theoretical density, a hot press has been employed recently. With this piece of equipment the powder is sintered while simultaneously applying pressure. The sintering temperature and pressure used are 1450 °C and 1500 psi. Densities of 95% or greater have been obtained. Two concerns, however, are that the specimens pressed so far have fractured and have slowly splintered and become discolored over time in air. The latter problem has been solved by reoxidizing the electrolytes at 800 °C over a period of a couple of days. The fracturing of this material is probably due to the membrane adhering to the carbon die which then upon cooling causes the barium cerate to crack due to differences in the thermal coefficients of expansion generating significant stress on the piece. This should be able to be solved by using zirconia paint in between the die and the specimen and by cooling the die down at a slower, more controlled rate. On the other hand, another solution may be to press thicker membranes and slice them with a diamond saw.

Electrode Application

For all of the fuel cell experiments sputtered platinum electrodes were utilized; however, it became apparent that these electrodes became nonconductive over time at the high temperature

of operation. After use in a fuel cell run the resistance between any two points on the electrode would often be greater than 20 M Ω ; whereas, before the experiment this resistance would be well under 1 Ω . As a result, applying the electrodes by painting platinum paste on the electrolytes and then actually sintering them to the electrolyte surface was examined. The electrodes applied in this manner were porous, as verified by SEM, conductive, with a lower resistance than the sputtered ones, and remained conductive for a longer period of time at the high temperatures of operation.

The sintering of platinum paste electrodes has not been without problems. During the firing cycle, in which the electrode is sintered to the electrolyte at a temperature of 1050 °C, the electrolytes would crack in some cases. This is believed to be due to physical or structural defaults within the electrolyte to begin with which then are able to propagate due to the heat cycling. This is another reason for the necessity of fabricating totally dense, hence defect-free, electrolytes.

Fuel Cell Experiments

Fuel cell tests have been performed using all three electrolytes. All of these runs have used the planar cell configuration shown in figure 5. The fuel gas flows to the platinum anode electrode which has been deposited on the ionic conductor, and air is blown to the cathode side where the oxygen is reduced at the similarly-deposited positive electrode. The gases with the reaction products then exit through the other tube on the same side of the cell housing. Thin glass o-rings, which soften at the elevated temperature of fuel cell operation, are placed between the membrane and the cell housings in order to obtain gas tight seals on both the anode and cathode

sides. In order to have a reasonable basis for performance comparison, all tests using hydrogen sulfide as the fuel are preceded with hydrogen.

No experiments with the samaria-doped ceria electrolyte have been run recently. This electrolyte has proven its stability in a hydrogen sulfide environment and has given the best results ever obtained using hydrogen sulfide as the fuel in a solid oxide fuel cell. Open circuit potentials of 0.7 V have been observed, and short circuit current densities of up to 46.0 mA/cm² at 700 °C have been achieved with this electrolyte. Furthermore, with a membrane that was 0.64 mm thick, a maximum power density of 5.05 mW/cm² at 686 °C was obtained. The next step to be taken with this electrolyte is to examine the kinetics of the two anode half-cell competing reactions (reactions 3 and 4). This will be discussed in the Future Work section.

The results obtained with the proton conductor SrCe_{0.95}Yb_{0.05}O₃ are a significant improvement over those seen in the past with this electrolyte. A short circuit current density of 0.771 mA/cm², which is five times greater than observed previously, with an open circuit potential of 0.763 V at a temperature of 710 °C has been obtained with H₂S as the fuel. At this same temperature a maximum power density of 0.12 mW/cm² was acquired. This is displayed in the power density curve given in figure 6. The primary reason for this increase in performance is because the electrolyte was successfully fabricated in a much thinner form. However, cell performance deteriorated over time which can be attributed to the formation of the layer of strontium sulfate on the surface of this electrolyte and possibly the sputtered platinum electrodes' loss of conductivity.

As for the other two electrolytes, the first reported experiments utilizing samaria-doped barium cerate with hydrogen sulfide as the fuel were carried out in this study as were those for

the other two electrolytes. The short circuit current density and power density obtained had values between those acquired for the other two electrolytes. This is expected considering that its ionic conductivity lies between those of the other two electrolytes. Experiments with this electrolyte gave short circuit current densities of up to 1.75 mA/cm^2 with open circuit potentials of 0.67 V at $757 \text{ }^\circ\text{C}$. A power density curve obtained at this same temperature, displayed in figure 7, showed a maximum power density of 0.25 mW/cm^2 . Some preliminary gas chromatographic analysis of the temperature dependence of the reaction kinetics of hydrogen sulfide has been undertaken. The results obtained correlate well with the expected ionic conductivity behavior of this electrolyte in the temperature ranges considered. At higher temperatures ($T > 800 \text{ }^\circ\text{C}$) the dominating species was sulfur dioxide, which is indicative of oxide conduction, while at lower temperatures ($T < 700 \text{ }^\circ\text{C}$) sulfur is the primary product. Sulfur can be produced by either oxide or proton conduction, but in either event, this product distribution at lower temperatures looks promising.

Future Work

Despite some progress in the fabrication of suitable electrolytes for use in fuel cell runs, there is still room for improvement, especially with the proton conductor and the mixed-ionic conductor. More attempts will be made with the hot press to produce samaria-doped barium cerate electrolytes. Within a couple of more trials success should be achieved. This technique will also be attempted with ytterbia-doped strontium cerate.

An isostatic press will also be utilized in an attempt to increase the membrane's density. This press compacts the powder uniformly in all directions (i.e. presses it hydrostatically).

Furthermore, its pressure rating, 60,000 pounds, is significantly higher than that of the uniaxial press currently being used. These factors should result in an improvement in the green-body density of the electrolyte. This will in turn increase the ease with which the individual granules sinter together resulting in a higher final, sintered density.

Since the main cell resistance is associated with the electrolyte, one way to improve the power output of the fuel cell is to decrease the thickness of the electrolyte. The membranes formed by dry pressing are usually between 0.7 and 0.8 mm thick. Two ceramic processing techniques that can fabricate membranes on the order of 100 μm are tape casting and sol-gel processing. Time permitting, these will be examined; doing so will decrease the electrolyte resistance by a factor 7 or 8, resulting in an appreciable improvement in the power output of the fuel cell.

The use of electrodes applied by platinum paste should increase the longevity of the fuel cell experiments. After full evaluation of the electrolytes and the reaction kinetics of hydrogen sulfide, it will become necessary to investigate other, less expensive materials to replace platinum. The anode material must be thermodynamically and electrochemically stable and must be resistant to hydrogen sulfide as well as possess all of the other characteristics common to good electrodes. Metal or metal sulfides and materials based on a perovskite-type lattice structure are possible choices for the electrode material. Some candidates, which have been used before with H_2S , include NiFe_2S_4 , CuCo_2S_4 , WS_2 , and NiS [6]. The cathode materials to be examined will be limited to oxide perovskites with the composition $\text{La}_{1-x}\text{A}_x\text{MO}_3$ where $\text{A} = \text{Sr}$ or Ba and $\text{M} = \text{Co}$ or Mn . These tend to have high activity for the reduction of oxygen, have a relatively high electrical conductivity, and have been successfully used as cathodes in the past [4,7,8]. A

perovskite-type oxide of this nature would also result in a better matching of thermal expansion coefficients between the electrode and electrolyte.

With the use of other electrodes beside platinum, it will become necessary to incorporate a reference electrode into the fuel cell configuration in order to allow for the determination of the performance characteristics of each electrode individually during a fuel cell run. This inclusion of a reference in the system will allow for the optimization of the complete fuel cell design - electrolyte, anode, and cathode.

Fuel cell experiments will be run using all three electrolytes. Efforts will be made to try to increase the power density and to see what effects denser and thinner electrolytes have on it. Post-mortem analysis of the electrolyte will be carried out to definitively determine the stability of the electrolytes in actual fuel cell operation. In addition to x-ray diffraction, SEM and chemical surface analysis techniques will be employed.

With the oxide conducting electrolyte, $(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$, the next step is to analyze the reaction kinetics of the two possible anode half-cell reactions. The conditions under which the reaction producing sulfur is favored, without the formation of sulfur dioxide, will be determined. Variation of the temperature and gas composition could have an effect on this product distribution. Furthermore, it is believed that the anode material may selectively catalyze one of the reactions. Gas analysis of the effluent streams will be performed to carry out this analysis.

The effluent streams for experiments with doped BaCeO_3 electrolytes will also be examined. The product distribution as a function of temperature will be determined more accurately. Furthermore, a maximum temperature will be found at which the fuel cell can operate without significant sulfur dioxide formation resulting from oxide conduction.

