

# DEGRADATION OF SOLID OXIDE FUEL CELL METALLIC INTERCONNECTS IN FUELS CONTAINING SULFUR

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## ABSTRACT

Hydrogen is the main fuel for all types of fuel cells except direct methanol fuel cells. Hydrogen can be generated from all manner of fossil fuels, including coal, natural gas, diesel, gasoline, other hydrocarbons, and oxygenates (e.g., methanol, ethanol, butanol, etc.). Impurities in the fuel can cause significant performance problems and sulfur, in particular, can decrease the cell performance of fuel cells, including solid oxide fuel cells (SOFC). In the SOFC, the high (800-1000°C) operating temperature yields advantages (e.g., internal fuel reforming) and disadvantages (e.g., material selection and degradation problems). Significant progress in reducing the operating temperature of the SOFC from ~1000 °C to ~750 °C may allow less expensive metallic materials to be used for interconnects and as balance of plant (BOP) materials. This paper provides insight on the material performance of nickel, ferritic steels, and nickel-based alloys in fuels containing sulfur, primarily in the form of H<sub>2</sub>S, and seeks to quantify the extent of possible degradation due to sulfur in the gas stream.

## INTRODUCTION

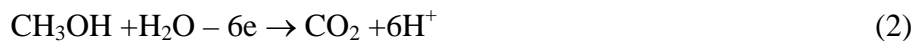
Fuel cells are energy conversion devices that generate electricity and heat by electrochemically combining a gaseous fuel and an oxidizing gas via an ion-conducting electrolyte. Hydrogen is the primary gaseous fuel in fuel cells and is used in the following major fuel cell types:

- Alkaline Fuel Cells (AFC)
- Phosphoric Acid Fuel Cells (PAFC)
- Proton Exchange Membrane Fuel Cells (PEMFC)
- Molten Carbonate Fuel Cells (MCFC)
- Solid Oxide Fuel Cells (SOFC)

The Direct Methanol Fuel Cell (DMFC) is the one exception. Here, the fuel is oxygenate-based, methanol, and it is directly supplied to the anode. Therefore, in fuel cells, fuel utilization at the anode proceeds either via the direct oxidation of hydrogen:



or through the oxidation of methanol:



Oxygen reduction occurs at the cathode, usually from air <sup>1</sup>, and proceeds in the following manner:



Among all fuel cells currently being developed, the SOFC is the most promising for the U.S. Department of Energy in terms of stationary applications due to the following advantages compared with other fuel cell types: <sup>2</sup>

- Few problems are associated with electrolyte management since SOFCs are constructed from solid state materials;
- Very high efficiencies are achieved, reaching 80% in hybrid configurations;
- Anode is not sensitive to CO;
- High-grade waste heat is produced for combined heat and power applications;
- Internal reforming of hydrocarbon fuels is possible, leading to fuel flexibility;
- Inexpensive construction materials are possible for interconnection and BOP.

However, when considering all the possible advantages associated with SOFCs, the most desirable one is fuel flexibility.

## FUEL PROCESSING

Fuel processing is defined as the conversion of raw primary fuel, supplied to the fuel cell system, into the fuel gas required by the stack in that fuel cell system. Each type of fuel cell stack has a particular set of general fuel requirements. These are shown in Table 1.

Table 1  
Fuel Requirements for Principal Fuel Cells<sup>3</sup>

Gas Species	PEMFC	AFC	PAFC	MCFC	SOFC
H <sub>2</sub>	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (> 10 ppm)	Poison	Poison (> 0.5%)	Fuel <sup>a</sup>	Fuel <sup>a</sup>
CH <sub>4</sub>	Diluent	Diluent	Diluent	Diluent <sup>b</sup>	Diluent <sup>b</sup>
CO <sub>2</sub> & H <sub>2</sub> O	Diluent	Poison <sup>c</sup>	Diluent	Diluent	Diluent
S (as H <sub>2</sub> S & COS)	Few studies to date	Unknown	Poison (> 50 ppm)	Poison (> 0.5 ppm)	Poison (> 1.0 ppm)

<sup>a</sup> In reality, CO reacts with H<sub>2</sub>O producing H<sub>2</sub> and CO<sub>2</sub> via the shift reaction and CH<sub>4</sub> with H<sub>2</sub>O reforms to H<sub>2</sub> and CO faster than reacting as a fuel at the cathode.

<sup>b</sup> A fuel in the internal reforming MCFC and SOFC.

<sup>c</sup> The fact that CO<sub>2</sub> is a poison for the AFC, more or less rules out its use with reformed fuels.

