A Solid Oxide Fuel Cell Running on H_2S/CH_4 Fuel Mixtures

Zhe Cheng,[a,*] Shaowu Zha,[a,**] Luis Aguilar,[b] Dean Wang,[c] Jack Winnick,[b,**]
and Meilin Liu[a,**,z]

[a]*School of Materials Science and Engineering,* [b]*School of Chemical and Biomolecular Engineering,*
Georgia Institute of Technology, Atlanta, Georgia 30332, USA
[c]*Shell Global Solutions, Houston, Texas 77252, USA*

Solid oxide fuel cells (SOFCs) that were capable of running on sour natural gas were fabricated and tested. The electrolyte of the SOFCs was yttria-stabilized zirconia (YSZ), the anode material was a strontium-doped lanthanum vanadate with a nominal composition of $La_{0.7}Sr_{0.3}VO_3$ (LSV), and the cathode was a porous composite of $La_{0.85}Sr_{0.15}MnO_3$ (LSM) and YSZ. The observed peak power density at 950°C was 280 mW/cm^2 when 5% H_2S/95% CH_4 gas mixture was used as the fuel and ambient air as the oxidant. Analysis of the effluent gas from the SOFC indicated that, apart from being oxidized electrochemically to sulfur and SO_2, a significant portion of the H_2S was transformed to carbon disulfide (CS_2), an important solvent currently used to dissolve heavy hydrocarbon deposits. The results indicated that SOFCs with a LSV anode might be used for the processing of sour natural gas (containing CH_4, H_2S, etc.) in which both electricity and high value chemicals (i.e., sulfur and CS_2) are produced simultaneously.
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Sour natural gas usually contains a significant amount of hydrogen sulfide (H_2S), which must be removed before the fuel source may be utilized. In some instances (e.g., the production of the natural gas is relatively low compared to the production of crude oil or the facility is in a remote and desolate location), there is little financial incentive for sour natural gas clean-up, transport, and storage facilities at the drilling site, and it is usually flared. In addition to the lost fuel credits, the flaring of sour natural gas would result in increased emissions of carbon dioxide (CO_2) and sulfur dioxide (SO_2). How to use the sour natural gas more effectively is a problem of great ecological and economical interests to the oil and gas industry. In recent years, it was proposed that the sour natural gas could be used for hydrogen generation through the reaction between methane (CH_4) and hydrogen sulfide[,2]

$$CH_4(g) + 2H_2S(g) \rightarrow CS_2(g) + 4H_2(g) \qquad [1]$$
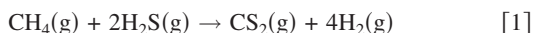
This process consumes H_2S and CH_4 and produces H_2 and CS_2, both of which are higher value chemicals and have wide applications.

However, an alternative way of processing and utilizing sour natural gas could be realized via a specially designed solid oxide fuel cell (SOFC) system. A SOFC is known to be capable of using a variety of fuels from hydrogen to hydrocarbons. Recently, it has been demonstrated that the SOFC could operate on fuels containing high concentrations of H_2S if the Ni/YSZ anode is replaced by other candidate anode materials.[3-10] In particular, it has been shown that certain anode materials even exhibited enhanced activity when H_2S was present.[6-8,10] Therefore, a promising alternative to the flaring of sour natural gas is to use SOFCs for its treatment. H_2S could be selectively oxidized through the electrochemical reaction at the anode, which generates electricity. At the same time, higher value chemicals may also be produced in the system: elemental sulfur could be generated through thermal cracking and partial electrochemical oxidation of H_2S; carbon disulfide (CS_2) may be produced via the reaction between sulfur and methane

$$CH_4(g) + S_2(g) \rightarrow CS_2(g) + 2H_2(g) \qquad [2]$$
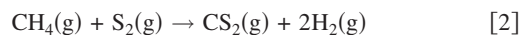
Reaction 2 is thermodynamically favorable and is expected to proceed to a greater extent when the generated H_2 is consumed through electrochemical oxidation on the anode. As a result, in addition to providing the drilling site with a viable source of electricity for daily operations, such a SOFC system might also produce CS_2, an important chemical which is currently used to dissolve heavy hydrocarbon

deposits and facilitate their removal from ground wells. Figure 1 is an ideal schematic to illustrate such a fuel cell system. The CH_4/H_2S fuel mixture is fed directly to the SOFC, where the electrochemical and chemical reactions proceed simultaneously to produce electricity and high value chemicals. The SOFC effluent (containing CH_4, sulfur, CS_2, and oxidation products such as H_2O, CO_2, and SO_2) could be separated; the methane and sulfur would be collected for commercial use while the rest of the gas (CS_2, CO_2, and SO_2, etc.) would be compressed and reinjected to the ground. This would bring CS_2 to the ground as a solvent for heavy crude oil and, at the same time, capture any CO_2 or SO_2 as opposed to their release into the atmosphere. A series of recycles could be incorporated as part of the design to optimize the total fuel utilization of the system.