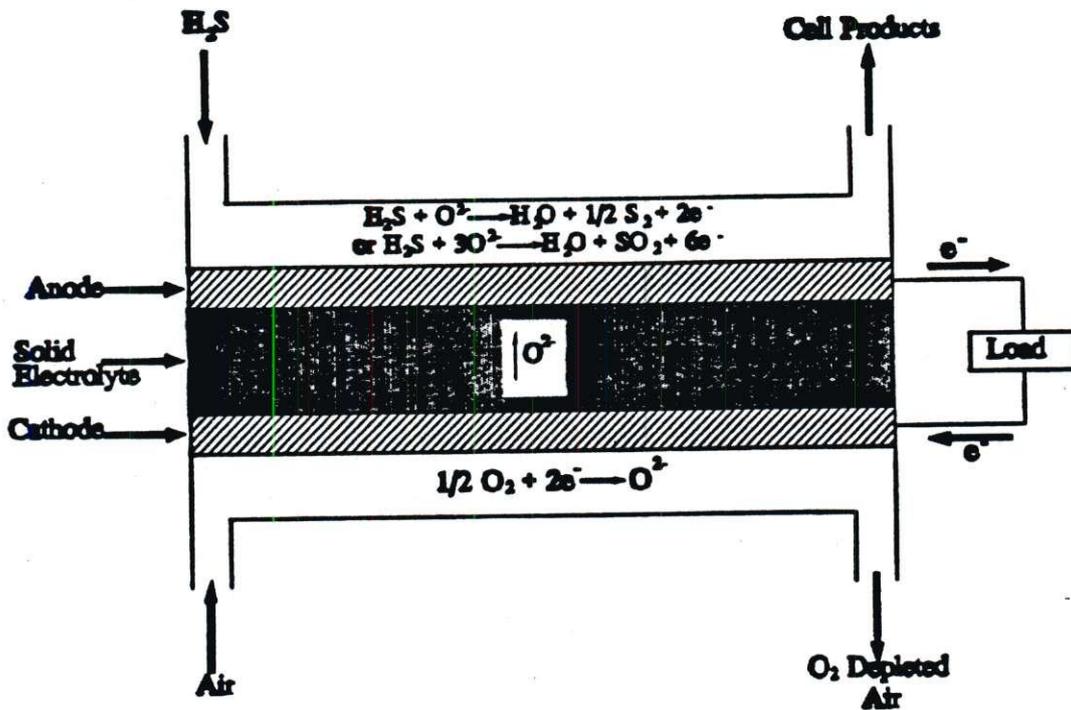


Figure 1A: Schematic of Operation of an Oxide Conducting SOFC with H_2S

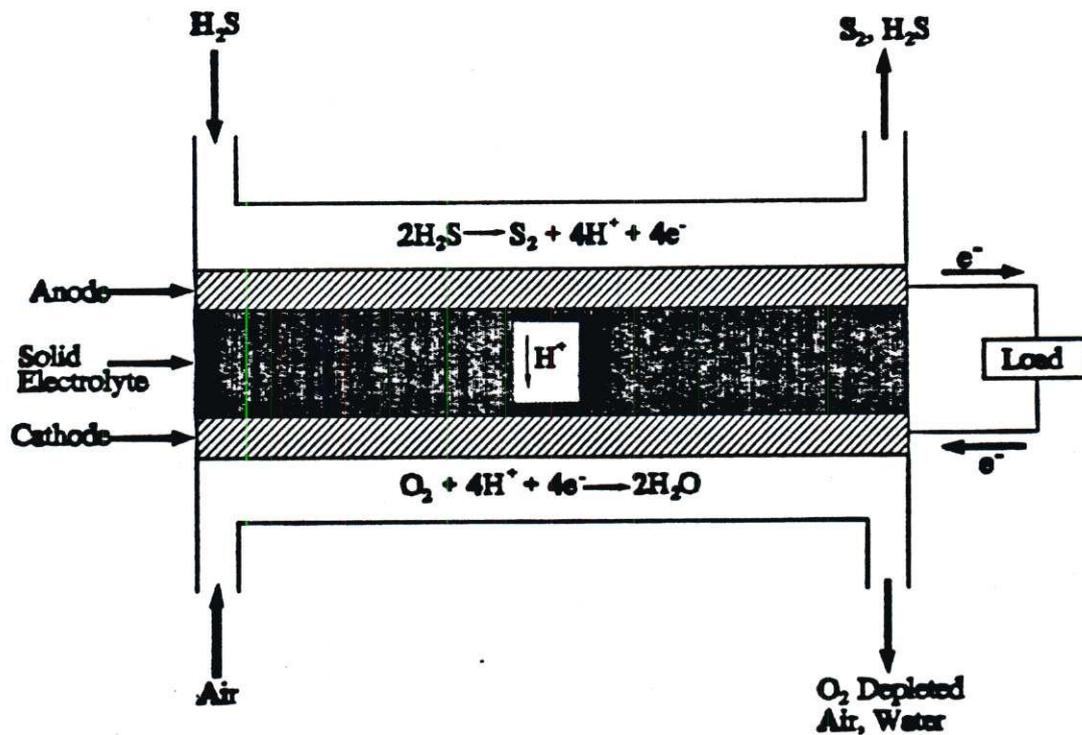


Figure 1B: Schematic of Operation of a Proton Conductor SOFC With H_2S

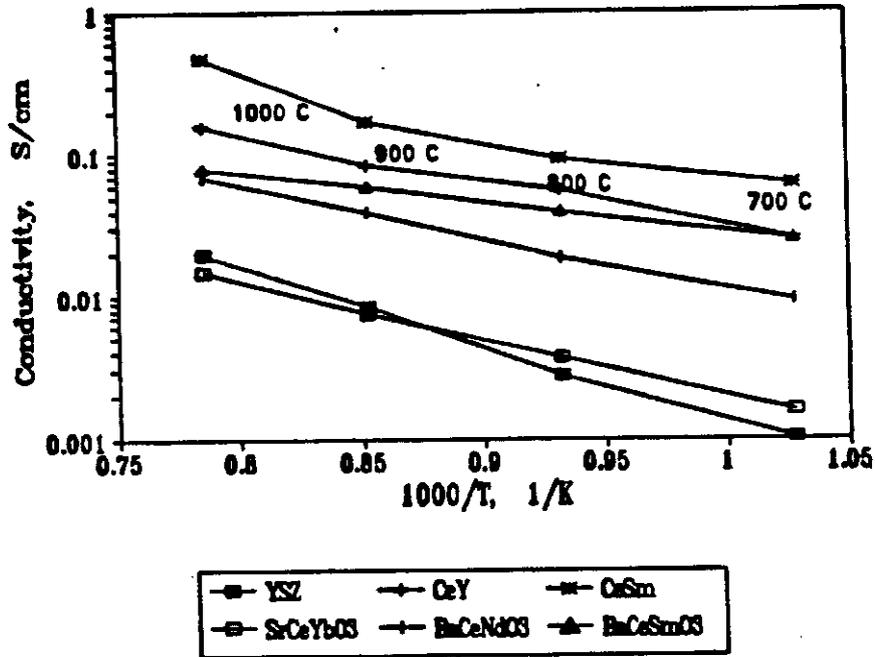


Figure 2: Conductivity of Various Ceria-Based Solid Oxide Electrolytes [3,4]

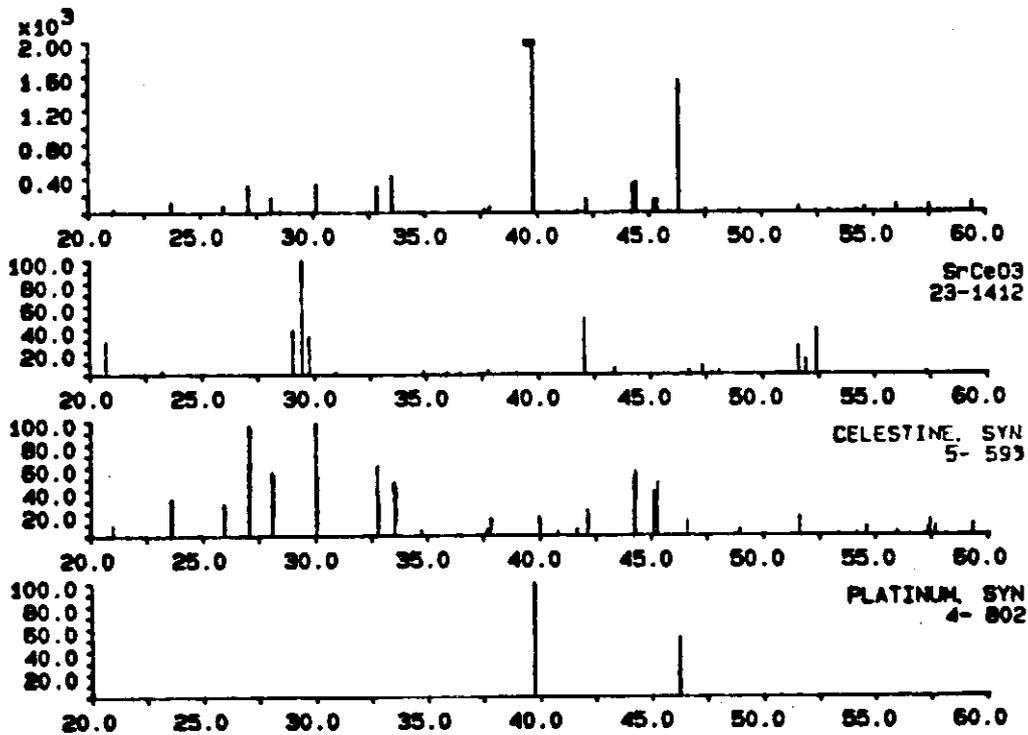


Figure 3: XRD Pattern of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ Electrolyte Exposed to H_2S