The main means of producing hydrogen gas from fossil fuels are steam reforming of hydrocarbons. One example of this is the reforming of methane<sup>4</sup>, where the reaction proceeds in the following manner:



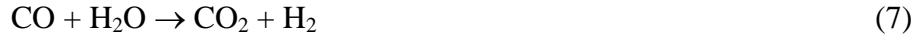
And with partial oxidation:



And for coal gasification:



Mixtures of CO and H<sub>2</sub> produced in coal gasification are called synthetic gas or syngas. A further process involves the conversion of CO in the water-gas shift reaction:



At present, the most common fuel is natural gas, which is relatively inexpensive, clean (compared to coal, gasoline and diesel), abundant and with an existing supply infrastructure. Natural gas, however, varies in composition especially impurity species. Besides methane, natural gas may contain higher hydrocarbons, the amount of which decreases logarithmically with increasing carbon chain length. The presence of the higher hydrocarbons can cause carbon deposition problems (coking), and if the natural gas contains sulfur compounds, sulfur poisoning may occur. Coking can occur on the anode and/or in the fuel supply manifold.<sup>5</sup>

Sulfur-containing compounds, such as dimethyl sulphide (CH<sub>3</sub>)<sub>2</sub>S, diethyl sulphide (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S, tertiary butyl mercaptan (CH<sub>3</sub>)<sub>3</sub>CHS, and tetrahydrothiophene (C<sub>4</sub>H<sub>8</sub>)S, are added to natural gas as odorants at the level of ~5 ppm of sulfur, while hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS) are often present in natural gas as impurities. At very low concentrations, the adsorption of sulfur on nickel is reversible. Thus, low concentrations of sulfur in the feed gas can be tolerated in SOFCs, particularly at higher operating temperatures, since the tolerance of the anode and reforming catalyst to sulfur progressively increases with increasing temperature. However, at higher concentrations, sulfidation, which is irreversible, can occur on the anode or catalyst.

SOFCs can also operate on output from coal gasification systems.<sup>6</sup> Figure 1 shows a typical simplified processing sequence for coal gasification.

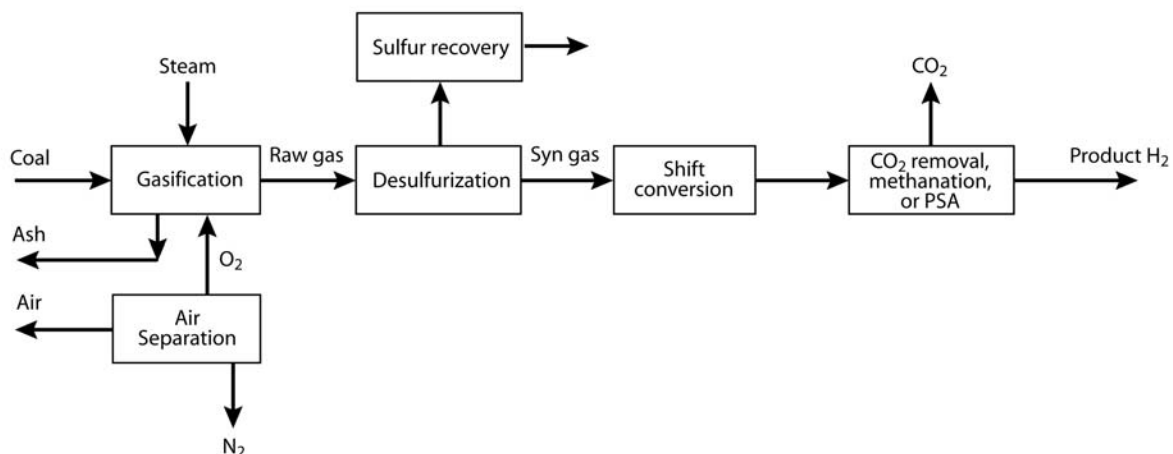


Figure 1. Scheme of coal gasification process; PSA-press-swing adsorption (from Ref. 4).

Depending upon the source of the gases, and the cleanup processes used, the levels of impurities will vary.<sup>7</sup> Sulfur in the form of H<sub>2</sub>S has the greatest impact on SOFC performance. However, if the sulfur contamination is low, it is possible for fuel cell performance to recover fully upon switching to a “clean” fuel as shown in Figure 2.

