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Solid Oxide Fuel Cell Process and Apparatus

Mathew Ellis Cooper

David J. Bayless Missouri University of Science and Technology, dbayless@mst.edu

Jason P. Trembly

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(12) United States Patent

Cooper et al.

(54) SOLID OXIDE FUEL CELL PROCESS AND APPARATUS

- (75) Inventors: Matthew Ellis Cooper, Morgantown, WV (US); David J. Bayless, Athens, OH (US); Jason P. Trembly, Durham, NC (US)
- (73) Assignee: Ohio University, Athens, OH (US)
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- (52) **U.S. Cl.** 429/479; 429/484; 429/485; 429/486; 429/487; 429/488; 429/490; 429/502:429/505
- (58) Field of Classification Search None See application file for complete search history.

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Primary Examiner — Krishnan S Menon

(74) Attorney, Agent, or Firm — Jason H. Foster; Kremblas & Foster

(57) ABSTRACT

Conveying gas containing sulfur through a sulfur tolerant planar solid oxide fuel cell (PSOFC) stack for sulfur scrub bing, followed by conveying the gas through a non-sulfur tolerant PSOFC stack. The sulfur tolerant PSOFC stack utilizes anode materials, such as LSV, that selectively convert $H₂S$ present in the fuel stream to other non-poisoning sulfur compounds. The remaining balance of gases remaining in the as the fuel for the conventional PSOFC stack that is downstream of the sulfur-tolerant PSOFC. A broad range of fuels such as gasified coal, natural gas and reformed hydrocarbons are used to produce electricity.

19 Claims, 6 Drawing Sheets

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FIG. 2 PRIOR ART

Sheet 2 of 6

Current Density (mA/cm²)

25

30

35

65

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SOLID OXIDE FUEL CELL PROCESS AND APPARATUS

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/786,640 filed Mar. 28, 2006.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

I has invention was made with Government support under 15 contract awarded by the United States Department of Energy. The Government has certain rights in the invention.

REFERENCE TO AN APPENDIX

(Not Applicable)

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to fuel cells and more particularly to fuel cell systems that can be used in sulfur environments.

2. Description of the Related Art

Fuel cells liberate electrochemical energy from fuel streams containing hydrogen and/or other gases. A particular type of fuel cell, known as a solid oxide fuel cell (SOFC), has the ability to produce energy from hydrocarbon fuels at effi-
ciencies far greater than traditional combustion engines, potentially as high as 80% for integrated systems. The discovery of a feasible energy production process is very impor tant, given that natural gas and oil reserves are at low levels and continue to diminish. Though coal is also a limited resource, very large quantities still exist in many countries, including the USA. Coal can be used as a fuel for SOFCs if it is gasified to form a fuel known as "coal syngas". 40

A diagram demonstrating how a typical SOFC works is shown in FIG. 1. Another simple diagram of a basic SOFC is $_{45}$ shown in FIG. 2. Since SOFC are electrochemical devices, they consist of three main components: an anode, a cathode and an electrolyte. As shown in FIG. 1, available CO and H in the fuel stream are utilized at the SOFC anode. H_2 oxidizes more readily than CO due to the faster diffusion rate of H_2 into the porous anode. The fuel stream reacts in the triple phase boundary (the area where the fuel, oxygen ions, and electrons produced by the oxidation are present) of the anode. The electrons produced by oxidation constitute the electrical power produced by the fuel cell. After reaching a power load, 55 The elemental sulfur and hydrogen produced by this chemical the action of the SOEC where existence is the elemental sulfur and hydrogen produced by this chem the electrons travel to the cathode of the SOFC where oxygen from air is reduced to oxygen ions ($O²$). The oxygen ions then travel across an electrolyte, such as yttria stabilized zirconia (YSZ), that only allows the passage of oxygen ions. The ions then complete the circuit when they reach the anode. $60₆₀$ 50

During operation, a fuel stream containing H_2 and/or CO flows over the anode, while the cathode is exposed to either oxygen or air. When a load is applied to the system, oxygen reduces at the cathode to form oxide ions as noted above and according to the following:

$$
O_2 + 4e^- \rightarrow 2O^2 \tag{1}
$$

These ions migrate through the electrolyte to the anode, where they react with the fuel stream components to produce an electrical charge according to the following:

$$
2\text{CO} + 2\text{O}^2 \rightarrow 2\text{CO}_2 + 3e^-
$$
 (2)

$$
2H_2 + 2O^2 \rightarrow 2H_2O + 4e^-
$$
\n⁽³⁾

10 $H₂S$ is a colorless, poisonous gas that is present in gasified coal and can cause many problems throughout SOFC sys tems, most notably to the anode. The SOFC shown in FIG. 1 shows little to no resistance in $H₂S$ -containing environments. The activity of a typical SOFC anode drops considerably after exposure to H_2S concentrations as small as 2 ppm. In the presence of larger concentrations of H_2S , this effect can be irreversible.