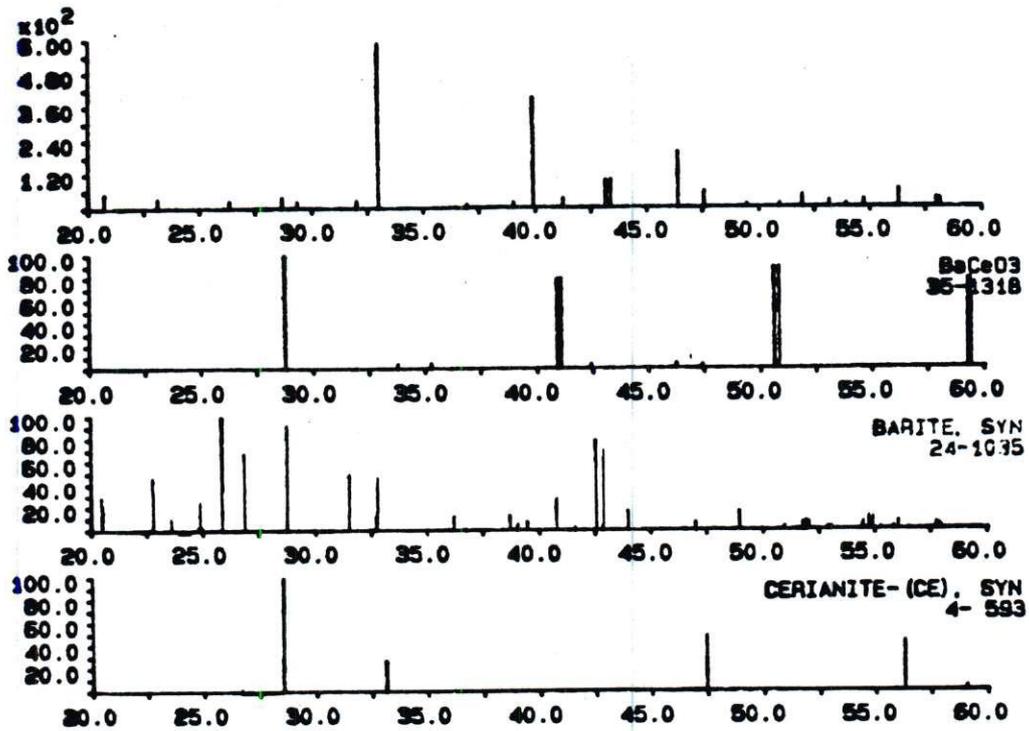


Figure 4: XRD Pattern of $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$ Electrolyte Exposed to H_2S

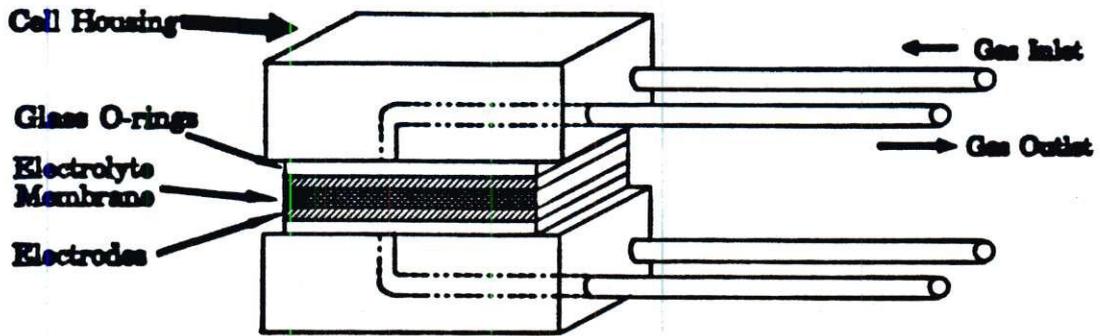


Figure 5: Fuel Cell Design

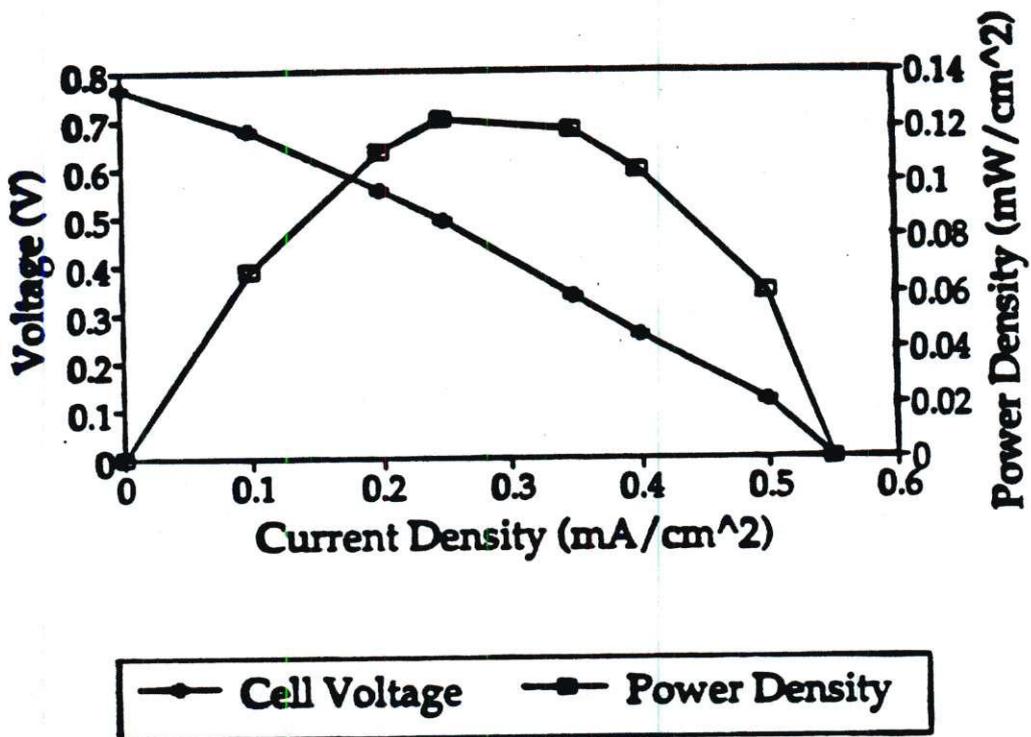


Figure 6: Power Density Curve with $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ Electrolyte and H_2S as the Fuel

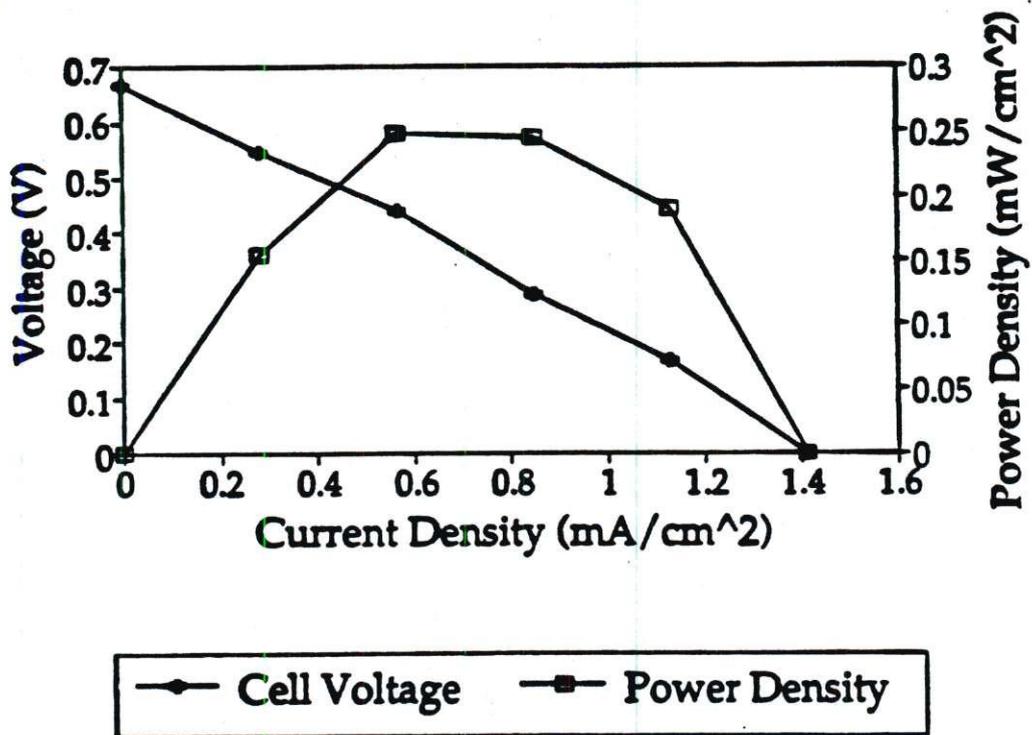


Figure 7: Power Density Curve with $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$ Electrolyte and H_2S as the Fuel

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November 20, 1995

Dr. Maria Burka
Engineering Division
National Science Foundation
4201 Wilson Blvd. Rm. 526
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Dear Maria:

re: CTS-9321968

Enclosed is the second annual report for our project, "A Hydrogen Sulfide solid Oxide Fuel Cell." As you will see, we have applied for a patent on our results with lithium sulfate.