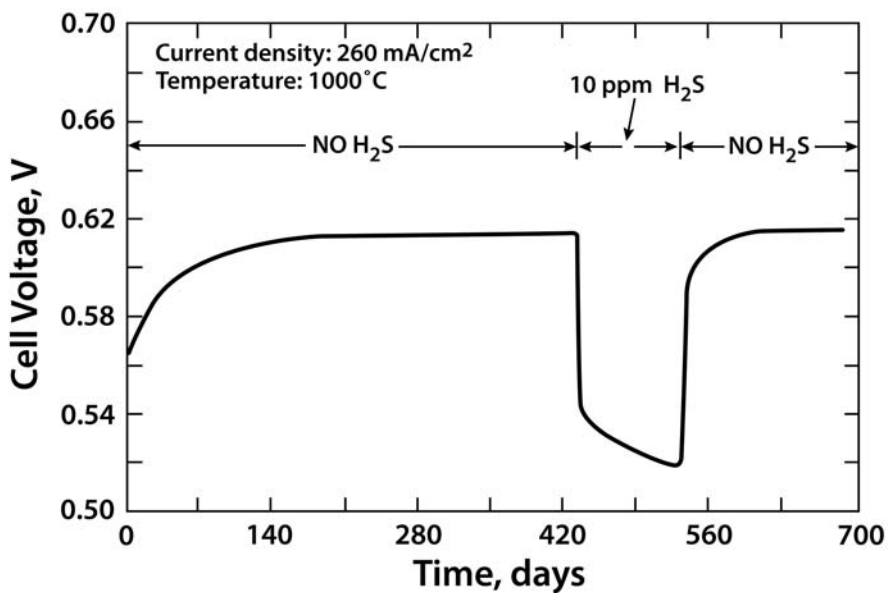


Figure 2. Effect of H<sub>2</sub>S on cell voltage (from Ref. 7).

Operation of a SOFC at sulfur levels greater than 100 ppm can result in severe performance degradation. At these high levels, sulfur may be incorporated into the electrolyte, and this incorporation provides an explanation as to why the sulfur effect is

not reversible. However, the upper limit for  $H_2S$  in SOFC fuel cells has not been established.

## METALLIC MATERIALS FOR PLANAR SOLID OXIDE FUEL CELL

Tubular, planar, and monolithic cell and stack SOFC configurations are currently being developed for civilian and military applications. The current SOFCs use a Yttria (Y) stabilized Zirconia ( $ZrO_2$ ), or YSZ, electrolyte, a Ni/Y-stabilized  $ZrO_2$  cermet anode, a doped  $La_{0.8}Sr_{0.2}MnO_3$  (LSM) cathode electrode, and ceramic ( $La_{1-x}(Sr,Ca)_xCrO_3$ ) or metallic (ferritic stainless steels) interconnection.<sup>8,9</sup> A single cell typically produces 0.5-0.9 V, and in order to generate a reasonable voltage, these cells are stacked together and electrically connected in series to increase voltage and power delivery capability. Although several stack designs are under development around the world, the most common configuration is the planar, or flat, SOFC shown in Figure 3.<sup>10</sup>

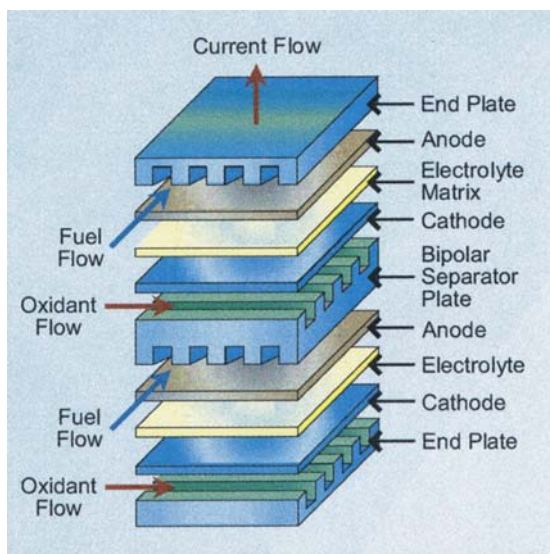


Figure 3. Schematic diagram of a planar SOFC stack (from Ref. 10).

A reduction in the cell operating temperature from  $\sim 1000^\circ C$  to  $\sim 750^\circ C$  may allow the more widespread use of metallic materials for the interconnections.