Therefore, in order to use gasified coal as a fuel source for SOFCs, either the anodes in the SOFC must be tolerant to $H₂S$, or there must be no $H₂S$ present in the inlet fuel stream. The removal of $H₂S$ from fuel streams is expensive. Such $_{20}$ costly fuel treatments to remove impurities as H₂S prevent SOFC from competing with more traditional power genera tion methods. State-of-the-art sulfur tolerant anodes effec tively react H_2S , but show poor results when attempting to oxidize H_2 , making them inappropriate for power production.

 $H₂S$ is typically removed during coal gasification by the Claus process, where a partial oxidation with air produces elemental sulfur and water. This process consists of two consecutive steps:

$$
2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \tag{4}
$$

$$
2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{5}
$$

The former reaction is carried out at temperatures nearing 1400 K as a non-catalytic combustion, while the latter reac tion is a reversible catalytic process taking place over an equilibrium reactor train. The efficiency of this reaction scheme is limited by multiple side reactions, including the oxidation of sulfur:

$$
S + O_2 \rightarrow SO_2 \tag{6}
$$

and a reverse Claus process:

$$
3S + H_2O \leftrightarrow SO_2 + H_2S \tag{7}
$$

The largest contemporary obstacles to industrial or distrib uted use of SOFC are their susceptibility to poisoning by H_2S impurities and the necessary costs of fuel treatment to remove H₂S from syngas. While SOFC have shown encouraging stability and performance in systems containing only H_2 and H_2O , it is costly and difficult to locate and/or produce large quantities of pure elemental hydrogen. The damage to SOFCs if the $H₂S$ is not removed is unacceptable.

Due to the high operating temperature of the SOFC, H_2S can also thermally decompose:

$$
H_2S \rightarrow \frac{1}{2}S_2 + H_2 \tag{8}
$$

reaction may further react in the electrochemical reactions

$$
H_2 + O^{2-} \rightarrow H_2O + 2e - \tag{9}
$$

$$
2S_2 + 2O^2 \rightarrow SO_2 + 4e \tag{10}
$$

where E^0 for the reactions described by Equations (11) and (12) are 1.185 and 0.883 V, respectively. The simultaneous presence of H_2S along with SO_2 produced by the reaction described by Equation 12 at the SOFC anode may lead to their consumption via the reverse Claus process.

The contemporary standard for SOFC anodes is a metal such as Ni or Pt. These metals possess excellent catalytic activity toward H_2 and CO oxidation at the temperatures (~1000°C.) reached during SOFC operation. However, con ventional SOFC anodes such as Ni or Pt are poisoned by H_2S present in Syngas, causing poor electrochemical performance and even irreversible system failure. For example, platinum catalyzes the oxidation of H_2S to sulfur oxides at temperatures above 300° C. Researchers have examined the use of Pt as an anode in a SOFC utilizing an H_2S -containing fuel stream, but Pt anodes have poor longevity when used with $H₂S$ -containing fuel streams due to the formation of PtS, which increases the interfacial resistance between the Pt anode and the YSZ electrolyte leading to detachment of Pt from YSZ. Fuel streams containing both 5% H_2S (balance H_2) and pure H_2S have been tested, and it was found that longer anode lifetimes were achieved when using the dilute H_2S 15 feed. 10

Prior studies utilizing Pt as a SOFC anode in H_2S -containing systems predominantly tested systems containingYSZ as the electrolyte. Such studies utilized ceria-based electrolytes in an effort to reduce the SOFC operating temperature. While 20 low overpotentials and high current exchange densities were observed in such systems as in other Pt anode SOFC systems, the ceria electrolyte has been found to develop electronic conductivities in reducing environments and demonstrate poor long-term stability in a H_2S environments. Corroborat- 25 ing the results of the previous researchers mentioned, the Pt anode demonstrated a steady loss in activity with time due to the formation of PtS.