Sincerely,



A Hydrogen Sulfide Solid Oxide Fuel Cell

**Annual Progress Report to the National Science Foundation
on Grant No. CTS-9321968**

November 10, 1995

Jack Winnick, Principal Investigator
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0100

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Project Summary

An intermediate to high temperature solid electrolyte fuel cell which utilizes hydrogen sulfide as the fuel and air as the oxidant is under development. Removing this toxic gas in a fuel cell would utilize its high chemical potential much more effectively than simply oxidizing it in the conventional Claus process which releases this energy as heat. Use in this manner would result in the removal of a pollutant while simultaneously generating electricity as opposed to heat and producing a saleable by product, sulfur.

To date, three different ceria-based materials, each with a different ionic conduction method, have been examined as the potential electrolyte. The oxide conductor samaria-doped ceria has shown the most success. A reliable fabrication technique has been developed, the best results ever reported using H_2S as the fuel in a solid oxide fuel cell have been obtained, and this electrolyte is apparently stable to hydrogen sulfide. However, the major obstacle to be overcome is that with an oxide conducting electrolyte there is a very good chance that sulfur dioxide, which is a pollutant itself, will be produced at the anode. The other two electrolytes being examined are the proton conductor ytterbia-doped strontium cerate and the mixed ion conductor barium cerate. With a proton conductor the possibility of producing SO_2 is eliminated. Significant improvement in the performance of fuel cells using both of these electrolytes has been demonstrated. However, it also has been determined, via x-ray diffraction, that both of these cerates convert to their nonconductive sulfates, $SrSO_4$ and $BaSO_4$ respectively, upon exposure to H_2S at high temperatures.

As a result, a search for other high temperature, proton conducting solid electrolytes was undertaken, and some based on sulfate, which are thermodynamically stable to hydrogen sulfide,

were discovered. In particular, the oxyacid salt lithium sulfate seems to show great promise. Preliminary fuel cell results using a crude Li_2SO_4 electrolyte verify this.

Background

Hydrogen sulfide (H_2S) is a poisonous, corrosive gas that is produced annually in excess of ten million tons in the United States alone. Most of this production results from the "sweetening" of fossil fuels: coal, natural gas and petroleum. Sulfur exists naturally in these fuels in varying amounts, both organically bound and as inorganic minerals within the coal. During direct combustion of raw coal, this sulfur is converted to sulfur dioxide (SO_2), an environmental pollutant. Advanced processes for coal utilization involve conversion of the coal to fuel gas (or liquid) prior to combustion. In this transformation, the sulfur is converted almost entirely to H_2S , the thermodynamically favored form at the temperatures and pressures in the gasifiers. It is then necessary to remove the H_2S to the ppm level for most of the downstream processes since it is corrosive to turbines and most fuel cells, as used, for example, in combined cycle plants.

The classical methods for removal of this pollutant from fuel gas, which typically requires a cooling of the process stream, involve absorption in a liquid solvent, such as methanol, followed by regeneration of the solvent. In the regeneration process, concentrated H_2S is evolved, and the solvent is returned to the absorber. Because H_2S has no large-scale commercial use and due to its toxic nature following evolution from the regenerator, it is typically sent to a "Claus" plant where it is partially oxidized to elemental sulfur and water vapor:



During this exothermic process a large amount heat is released, much of which is captured in the form of steam. This exothermicity is due to the energy content of the H₂S which at 1000 K has a standard heat of formation of -90.024 kJ/mole and a standard free energy of formation, ΔG_f, of -40.984 kJ/mole.

Electrical energy, as opposed to heat, would certainly be the preferred byproduct of the conversion of hydrogen sulfide to sulfur. One way to achieve this would be to utilize hydrogen sulfide as the fuel in a fuel cell. This would utilize its chemical potential much more effectively than directly oxidizing it in the Claus process due to the fuel cell's inherently high efficiency and would not require the cooling and reheating of the process gas stream. The high value of ΔG_f indicates oxidation in a fuel cell may be possible. This potential for using hydrogen sulfide as the fuel in a fuel cell has been known for quite sometime; the problem has been the implementation. H₂S is known to be a poison to most fuel cells, even at low concentrations, reacting with the electrolyte to drastically reduce the power output^{1,2}.

An advance was made when it was discovered not only that the solid oxide fuel cell was tolerant to relatively high levels of H₂S in the fuel (H₂), but also that highly concentrated streams of H₂S could be used as the fuel in the absence of hydrogen³. While the original work utilized Pt electrodes, it was soon found that other, more economical electrode materials could work as

well⁴. However, the electrolyte material in these early tests was yttria-stabilized zirconia (YSZ), an oxide conductor which reaches operational conductivity only near 1000°C. Furthermore, the oxide conduction leads to the possibility of two different reaction paths for the anodic oxidation of H₂S:



The half cell reaction occurring at the cathode is the reduction of oxygen to oxide ions, which migrate to the anode:

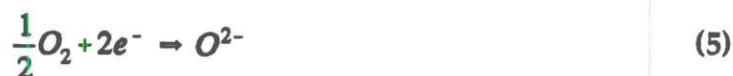


Figure 1A shows a schematic of the operation of this fuel cell. The first of the anode reactions, reaction 3, is preferred, since elemental sulfur is the byproduct of choice. Production of SO₂ would create another pollution control problem. Thermodynamics shows almost no difference between these competing paths. At 700 °C the standard full cell potential of reactions 3 & 5 is 0.789 V while that of reactions 4 & 5 is 0.774 V. As a result, kinetic studies need to be undertaken in order to determine the extent of the reactions and what factors, if any, affect the resulting product distribution. While effluent analysis in early experiments showed no SO₂ formation, this could be because these were performed at low utilization in which any SO₂ generated would be chemically reduced by excess H₂S via the same reaction (reaction 2) that occurs in the Claus Process.

In commercial operation, a fuel cell will always be under high utilization conditions; thus, a cell which does not permit reaction 4 is necessary. Some reaction selectivity may be accomplished by use of electrode materials with low activation energy for one of the paths; however, at these temperatures, activation overpotential is generally insignificant compared to other irreversibilities, such as ohmic polarization. Finally, H₂S utilization with the YSZ electrolyte failed to produce current densities of the same order of magnitude as reached with hydrogen.

A departure from the use of an oxide conducting electrolyte is to use one which conducts protons. In this case hydrogen ions migrate across the electrolyte from the anode to the cathode. Here the anode reaction could only be:



The reaction at the air cathode would remain the reduction of oxygen except with the protons combining with the oxygen to produce water vapor:



Figure 1B shows the schematic operation of this. With such an arrangement the possibility of producing sulfur dioxide is eliminated since sulfur and oxygen species are never exposed to one another.

As can be seen the choice of an appropriate material for the electrolyte is a major consideration. Obviously, a proton conducting electrolyte is preferable here, and it is essential that it is stable, both chemically and electrochemically, in a hydrogen sulfide environment.

Furthermore, since the electrolyte resistance is the major source of performance loss in this fuel cell system, the ionic conductivity of the electrolyte should be as high as possible with negligible electronic conductivity.

The efficiency of a fuel cell is related to its total cell resistance which consists of ohmic and nonohmic components. The ohmic part is the electrical resistance or IR drop, and the nonohmic portion includes the anodic and cathodic polarizations which can be attributed to activation and/or concentration overpotentials. However, in solid electrolyte fuel cells these electrode polarizations are typically small compared to the resistance of the electrolyte. The high temperature at which these fuel cells operate has a beneficial effect on the reaction kinetics of and mass transfer at the electrodes allowing high current and power densities to be obtained without much polarization loss or the need for noble metal catalysts⁵. In order to allow for the flow of electrons to and from the reaction sites, the material from which the electrodes are fabricated must have high electronic conductivity. Preferably, some ionic conduction should also be present. This could enhance current production by allowing oxidation/reduction to occur over the entire surface of the electrode as opposed to only at the region of the three phase interface. In addition, the electrodes must have appropriate reactivity for catalyzing the reactions. Because different half-cell reactions occur at the two electrodes, which are physically separated, it is possible to optimize each electrode individually.

State of Research

This project can be divided into two primary areas: 1) electrolyte and electrode selection, fabrication, and analysis and 2) fuel cell experiments using these components. Both of these topics are important in the overall success of this project.

Electrolyte

The fabrication of suitable electrolyte membranes has played a major role in this research. In order to be used successfully as the electrolyte in an intermediate temperature fuel cell, the membranes formed must be thin, homogeneous in nature, dense, and stable in the presence of hydrogen sulfide. Since the electrolyte is the primary resistance to ion transfer in a solid electrolyte fuel cell, decreasing the electrolyte thickness will improve the fuel cell performance by lowering the IR drop across the cell. Furthermore, the density of the electrolyte should be greater than 95% of the theoretical density. This will insure that the gases do not mix chemically, as opposed to electrochemically, and will decrease the number of physical defects, such as voids, resulting in a substantial improvement in the ionic conductivity of the electrolyte. Having a completely homogeneous electrolyte will also improve the conductivity. Finally, and most importantly, the electrolyte must not react with the gases to which it is exposed (H_2S and O_2 here).

The solid electrolytes utilized to date have been based on cerium dioxide (CeO_2) as opposed to the more common stabilized-zirconia. The ionic conductivity of doped-ceria is significantly greater than that of stabilized-zirconia at a given temperature. This allows the operating temperature of the fuel cell to be about 200 °C lower than when stabilized zirconia electrolytes are utilized. Figure 2^{6,7} shows a comparison of the conductivity of yttria-stabilized

zirconia to that of several ceria-based electrolytes with different dopants as a function of temperature.