High-temperature ceramic materials based on  $LaCrO_3$  are currently used at temperatures up to  $\sim 1000^\circ C$  because they possess good electrical conductivity, are chemically compatible with the adjacent components of the fuel cell, are chemically stable in oxidizing atmospheres, and match the thermal expansion coefficients of the other cell components. The good mechanical strength, good electrical and thermal conductivity, and low price, however, make metallic interconnects very attractive in comparison. This attractiveness arises because ceramic materials are brittle and difficult to fabricate with more rejects and wastage during processing. As such, ceramic interconnects will remain expensive. Metallic interconnects, on the other hand, can be

mass produced using a variety of techniques: machining, pressing, stamping, and near-net-shape sintering of powders. From a component design standpoint, the parallel channels on the broad surfaces of the interconnection distribute the fuel and air to the electrode assembly, while the ridges separating the channels serve as the electrical contacts with the electrodes. Generally speaking, any material selected for interconnect applications should possess:<sup>8,11</sup>

- Good chemical and physical stability in the dual gas environment (i.e., air on the cathode side and fuel on the anode side) at the SOFC operational temperature;
- Good thermal fatigue resistance when cycled between room and the operating temperature;
- A coefficient of thermal expansion (CTE) compatible with the other components in the fuel cell stack, i.e., the cathode, the anode, and the electrolyte assembly;
- Good electrical and thermal conductivity; and
- Compatibility with seals and other electrical contact materials.

In addition, materials and component costs must remain reasonable in terms of selection criterion.

Attempts have been made to use heat-resistant steels containing significant Ni as interconnect materials. However, this has led to a thermal expansion mismatch between the metallic interconnect and the ceramic SOFC components which caused problems with seals and residual stresses from thermal cycling. The situation has changed somewhat with the use of low-CTE chromia-forming steels.<sup>12</sup>

### **CHROMIA-FORMING METALLIC MATERIALS**

Scales formed on Fe-Cr steels in H<sub>2</sub>-H<sub>2</sub>S mixtures exhibit less adherence to the substrate, and can be porous and cracked. These scales consist of at least two layers, with sulfides of the steel alloying additions occurring in the inner layer adjacent to metal. The corrosion rate depends on the H<sub>2</sub>S concentration. This behavior is shown in Fig. 4.<sup>13</sup>

The higher concentration of H<sub>2</sub>S, the higher the corrosion rate will be. It is worth pointing out that low-alloyed Cr steels, containing up to 12% Cr, practically corrode at the same rate as plain carbon steel.

It was found that sulfur corrosion of stainless steel, high-Cr ferritic steel and a low-Cr steel had a non-uniform character, as shown in Figure 5. It was also clear that the Cr and Ni content affected the overall corrosion rate. At higher temperatures, corrosion rate decay is observed.

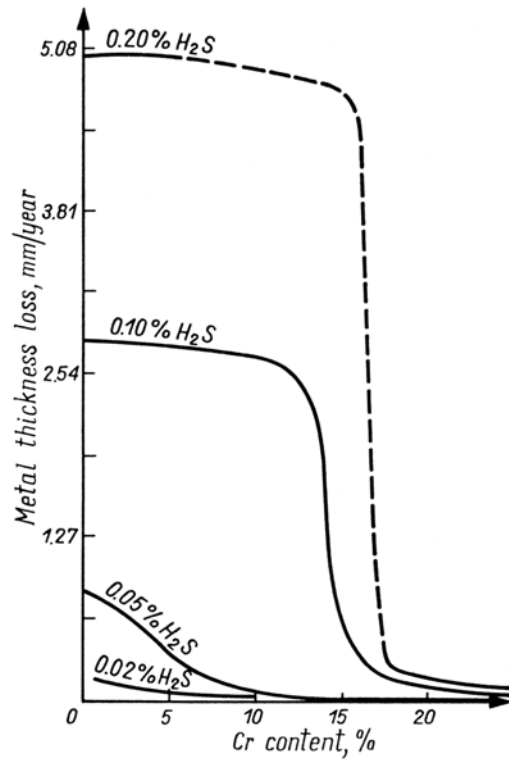


Figure 4. Sulfur corrosion rate of Fe-Cr alloys as a function of alloy composition and  $H_2S$  concentration (from Ref. 13).

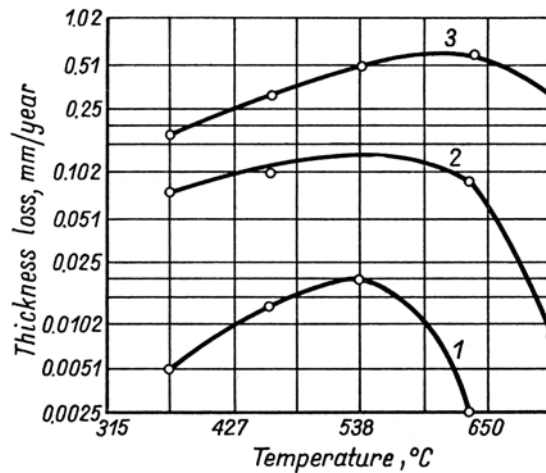


Figure 5. Sulfur corrosion rate of alloyed steels as a function of temperature in an  $H_2$ - $H_2S$  environment: 1) 18-8 Cr-Ni austenitic steel; 2) ferritic steel with 7 to 16% Cr; 3) steel with 3% Cr (from Ref. 13).