Given that Pt anodes proved to be inappropriate for SOFC systems utilizing H_2S -containing feeds, attention was given 30 to contemporary Ni/YSZ anode SOFCs. A study using impedance analysis and DC polarization showed extensive sulfur poisoning due to the formation of NiS during operation. Since NiS has a melting point below the operating tem perature of SOFCs, Ni-based anodes are susceptible to melt- 35 ing during operation with H_2S -containing fuels. Differences
in thermal expansion between Ni/YSZ and NiS can also prove problematic. Analogous to the results found for Pt anodes, it was found that the degree of sulfur poisoning on Ni/YSZ anodes is proportional to the total H_2S content in the incom-40 ing fuel stream. Another study found that the polarization resistance for Ni/YSZ anodes doubled when a H_2 fuel stream containing 5% H_2S was utilized, while yet another study found that sulfur poisoning on Ni/YSZ anodes became irre versible after exposure to 105 ppm H_2S at 1273 K. 45

Due to the infeasibility of Pt and Ni-based SOFC anodes in HS environments, researchers have turned their attention to anodes made of perovskite oxides, which is a term for com pounds having the generic composition ABO_3 . One study examined the properties of a wide range of perovskites based 50 are 0.801 and 0.855V, respectively. It has been found that the on lanthanum chromite $(La_{1-x}A_xCr_{1-y}B_yO_3)$. While most of the materials tested somewhat fulfilled the requirements of an SOFC anode, none of the materials were found to have a combination of properties superior to Ni/YSZ. Poor conduc tivity, lacking activity toward hydrogen oxidation, and ther- 55 mal expansions not matching those of YSZ or ceria-based electrolytes were among the disadvantages associated with using these materials as SOFC anodes.

Conventional studies of the properties of $La_{\rm s}Sr_{\rm 1-r}TiO_3$ (LST) found it to meet all requirements for SOFC anodes, and 60 others successfully tested SOFCs utilizing LST anodes using fuel streams with concentrations of H_2S ranging from 10 to 5000 ppm. These anodes showed little degradation over time and even showed an increase in activity when 5000 ppm $\rm H_2S$ was present. This phenomenon was attributed to the SOFC oxidizing \sim 12% of the available H₂S, producing additional electricity. 65

4

LST anodes also oxidize other fuel gas species present in the fuel stream, such as H_2 , along with H_2 S, although the literature shows that LST does not have high electrocatalytic activity toward any fuel species. The overall electrocatalytic performance of LST anodes was noted in the literature to be far below that found using existing anode materials, such as Ni/YSZ. The maximum power density found using LST anodes is 175 mW/cm^2 , while power densities of up to 1.8 W/cm² have been demonstrated by other contemporary systemS.

More recent studies have shown that a perovskite known as lanthanum strontium vanadate $(La_x Sr_y VO_x$ or LSV) is not only resilient to H_2S when used as a SOFC anode in 0-10% $H₂S$ environments, but further shows excellent activity toward $H₂S$ oxidation. LSV, however, does not show strong activity toward oxidation of other fuel gas species.

Studies using a Pt anode were also carried out for compari son. Performance of SOFCs utilizing LSV anodes showed no significant deterioration during a 48 hour period of operation in $H₂S$ environments. Moreover, the performance of the LSV anode appeared to increase as $H₂S$ concentration increased.

BRIEF SUMMARY OF THE INVENTION

The invention is a solution to the problem of damage to conventional SOFC by $H₂S$ without the added cost of fuel treatment by taking advantage of the strengths of certain anode materials rather than attempting to overcome their known weaknesses. Thus, coal syngas can be used as a fuel for SOFCs if the levels of H ₂S present in coal can be accommodated by the SOFCs. The invention shows promise in making reformed fuel containing sulfur species a viable fuel source for energy production via SOFCs.

Though low grade thermal energy may be recovered from the Claus process, it is more desirable to replace the combus tion furnace of the first step in fuel treatment with a H_2S/Air SOFC with a LSV anode, which oxidizes $H₂S$ electrochemically. This allows direct conversion of the energy released to electricity at efficiencies as high as 80% for integrated sys temS.