This project has examined three different ceria-based materials, each with a different ionic conduction mechanism, as the potential solid electrolyte. The oxide conducting electrolyte being examined is ceria doped with 20 m/o samaria ($(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$). It was chosen because it has the highest conductivity of the ceria family, has an oxide conduction number of close to unity, and is less reducible than pure and alkaline earth-doped ceria⁸. The proton conductor ytterbia-doped strontium cerate ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$) and the mixed-ion conductor samaria-doped barium cerate ($\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$) are the other two electrolytes being studied. The mixed conductivity of samaria-doped barium cerate is temperature dependent. At lower temperatures (<750 °C) the conductivity is primarily protonic in nature, at high temperatures (>850 °C) oxide ions are the dominant conducting species, and at temperatures in between both forms of ionic conduction are present. Furthermore, this conductivity is higher than that seen in other proton or mixed-ion conducting ceramic electrolytes⁶. Because the ideal temperature for this fuel cell system in power plant applications is in the lower range mentioned above, this material is a candidate for the electrolyte.

The oxide conductor samaria-doped ceria has not been examined recently because of the emphasis that has been place on finding a suitable proton conductor. Reviewing briefly previous work with this electrolyte, a successful fabrication technique has been developed⁹. This consists of coprecipitating the nitrate forms of cerium and samarium followed by a series of acetone and toluene washes, calcining the resulting powder, uniaxially pressing the calcined powder, and finally sintering the resulting membrane at a temperature of 1600 °C. This procedure has

produced thin and dense membranes. Furthermore, samaria-doped ceria is apparently stable to H_2S . X-ray diffraction analysis of membranes used in fuel cell runs has revealed no degradation of the electrolyte. Even though this oxide conducting electrolyte shows the most promise, there still is the major obstacle of producing sulfur dioxide at high utilization.

Much of the effort in the past year has been spent examining the two cerate-based electrolytes. The problems encountered with both have paralleled one another in many respects. There have been problems obtaining dense specimens on a consistent basis. Hot pressing, in which the powder is sintered while simultaneously applying pressure, of samaria-doped barium cerate was attempted. Very dense specimens were obtained, but ultimately this fabrication technique was abandoned because mechanical stress fractures throughout the membranes rendered them unusable.

Another way of obtaining a better final density is to start with a higher green body density for firing. An isostatic press was repaired and subsequently utilized for this purpose. This press compacts the powder uniformly in all directions (i. e. presses it hydrostatically). The membranes were prepressed in a 1.25" die in a uniaxial press at pressures of less than 1000 psi to 13,000 psi and placed in rubber balloons which were then partially or completely evacuated. These balloons were then submerged in a water/oil mixture in the pressure vessel of the isostatic press and pressed at 30,000 to 38,000 psi. Some improvement in the density was seen from using the isostatic press. The resulting densities were consistently 90% or greater of the theoretical. One concern though is that the membranes often warped after isostatically pressing them. This was solved adequately by uniaxially pressing at only 1000 psi or less and/or placing the membrane between two thick pieces of rubber the same size as the membrane before evacuating the balloon.

Of greater concern is the stability of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$ in a hydrogen sulfide atmosphere at high temperatures. In the presence of this gas the surface of these two electrolytes apparently convert to their nonconductive sulfate forms, strontium sulfate (SrSO_4) and barium sulfate (BaSO_4). This sulfate formation was believed to be due to a lack of homogeneity in the initial powders in which there was excess strontium or barium, not present as strontium cerate or barium cerate, reacting with hydrogen sulfide to form the sulfates¹⁰. Additionally, electrolyte membranes ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$) were obtained from other sources to help determine if our fabrication was at fault, and in fuel cell experiments these also converted to their sulfate forms.

Because there is reason to believe that the powder fabrication step is the most important one in the overall success of producing these electrolyte materials and because the level of homogeneity required to obtain membranes with the characteristics desired may not be able to be obtained on site, $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$ powders were purchased from Seattle Specialty Ceramics. This company uses a patented spray pyrolysis powder manufacturing process which guarantees a phase pure (i.e. homogeneous powder) powder with a fine particle size. It operates by atomizing a stoichiometric solution of the precursor powders, dehydrating it in a hot spray dryer chamber, and igniting the droplets in a tube furnace to initiate an explosive exothermic reaction which generates enough heat (>1000 °C) to cause an instantaneous conversion to the final phase while maintaining microscale mixing. The use of these powders alleviates any concerns about the homogeneity of the powder. As a result, determination of whether or not these two electrolytes are stable in a hydrogen sulfide atmosphere should be able to be decided definitively.

Not only were tests run on membranes formed from the purchased powders, but stability tests on the powders themselves were performed. For these powder stability tests, electrolyte powder was placed in an alumina tube with one end blocked off and heated up to around 700 °C. A 10,000 ppm hydrogen sulfide mixture with a balance of nitrogen was then flown past the powders at a slow rate and allowed to exit. For both doped-barium cerate and doped-strontium cerate a conversion to their sulfate forms was observed via x-ray diffraction analysis. Figures 3A and 3B display representative diffraction patterns with the top pattern in each figure being the experimental one. Similar tests were run on fabricated membranes by running H₂S over one side of it at a high temperature for several days. These, along with electrolytes used in actual fuel cell experiments, all indicate that neither a barium cerate nor a strontium cerate-based electrolyte is stable to hydrogen sulfide.

Because these cerates apparently convert to their sulfate forms upon exposure to H₂S, it would appear that a solid sulfate-based material that is a proton conductor at intermediate to high temperatures would be ideal for this project. In fact, there is a group of sulfates, which belong to a class of materials known as oxyacid salts, that have long been known to be cation conductors, conducting, for example, lithium ions. Oxyacid salts include a wide range of components including some sulfates, nitrate, phosphates, and carbonates. More recently, it has been discovered that in a hydrogen-containing atmosphere some of these materials are proton conductors as well¹¹. These materials would have several advantages over the ceramic oxides when utilized as an electrolyte in a fuel cell. The use of some of these oxyacid salts would be clearly beneficial in economic terms as well as in ease of preparation. Furthermore, the temperature at which these materials shows appreciable conductivity can be significantly lower.

Depending on the material, fuel cells based on oxyacid salts can operate at temperatures as low as 400 °C¹².

To date, the oxyacid salts have been studied inadequately as solid electrolytes for intermediate temperature fuel cells. One recent study though examined several sulfates (Li_2SO_4 , Na_2SO_4 , and K_2SO_4) as electrolytes in a fuel cell with hydrogen as the fuel. The material that showed the greatest promise is lithium sulfate. At a temperature of 600 °C a current density of over 300 mA/cm² was obtained with an open circuit potential of greater than 1 V¹¹. A study of its conductivity showed that in its high temperature α -phase (face-centered cubic), it is almost purely a cation (or proton conductor) with a proton conductivity of 10^{-2} to 10^{-1} S/cm at 600 °C, which is comparable to that of yttria-stabilized zirconia at 1000 °C.^{11, 12}

Since fuel cell experiments using Li_2SO_4 as the electrolyte with H_2 as the fuel have been successful, extending this to using hydrogen sulfide as the fuel seems very reasonable. Furthermore, based on Gibb's free energy calculations for all possible reactions between lithium sulfate and hydrogen sulfide or oxygen, this electrolyte is thermodynamically stable in the environments to which it would be exposed.

The fabrication technique for electrolytes based on Li_2SO_4 is still being developed. Anhydrous lithium sulfate is ground up and heated at 250 °C for a period of 30 minutes before being pressed uniaxially at 13,000 psi in a 1.25" diameter die. It is then pressed isostatically at 37,000 psi and "fired" at 500 °C for 24 hours. Electrolytes of between 1.0 and 1.5 mm have been obtained with densities of around 90% of the theoretical. One concern is that membranes which are isostatically pressed and fired form a very thick black surface layer; whereas, those only pressed uniaxially remain white after firing. The exact cause of this color change is not

currently known. It may be due to a reaction between lithium sulfate and the latex balloon; however, x-ray diffraction analysis of discolored electrolytes still shows a good match with lithium sulfate.

Electrodes

Since determining an appropriate electrolyte material has been the focus of this research to this point, platinum has been used for both electrodes in all of the experiments. Applying platinum paste (Engelhard 6926) to both faces and sintering at 1050 °C for 30 minutes results in porous electrodes which remain conductive for an extended period of time at the high temperatures of fuel cell operation. Because lithium sulfate is a liquid at 1050 °C, with these electrolytes the platinum is sintered during heat up for the fuel cell run which appears to work fine.

For economic reasons, platinum will need to be replaced. The material used for the anode is of greater concern because of the makeup of the gas to which it is exposed. It will need to be both thermodynamically and electrochemically stable in a hydrogen sulfide atmosphere as well as being electrocatalytically active to this fuel. The cathode material, on the other hand, only needs to be stable in air at high temperatures.

Fuel Cell Experiments

Fuel cell tests have been performed using the ceramic oxide electrolytes as well as the oxyacid salt. All of these runs have used the planar cell configuration shown in figure 4. The fuel gas flows to the anode, and air is blown to the cathode side where the oxygen is reduced at the positive electrode. The product gases then exit through the other alumina tube on the same side of the cell housing. The two cell housings are made of MACOR, a machinable ceramic.