## RESEARCH APPROACH

In order to facilitate incorporation of metallic interconnects into SOFC systems, the performance characteristics of the most promising metallic alloys must be investigated in simulated SOFC environments<sup>14-17</sup>, as well as environments containing small quantities of sulfur. As an additional benefit of this research, the knowledge gained can be used to better select alloys for BOP applications in heat exchangers, recuperators, fuel processors, de-sulfurization units, pipes and tubes, and other ancillary equipment.

Research at the U.S. Department of Energy, Albany Research Center (ARC), has focused on developing high temperature materials that can be used in various sections of a SOFC system with special emphasis on metallic interconnects. This research to date has investigated alloy design and development strategies whereby the CTE of the metallic interconnect can be controlled to match more closely the CTE of the electrode assembly. To date exposure studies have been performed on these and other candidate alloys in air and in an air-H<sub>2</sub> environment. In addition, surface modification strategies have also been pursued to extend the operational envelop of lower cost alloys to higher temperatures and more severe environments.

A next step in the ARC research program will be to expose developmental nickel alloys and steels, as well as standard stainless steels and nickel alloys, to a H<sub>2</sub>+H<sub>2</sub>S environment. The exposure environment will be varied as a function of H<sub>2</sub>S concentration and temperature, respectively. A tubular geometry was selected for its simplicity and utility. The advantages of a tube approach to these fundamental exposure studies include:

1. Multiple alloy sample exposure to the H<sub>2</sub>+H<sub>2</sub>S environment during one experimental test run. (The tubes will be made up of a series of alloys, welded together to create a tube of the appropriate length for the tube furnace.)
2. Ability to run control experiments in conjunction with the H<sub>2</sub>+H<sub>2</sub>S environment experiments. (In a multi-tube configuration, for example, three identical tubes could be run, one with air passing through the tube, one with H<sub>2</sub> passing through the tube, and one with H<sub>2</sub>+H<sub>2</sub>S mixture passing through the tube. In addition, air will surround the tubes in the furnace set-up.)
3. Assessment of welded joints between similar and dissimilar alloys under the various exposure environments. (In addition to assessing the corrosion performance of the developmental and commercial alloys, the effects usually associated with the welding of these materials can also be investigated and assessed. For example, possible element segregation leading to sensitization can be determined.)
4. Easy control of experimental parameters. (Since the tubes will be placed in a tube furnace, temperature, gas flow rate, gas chemistry, and surrounding environment can be precisely controlled and measured.)



5. Ease of sample characterization and analysis of metal loss due to corrosion after exposure. (The cylindrical geometry allows easy sectioning of samples for metallographic examination and analysis. Sectioning, mounting and polishing will preserve scales on the inside and outside of the tubes. Welded joints as well as the non-welded alloy can be examined at the same time for each set of exposure conditions. The cylindrical geometry allows for easy determination of material wastage.)

To quantify material wastage for tubular samples, the following equation will be used:

$$Metal\ Loss_{avg} = \frac{1}{N} \sum_i^{i=N} (D - D_i)^{-2} \quad (8)$$

where D is the original diameter of the tube before exposure,  $D_i$  is the diameter of structurally intact alloy after exposure, and N is the number of measurements on the test sample.<sup>18</sup>

As the research progresses a clearer picture of how iron- and nickel-base alloys perform in SOFC environments will emerge. It is hoped that these studies will lead to strategies of material selection for SOFC environments by understanding more completely the complex interaction of materials and environment.

## CONCLUSIONS AND SUMMARY

The types and levels of impurities in possible fuels streams for SOFC operations depend upon natural source of the fuel and the manner in which hydrogen production occurs.

Sulfur is one of the major impurities found in natural gas, and it is intentionally added in a variety of forms as a safety precaution. However, H<sub>2</sub>S may also occur in natural gas and other hydrocarbon fuel precursors, and its presence causes a reduction in SOFC cell performance. Another complication factor to consider is that Fe-Cr and Ni-based metallic materials are susceptible to sulfur corrosion.

ARC has designed a research approach whereby Ni-based experimental and commercial alloys, as well as ferritic and austenitic steels will be tested in hydrogen fuels containing H<sub>2</sub>S.

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