The electrochemical oxidation of H_2S in a SOFC begins with the reaction of migrated oxide ions and H₂S, forming either elemental sulfur:

$$
H_2S + O^{2-} \rightarrow 4/2S_2 + H_2O + 2e - \tag{11}
$$

or SO_2 :

$$
H_2S + 3O^2 \rightarrow SO_2 + H_2O + 6e - \tag{12}
$$

where E^0 for the reactions described by Equations 11 and 12 reaction of Equation 12 predominates in the Sulfur-tolerant SOFC, especially at high levels of fuel utilization.

Although LSV anodes realize power densities of only 140 $mW/cm²$, comparing poorly with contemporary, sulfur-intolerant SOFC anodes, numerous observations suggest that the LSV anode preferentially oxidizes $H₂S$, even in the presence of a large amount of orthodox SOFC fuel gases such as H_2 . The ability of the LSV anode preferentially to oxidize H_2S while leaving behind benign fuel gas constituents makes it a seemingly excellent choice for "scrubbing" H_2S from a fuel gas stream while recovering electricity from the process. The gas constituents remaining in the fuel stream, such as H_2 , CO, $CH₄$, etc. are then more efficiently oxidized by contemporary sulfur-intolerant SOFCs downstream from the LSV anode SOFC.

The process includes conveying gas containing sulfur (as harmful sulfur species) through a sulfur tolerant planar solid

oxide fuel cell (PSOFC) stack for sulfur scrubbing, followed by sending the gas through a non-sulfur tolerant PSOFC stack. The sulfur tolerant PSOFC stack utilizes anode mate rials, such as LSV, that selectively convert $H₂S$ present in the fuel stream to other non-poisoning sulfur compounds. The 5 remaining balance of gases remaining in the completely or near H_2S -free exhaust fuel stream is then used as the fuel for the conventional PSOFC stack that is downstream of the sulfur-tolerant PSOFC. In this manner, a broad range of fuels Such as gasified coal, natural gas and reformed hydrocarbons 10 are used to produce electricity.

Utilizing the invention rather than conventional coal com bustion will effectively reduce the total amount of $CO₂$ emitted to the environment while reducing fuel costs. The process produces only negligible amounts of NO_x since combustion 15 reactions are not used, while the capture efficiency of other pollutants such as SO_x and particulate matter are greatly increased when a laminar flow electrostatic precipitator is used for the capture of these pollutants.

The invention thus includes a process for using a fuel 20 derived from "coal syngas" which contains H.S. Syngas is an attractive option for SOFC fuel due to the abundance of coal in the US. Current estimates place the amount of coal produced in the US at 1.1 billion short tons each year. Moreover, duced in the US at 1.1 billion short tons each year. Moreover, the production, storage and transportation of conventional 25 SOFC fuels such as hydrogen are both inefficient and dan gerous. Coal, conversely, has been mined, stored and shipped worldwide for centuries.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIG. 1 is a schematic illustration of a conventional solid oxide fuel cell.

FIG. 2 is a schematic illustration of a conventional solid 35 oxide fuel cell.

FIG. 3 is a graphical illustration of the relative perfor mances of SOFCs, one with a platinum anode and the other with a LSV anode, in an $H₂S$ containing fuel blend with V_{cell} =0.44V; T=1273K; fuel flow rate=14 sccm.

FIG. 4 is a graphical illustration of the impedance spectra for a LSV SOFC in 100% H_2 and 10% H_2 S/90% H_2 fuel gas.

FIG. 5 is a schematic illustration of a SOFC with a sulfur tolerant anode, where A is LSV, LST or other such sulfur tolerant anode materials; B is the combination of the material 45 used in layer Aalong with an electrolyte such as YSZ or GDC: and C is YSZ or GDC.

FIG. 6 is a schematic illustration of a SOFC with a sulfur intolerant anode, where D is a catalyst such as nickel (Ni); E is the combination of the catalyst used in layer D along with 50 an electrolyte such as YSZ or GDC; and F is YSZ or GDC.

FIG. 7 is a schematic illustration of a system according to the present invention in which the first stage is a Sulfur tolerant SOFC and the second stage is a sulfur-intolerant SOFC.

FIG. 8 is another schematic illustration of a system accord ing to the present invention in which the first stage is a sulfurtolerant SOFC and the second stage is a sulfur-intolerant SOFC.