Thin glass o-rings, which soften at the elevated temperatures of fuel cell operation, have been incorporated into the design to obtain a gas tight seal between the cell housing and the electrolyte on both the anode and cathode sides. In order to have a reasonable basis for performance comparison, all tests using hydrogen sulfide as the fuel are preceded with hydrogen.

Performance of the fuel cell system is monitored by observing various cell attributes. During a typical experiment the data collected include the open circuit potential and short circuit current. The cell resistance is estimated via current interrupt or an AC bridge, and the cell potential-current relationship, from which the power can be optimized, is acquired using a PAR 371 Potentiostat/Galvanostat in galvanostatic mode. Effluent analysis of the exit stream is performed using gas chromatography. After use in a fuel cell, x-ray diffraction is carried out on the membrane in order to determine if any conversion of the electrolyte material has occurred.

To date the best fuel cell performance results obtained with hydrogen sulfide as the fuel have still been with the oxide conductor samaria-doped ceria. Open circuit potentials of approximately 0.7 V have been observed, and short circuit current densities of up to 46 mA/cm² at 700 °C have been achieved with this electrolyte. A maximum power density of 5.05 mW/cm² at 686 °C was obtained with a 0.64 mm thick membrane.

Significant improvement in the performance of fuel cells using the two cerate-based electrolytes was seen. However, as observed previously, cell performance deteriorated over a period of several days when exposed to hydrogen sulfide at the high temperatures of operation. This can be attributed to the formation of strontium sulfate or barium sulfate on the surface of the electrolyte. These sulfate forms are nonconductive.

With ytterbia-doped strontium cerate both the short circuit current density and power density improved by over one order of magnitude of what was previously reported. A short circuit current density of 9.0 mA/cm^2 with an open circuit potential of about 0.6 V at a temperature of $783 \text{ }^\circ\text{C}$ was obtained using hydrogen sulfide as the fuel. At this same temperature a maximum power density of 1.5 mW/cm^2 was acquired. This is displayed in the power density curve in figure 5. The membrane used in this particular experiment was formed from the powder purchased from Seattle Specialty Ceramics. Along with this, two other factors believed to be responsible for this notable performance increase is that membrane was denser and thinner than those in the past. With the use of the isostatic press a density of greater than 90% of its theoretical was seen with this electrolyte, and its thickness was around 0.62 mm .

The increase in performance for samaria-doped barium cerate was not quite as profound as for the proton conductor but was still substantial. Experiments with this mixed-ion conductor gave short circuit current densities of up to 5.2 mA/cm^2 with open circuit potentials of 0.60 V at a temperature of $696 \text{ }^\circ\text{C}$. At this same temperature the maximum power density obtained was 0.82 mW/cm^2 as displayed in figure 6. This improvement is believed to be for similar reasons to those stated above for the proton conductor.

Some preliminary results have been obtained using a crudely made lithium sulfate electrolyte in a fuel cell experiment using hydrogen sulfide as the fuel. The electrolyte used was over 2 mm thick and was only about 75 to 80% dense. With this unrefined lithium sulfate electrolyte and platinum electrodes a maximum short circuit current density of 12 mA/cm^2 was obtained with an open circuit potential of 1.1 V at a temperature of $725 \text{ }^\circ\text{C}$. No power curve was obtained in this first experiment. This high open circuit potential, as compared with the standard

potential, is believed to be due to the Nernstian effect of very low product concentrations at both electrodes. The cell resistance was measured to be only 2 to 3 Ω despite this electrolyte's thickness. Furthermore, post mortem analysis of the electrolyte with x-ray diffraction showed that no conversion of the electrolyte had occurred¹³. The fact that H₂S performed as well as H₂ as the fuel gives further reason to expect that more sophisticated experiments (e.g. denser, thinner electrolytes, more adherent electrode films) will yield far better results.

Future Work

Work in the near future will focus specifically on examining utilizing lithium sulfate as the electrolyte in order to fulfill this project's objective of creating a moderate-temperature, solid-state fuel cell which operates on H₂S as the fuel and air as the oxidant. The first step will be to improve the fabrication of the membranes produced. Several methods for preparation of the electrolyte from the raw material will be examined. Uniaxial pressing followed by isostatic pressing has shown some success and will continue to be employed. The casting of liquid Li₂SO₄ in graphite molds will also be investigated. The desired product is a highly dense, thin, uniform structure with flat, parallel faces to permit cell sealing. In addition to mass and geometric measurements, the specimens will also be tested using scanning electron microscopy. If time permits, tape casting and sol-gel processing will be employed in order to make thinner membranes (on the order of 100 μm) than will be possible by pressing.

The lithium sulfate electrolytes produced will then be used in full cell tests, initially using platinum electrodes. Performance will be monitored in terms of power output, polarization versus current, percent utilization, and duration of the experiments. Under high utilization, gas analysis

of the effluent streams will be performed to insure that no oxide conduction occurs (i.e. no SO_2 produced on the anode side). If the electrolyte is totally proton-conducting, stoichiometric (with current) water will be seen in the cathode effluent. In addition to proving the reaction mechanism, these tests will also determine the lower limit of H_2S that can be reached. One of the targets of this study is to be able to oxidize hydrogen sulfide to sulfur and water at low H_2S concentrations. Furthermore, despite being theoretically thermodynamically stable, post mortem analysis of the electrolyte will still be carried out in order to definitively determine the stability of the lithium sulfate in actual fuel cell operation. X-ray diffraction will be utilized for this purpose.

If lithium sulfate does not perform at the standards required for use in an intermediate temperature fuel cell with hydrogen sulfide as the fuel, then other sulfate-based materials, either pure or as a composite, will be examined. Both sodium sulfate (Na_2SO_4) and potassium sulfate (K_2SO_4) are known to be proton conductors though they have a lower conductivity than lithium sulfate. One way of improving various properties of an oxyacid salt is to add one or more other components to it. These components can be other salts with a cation species of the same charge or a different charge or another type of component altogether. Among other effects, the addition of these materials can increase the ionic conductivity, increase the mechanical strength, change stability due to formation of other conductive phases, and lower the temperature at which a phase change occurs. Some examples of these composite materials are $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$, $\text{Li}_2\text{SO}_4\text{-ZnSO}_4$, or $\text{Li}_2\text{SO}_4\text{-Ag}_2\text{SO}_4$. Very little research has been performed on any of these materials as electrolytes in intermediate temperature fuel cells.

As a last resort, if a suitable proton conducting electrolyte can not be discovered the oxide conducting samaria-doped ceria can be further examined. Since this material performs very well as the electrolyte and shows much initial promise, the next step is to examine the reaction kinetics of the two possible anode half-cell reactions. Temperature, gas composition, and anode material will be varied in order to determine if these have an effect on favoring the half-cell reaction producing sulfur at the expense of the one yielding sulfur dioxide. In particular, it is believed that the anode material may selectively catalyze one of the reactions. Gas chromatography will be utilized to carry out this analysis on the effluent streams.

After a full evaluation of the electrolytes, it will become necessary to investigate other less expensive materials to replace platinum as the electrode. When possible the electrodes will be formed on the membranes prior to final densification, so that an intimate, intercrystalline solid-to-solid bond can be achieved. Most of the effort will concentrate on evaluating anode candidate materials since these have to be both thermodynamically and electrochemically stable in a hydrogen sulfide environment as well as be electrocatalytically active. Metal sulfides and thiospinels are possible choices for the electrode material. Some candidates that have been used successfully before with H_2S and that will be examined are $NiFe_2S_4$, $CuCo_2S_4$, WS_2 , and NiS . These have demonstrated rapid kinetics for promoting electrochemical oxidation of hydrogen sulfide⁴. Since the environment to which the cathode is exposed is the same as in commercial solid oxide fuel cells (i.e. H_2/O_2 cells), the choice of an appropriate material will be simpler. The cathode materials to be studied will be limited to oxide perovskites with compositions of $La_{1-x}A_xMO_3$ where $A = Sr$ or Ba and $M = Co$ or Mn . These tend to have high activity for the reduction of oxygen and have a relatively high electrical conductivity.^{7,14}

With the use of other electrodes beside platinum, it also will be necessary to incorporate a reference electrode into the fuel cell configuration. This will be accomplished by forming "islands" of electrode surface from which no current is drawn. This will allow for the determination of the performance characteristics of each electrode individually, via overpotentials, during a fuel cell run. This inclusion of a reference in the system will allow for the optimization of the complete fuel cell design - electrolyte, anode, and cathode.