In describing the preferred embodiment of the invention 60 which is illustrated in the drawings, specific terminology will be resorted to for the sake of clarity. However, it is not intended that the invention be limited to the specific term so selected and it is to be understood that each specific term includes all technical equivalents which operate in a similar 65 manner to accomplish a similar purpose. For example, the word connected or term similar thereto are often used. They

are not limited to direct connection, but include connection through other elements where such connection is recognized as being equivalent by those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

A solution to the problem of sulfur in the gas stream of SOFCs has been developed utilizing a two-stage reaction process, which is shown in FIGS. 7 and 8. The first stage includes a fuel cell stack utilizing sulfur tolerant anodes, while the second stage includes conventional fuel cells. The fuel gas flows first through the first stage SOFC, which preferably oxidizes at least the sulfur-containing species. The gas then exhausts from the first stage and flows downstream into the second stage, which has higher energy production levels, but cannot tolerate any substantial amount of sulfur in the fuel gas stream. Thus, after the fuel gas has been "scrubbed' of sulfur by the first stage, it flows downstream to the second stage, which produces a substantial amount of energy.

30 as fuel. At high levels of fuel utilization, the preferred product Diagrams of the cells used in each stack are shown in FIGS. 5 and 6. The anode in the sulfur-tolerant stack utilizes a catalytic material with high activity toward the electrochemi cal oxidation of H_2S , such as, but not limited to, lanthanum strontium Vanadium oxide (LSV), lanthanum strontium tin oxide (LST), etc. as disclosed in International Application No. PCT/US/2006010620, International Publication No. WO 2006/102525A2, which is incorporated herein by reference. The catalyst used combines a high affinity toward the oxida tion of $H₂S$ along with sustainable behavior using coal syngas of the reaction utilizing H_2S is SO_4 . Thus, H_2SO_4 , which has a commercial value, can be produced by the process. The outlet gas stream of the first SOFC stack is free of or containing very low concentrations of H_2S , such as a few parts per million (ppm). The first stage preferably selectively oxidizes all $H₂S$ present in the coal syngas fuel stream.

40 rials, such as, but not limited to, Ni/YSZ, Ni/gadolinium The outlet gases from the first stage are then conveyed downstream to the second stage. The second stage utilizes more conventional, sulfur-intolerant fuel cell catalyst matedoped cerium oxide (GDC), and others. Since most if not all HS has been removed (by the first stage) from the gas stream that enters the second stage, the SOFCs used in the second stage show enhanced stability. The combination of these two stages allow the system to utilize fuels containing sulfur species, and this dramatically improves the viability of SOFC technology for distributed generation purposes.

The two-stage reaction system has been designed to utilize a syngas feed. A simple schematic of the proposed system is shown in FIG. 7. The SOFCs in the first stage utilize LSV anodes. These SOFCs effectively "scrub" any H_2S present in the syngas stream via electrochemical oxidation. The outlet gases from this LSV SOFC are fed to another SOFC utilizing conventional Ni anodes. Thus, with no $H₂S$ remaining in the fuel stream, the Ni anodes more effectively oxidize the remaining fuel species by avoiding SOFC performance deg radation and improving system longevity.

The invention uses two different types of SOFC anodes one that is active toward $H₂S$ oxidation, the other that is active toward syngas oxidation-in separate SOFCs placed in series in a gas flow path. In this way, the two SOFC units are able to oxidize a syngas stream containing $H₂S$ impurities.

It is necessary that the material used as the SOFC anode in the second stage meet a number of stringent requirements.
Catalytic activity towards reactant oxidation as well as high electronic conductivity is required to minimize polarization losses. The porosity of the material must support effective gas

transport while possessing good chemical and mechanical compatibility with other parts of the SOFC. Stability over a wide oxygen partial pressure range is necessary due to the differences in oxidizing conditions at the fuel inlet and outlet. For fuel streams containing only H_2 and/or CO, Ni/yttria 5 stabilized zirconia (YSZ) is the standard anode of choice as it satisfies most of these requirements.