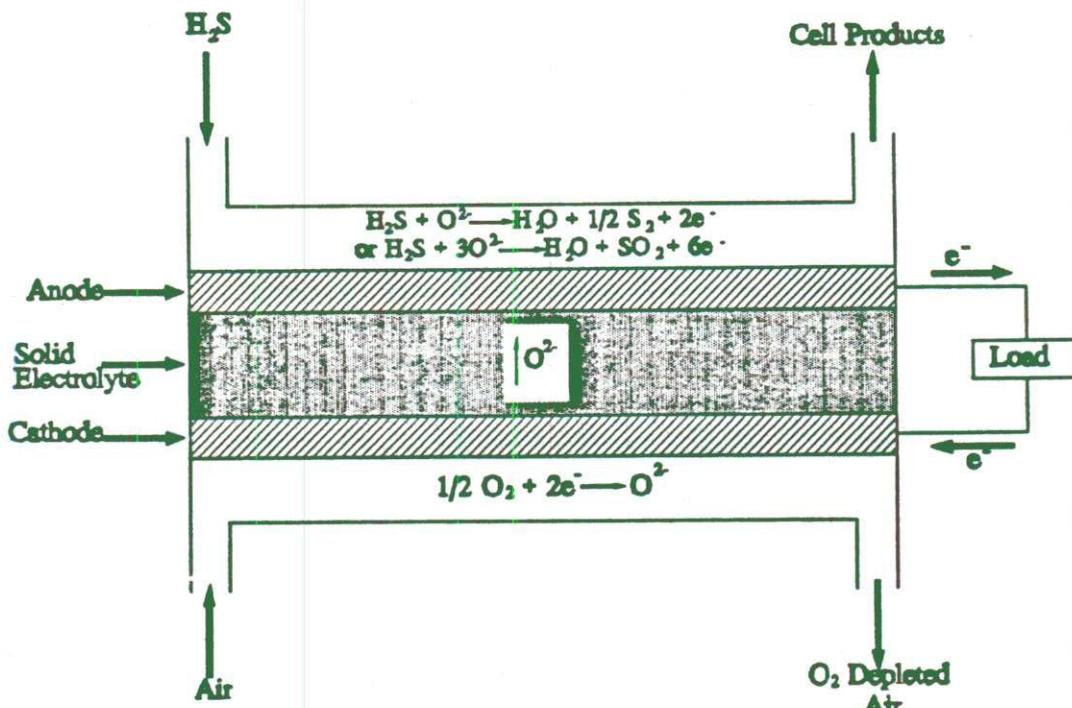


Figure 1A: Schematic of Operation of an Oxide Conducting SOFC with H₂S

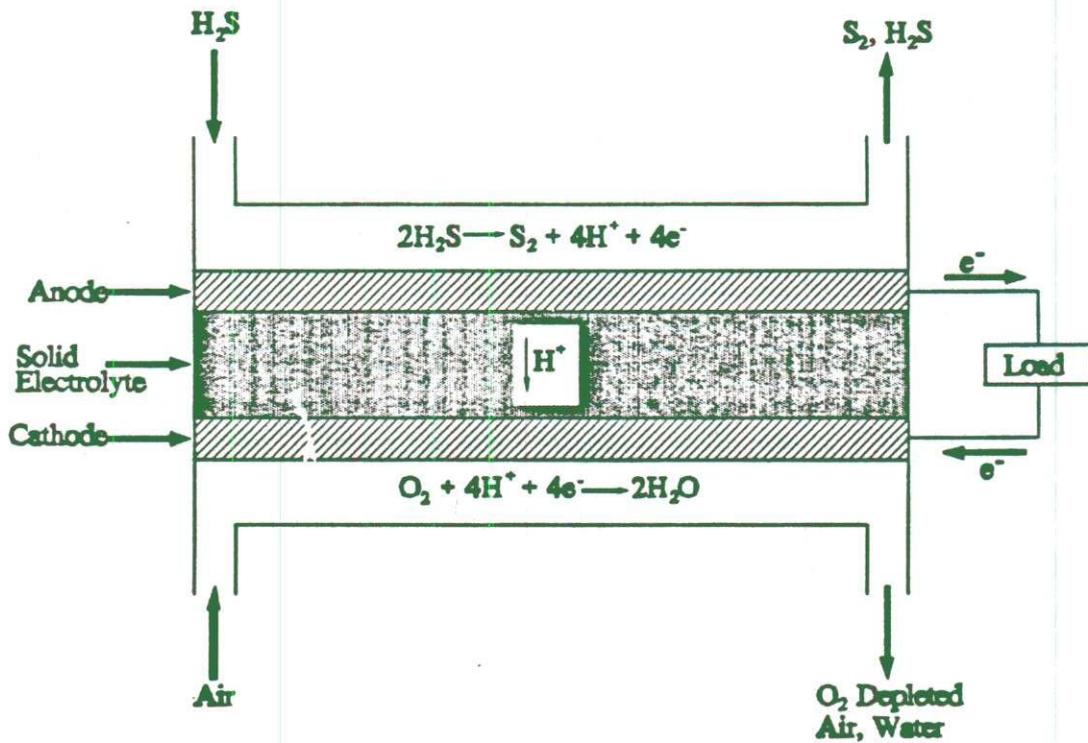


Figure 1B: Schematic of Operation of a Proton Conductor SOFC With H₂S

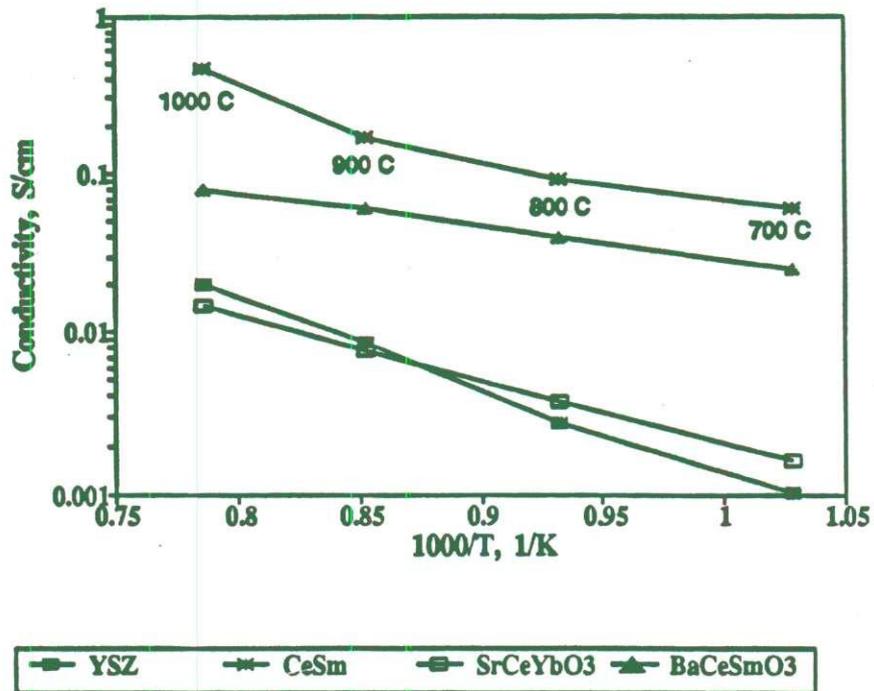


Figure 2: Conductivity of Various Ceria-Based Solid Oxide Electrolytes

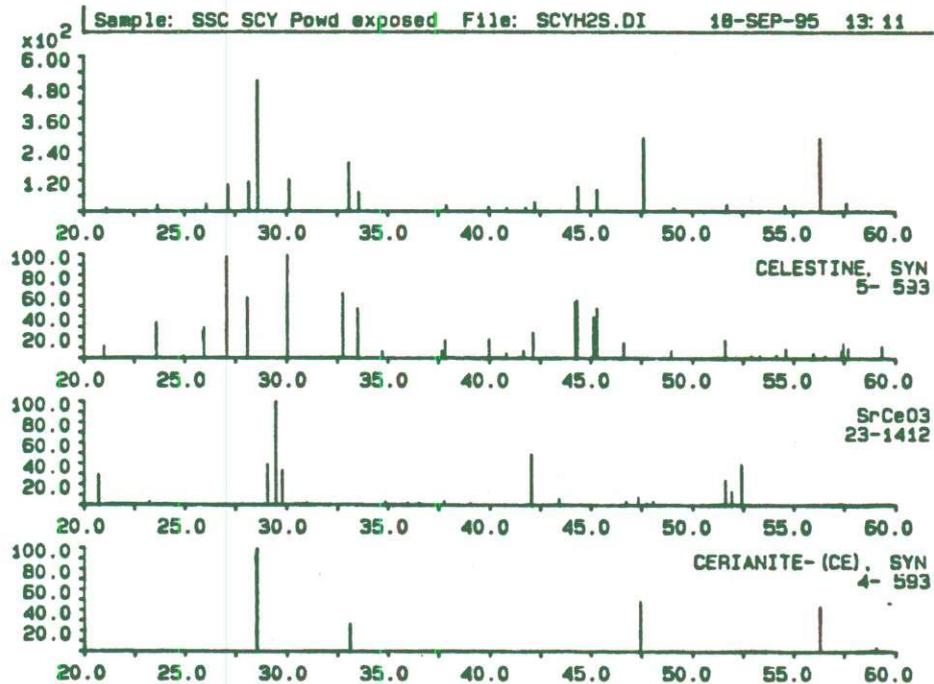


Figure 3A: XRD Pattern of SSC SrCe_{0.95}Yb_{0.05}O₃ Powder Exposed to H₂S

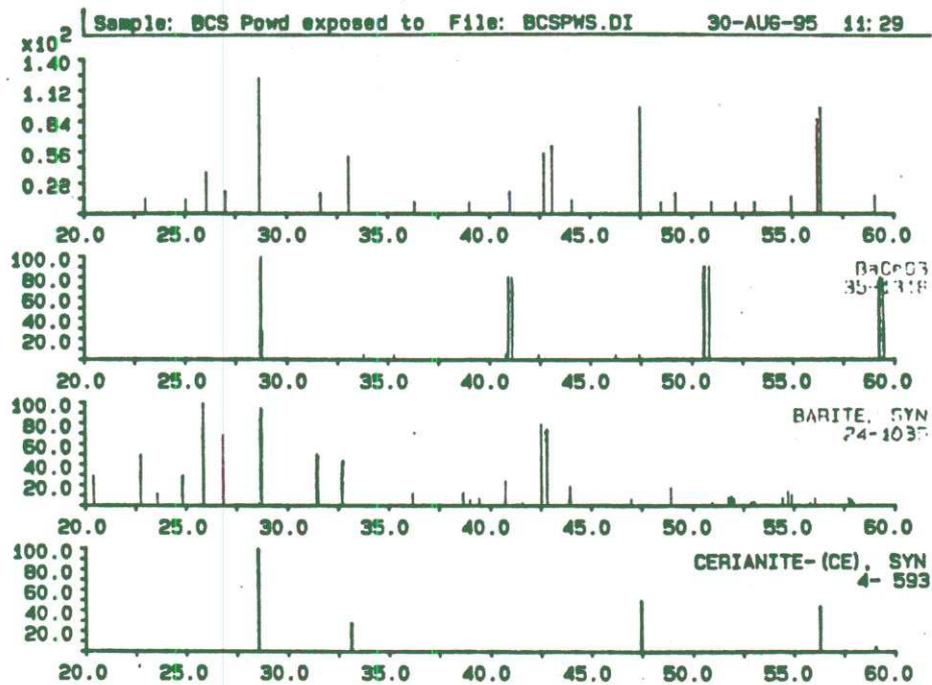


Figure 3B: XRD Pattern of SSC BaCe_{0.9}Sm_{0.1}O₃ Powder Exposed to H₂S

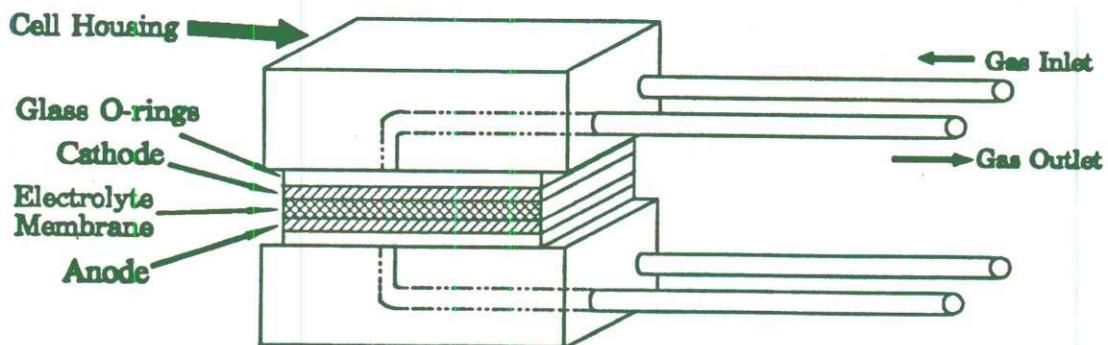


Figure 4: Fuel Cell Design

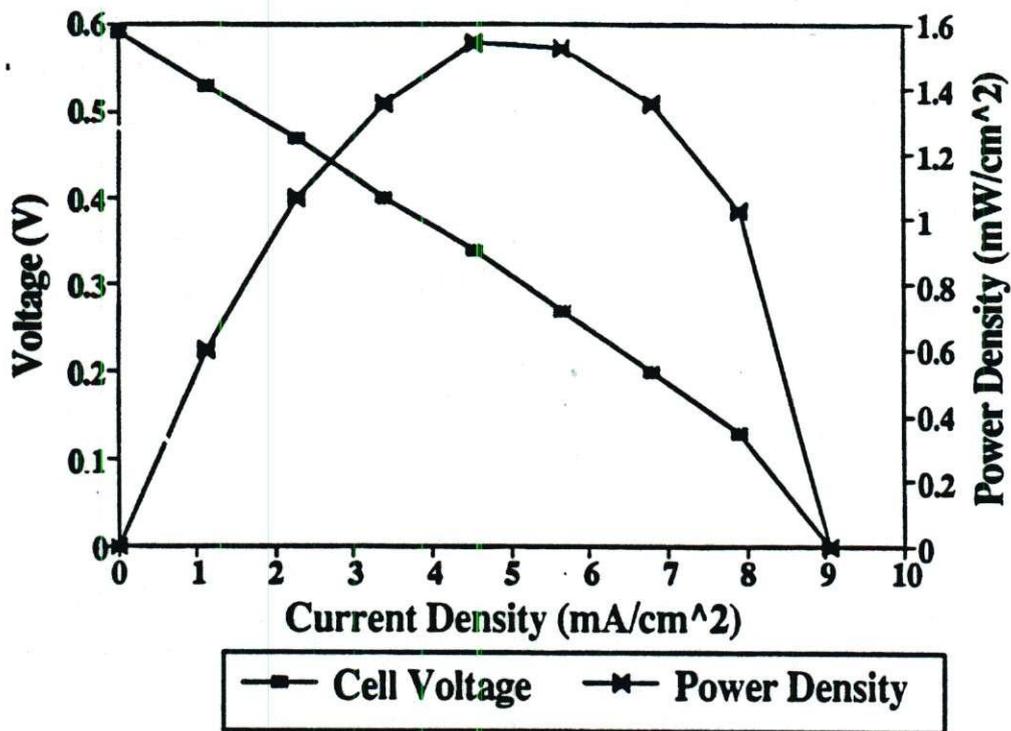


Figure 5: Power Density Curve with SrCe_{0.95}Yb_{0.05}O₃ Electrolyte and H₂S as the Fuel

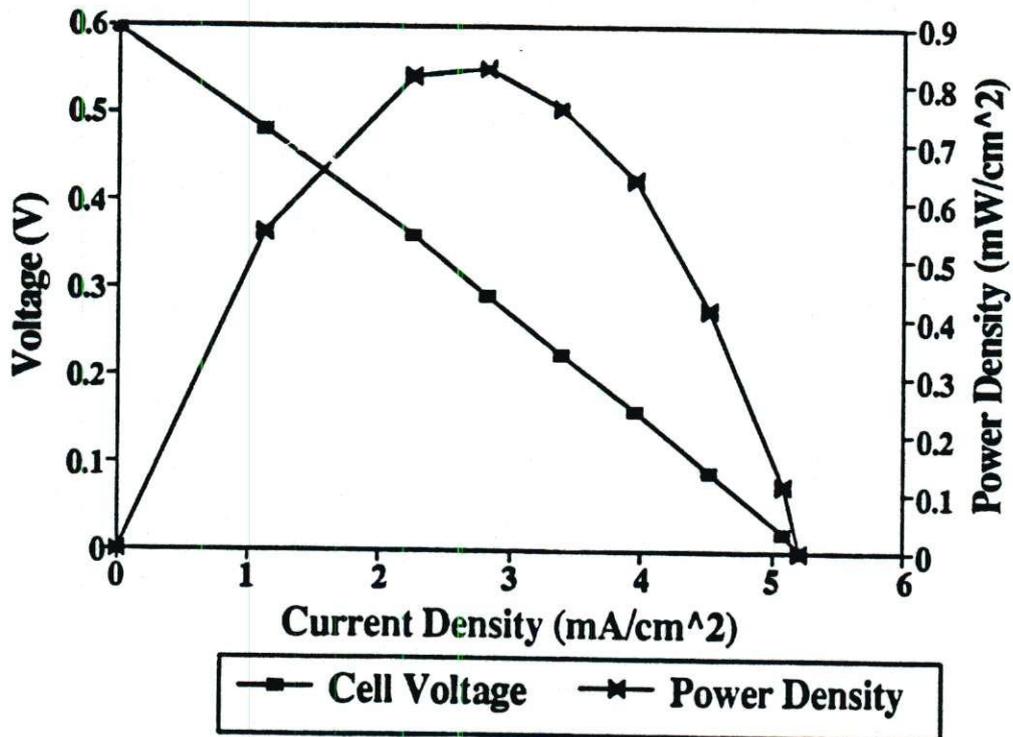


Figure 6: Power Density Curve with BaCe_{0.9}Sm_{0.1}O₃ Electrolyte and H₂S as the Fuel

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Publications, Presentations, and Patents

Publications

D. Peterson and J. Winnick, "Removal of H₂S in a Solid Oxide Fuel Cell with Ceria-Based Electrolytes," in *First International Symposium of Ceramic Membranes, PV 95-24*, The Electrochemical Society Proceedings Series, Pennington, NJ (1995).

D. Peterson and J. Winnick, "A Hydrogen Sulfide Fuel Cell Using a Proton-Conducting Solid Electrolyte", *Journal of the Electrochemical Society*, submitted for publication, 1995.

Presentation

D. Peterson, 188th Electrochemical Society Meeting, Chicago, IL, October 11, 1995.

Patents

In November 1995 a patent was applied for to use hydrogen sulfide as the fuel in a fuel cell that utilizes solid electrolytes based on lithium sulfate.