Cathodes used in the second stage of the SOFC system match electrolytes to avoid mechanical problems during SOFC operation. In addition, chemical stability, low interac tions with electrolyte, high electrocatalytic activity and adequate electronic and ionic conductivity are desired in an ideal SOFC cathode. The current orthodox choice for cathode material in SOFCs operating near 1000° C. is strontium- 15 doped LaMnO, (LSM), which represents a compromise of the above requirements. 10

For the electrolyte layer, three properties are necessary: high conductivity, little electronic conductivity and the ability to conduct oxygen ions. YSZ is the industry standard, as it boasts high conductivity above 700° C., negligible electronic conductivity below 1500° C. and is an oxygen ion conductor. An alternative electrolyte, gadolinium doped ceria (GDC) has greater conductivity than YSZ while also conducting oxygen ions, but has been reported to develop electronic conductivity 25 and is partially reduced in $H₂$ at temperatures above 600 $^{\circ}$ C.

Button cells containing sulfur-tolerant LSV anodes are used with a coal syngas feed to oxidize $H₂S$ present in the fuel stream. These cells, illustrative of the types of cells that can be used in the fuel stream, are shown in FIGS. 5 and 6.

The process and apparatus electrochemically "polish" H₂S from coal syngas. Lanthanum strontium vanadate (LSV) anodes are used in planar solid oxide fuel cells to effectively "scrub" any H_2S present in the hot syngas fuel stream via electrochemical oxidation, while leaving behind fuel compo- 35 nents such as $H₂$ and CO. The outlet gases from this LSV SOFC stage are available for combustion or reaction with another SOFC stage utilizing conventional Ni anodes. With no $H₂S$ remaining in the fuel stream, the Ni anodes are able to effectively oxidize the rest of the syngas while avoiding 40 SOFC performance degradation and improving system lon gevity.

The feasibility of the oxidation of $H₂S$ -containing fuel streams by LSV SOFCs has been demonstrated. FIG.3 shows a comparison of the performances of Pt and LSV anodes in 45 H_2S -containing environments. In this study, humidified H_2 was the fuel stream for the first 2 hours of the test. After 2 hours, the fuel stream was changed to a 5% $H_2S/95%$ H_2 mixture. Although the Pt anode failed quickly after the intro duction of H_2S into the SOFC fuel stream, the SOFC utilizing 50 LSV anodes actually showed an improvement in perfor mance. It is theorized that this phenomenon is attributable to the additional electricity produced from the electrochemical oxidation of H_2S .

FIG. 4 shows the impedance spectra for a LSV SOFC in 55 both H_2 and 10% H_2 S/90% H_2 environments. It can be seen that SOFC resistances were reduced by nearly 70% once the $H₂S/H₂$ fuel blend was introduced to the system. This rapid transition was also found to be fully reversible. The authors concluded that the reduction in overall polarization resistance 60 was due to easier charge transfer processes at the LSV anode upon introduction of the H_2S/H_2 fuel blend, and further claim this to be an indication of the preferential oxidation of H_2S over H₂ at the LSV anode.

The experimental syngas feed is comprised of 40 mole % 65 CO, 26.3 mole % H_2 , 33.7% N₂, 300 ppm H_2S and a relative humidity of 2% in order to approximate the average formu

lation for syngas derived from Pittsburgh No. 8 coal. Operating temperature (T_o) and electrolyte type (E) of the SOFC as well as porosity (ϵ) of the SOFC anode play a large role in cell performance. Operating temperature of the LSV SOFC has been tested in the range of 1173 K to 1273 K when utilizing H_2S/H_2 or H_2S/N_2 feeds.

It has been shown experimentally by others that, starting with a fuel gas containing 5% H_2S and 95% CH₄, a product gas (the gas downstream of the sulfur-tolerant SOFC) con tained the following amounts of H_2S after flowing through a SOFC having LSV anode material at the current densities (i) indicated:

Experiments performed on a LSV prototype with 30% fuel utilization and i=100 mA/cm², showed that 57% of the H_2S was converted to materials that would not damage the anode. At i=350 mA/cm², 41% of the H₂S was converted. Clearly in all cases, LSV (La_{o 7}Sr_o 3VO₃) is highly selective to H₂S. However, as power density increases, the reaction rates tend to move back towards higher utilization of H, or other fuel sources, not H_2S . Thus, the experiments show the viability of the system.

Although the system described herein describes gaseous fuel, it will become apparent that a liquid fuel can be used. Thus, suitable fuels in any fluidic (gas or liquid) form can be used with the present invention. Of course, other modifica tions can be made to the embodiments described above. For example, a plurality of SOFC can be mounted in series or in parallel within the first or second stages described above.

The term "sulfur-tolerant" is defined herein as being substantially unharmed by exposure to significant amounts of sulfur-containing molecules. Likewise, "sulfur-intolerant" is defined herein as being substantially harmed by exposure to significant amounts of sulfur-containing molecules. Something is "harmed" if its power density is diminished by more than about 25%.

This detailed description in connection with the drawings is intended principally as a description of the presently pre ferred embodiments of the invention, and is not intended to represent the only form in which the present invention may be constructed or utilized. The description sets forth the designs, functions, means, and methods of implementing the invention in connection with the illustrated embodiments. It is to be understood, however, that the same or equivalent functions and features may be accomplished by different embodiments that are also intended to be encompassed within the spirit and scope of the invention and that various modifications may be adopted without departing from the invention or scope of the following claims.

The invention claimed is:

1. A system for converting chemical energy in a fluid fuel, that contains sulfur and flows along a fuel path, to electrical energy, the system comprising:

(a) a sulfur-tolerant solid oxide fuel cell with an anode disposed in the fuel path for generating electricity and converting the sulfur-laden fluid fuel to a substantially sulfur-free fluid fuel in the fuel path downstream of the sulfur-tolerant solid oxide fuel cell; and

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(b) a sulfur-intolerant solid oxide fuel cell with an anode disposed in the fuel path spaced downstream of the sulfur-tolerant solid oxide fuel cell for generating elec trical energy from the substantially sulfur-free fluid fuel without substantial damage caused by sulfur.

2. The system in accordance with claim 1, wherein the sulfur-intolerant solid oxide fuel cell oxidizes molecules in the fluid fuel that do not contain sulfur.

3. The system in accordance with claim 1, wherein the sulfur-tolerant solid oxide fuel cell oxidizes sulfur-containing molecules in the fluid fuel.

4. The system in accordance with claim 3, wherein the sulfur-intolerant solid oxide fuel cell anode is made of Ni and YSZ.

5. The system in accordance with claim 3, wherein the sulfur-intolerant solid oxide fuel cell anode is made of Niand GDC.

6. The system in accordance with claim 4, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LSV.

7. The system in accordance with claim 5, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LSV.

8. The system in accordance with claim 4, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LST.

9. The system in accordance with claim 5, wherein the 25 sulfur-tolerant solid oxide fuel cell anode is made of LST.

10. A method of converting chemical energy into electrical energy, the method comprising:

- (a) conveying a fluid fuel containing Sulfur along a fuel path in which an anode of a sulfur-tolerant solid oxide 30 fuel cell is disposed; and then
- (b) the sulfur-tolerant solid oxide fuel cell generating elec tricity and converting the sulfur-laden fluid fuel to a

substantially sulfur-free fluid fuel in the fuel path down stream of the sulfur-tolerant solid oxide fuel cell; and then

- (c) conveying the substantially sulfur-free fluid fuel down stream from the sulfur-tolerant solid oxide fuel cell along the fuel path in which an anode of a sulfur-intolerant solid oxide fuel cell is disposed; and then
(d) the sulfur-intolerant solid oxide fuel cell generating
- electrical energy from the substantially sulfur-free fluid fuel without substantial damage caused by sulfur.

11. The method in accordance with claim 10, further com prising the step of the sulfur-intolerant solid oxide fuel cell oxidizing molecules in the fluid fuel that do not contain sulfur.

12. The method in accordance with claim 10, further com prising the step of the sulfur-tolerant solid oxide fuel cell oxidizing sulfur-containing molecules in the fluid fuel.

13. The method in accordance with claim 12, wherein the sulfur-intolerant solid oxide fuel cell anode is made of Ni and YSZ.

14. The method in accordance with claim 12, wherein the sulfur-intolerant solid oxide fuel cell anode is made of Ni and GDC.

15. The method in accordance with claim 13, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LSV.

16. The method in accordance with claim 14, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LSV.

17. The method in accordance with claim 13, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LST.

18. The method in accordance with claim 14, wherein the sulfur-tolerant solid oxide fuel cell anode is made of LST.

19. The method in accordance with claim 10, further com prising the step of producing H_2SO_4 .

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