In this paper, we report the initial results of our investigation on SOFCs running directly on a H_2S/CH_4 fuel mixture. The anode material was a strontium-doped lanthanum vanadate with a nominal composition of $La_{0.7}Sr_{0.3}VO_3$ (LSV). It has been shown that this material has good chemical resistance to H_2S at elevated temperatures, high electrical conductivity in a reducing atmosphere, excellent thermal match with YSZ electrolyte, and good catalytic activity.[8] The idea of producing electricity and higher value chemicals simultaneously by using a SOFC system is demonstrated. The effectiveness of the system is analyzed, and the directions for future research are discussed.

Experimental

The anode material, $La_{0.7}Sr_{0.3}VO_3$, was prepared using a solid-state reaction method. The precursors were La_2O_3 (Aldrich, 99.9%), $SrCO_3$ (Aldrich, 99.9+%), and V_2O_5 (Aldrich, 99.6%). The La_2O_3 and $SrCO_3$ were calcinated in air at 800 and 300°C, respectively, for 2 h to remove the adsorbed moisture. The powders were mixed, ground for 1 h, and cold-pressed into cylindrical pellets at 70 MPa. The pellets were calcinated at 1450°C for 5 h in 4% H_2 balanced by Ar (4% H_2/96% Ar) followed by repeated grinding and calcination until the complete reaction and uniform composition were achieved, as confirmed using powder X-ray diffraction (XRD, PW1800 X-ray diffractometer, Philips Analytical). The cathode material, $La_{0.85}Sr_{0.15}MnO_3$ (LSM), was synthesized using a glycine-nitrate combustion process described elsewhere.[11] 8% yttria-stabilized zirconia (YSZ, TZ-8Y, Tosoh) was cold-pressed at 75 MPa into cylindrical pellets, followed by firing at 1550°C for 5 h to obtain YSZ pellets (10 mm diameter and 250 μm thickness) with a relative density greater than 95%. A slurry consisting of LSM and YSZ (70:30 wt %), organic binder (V-006, Heraeus), and acetone was applied to one side of the YSZ pellets by brush-painting. The coated pellets were fired at 1200°C in air for 2 h to form a porous LSM-YSZ composite cathode. Another slurry consisting of $La_{0.7}Sr_{0.3}VO_3$ and V-006 was then applied to the other side of the YSZ pellets by
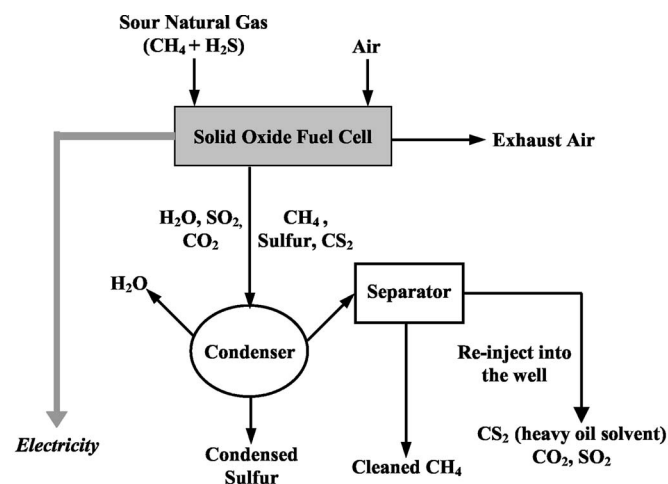
Figure 1. Schematic for the co-generation of electricity and high value chemicals (sulfur and CS_2) in a SOFC using sour natural gas as the fuel.

brush-painting. The nominal electrode area was ~ 0.25 cm^2. A thin layer of platinum paste was applied to both the anode and the cathode of each cell to enhance current collection. Pt gauzes (52 mesh, Alfa Aesar) and wires were used as the current collector and lead wires, respectively. The cell was sealed onto an alumina tube using a ceramic adhesive (Autostic™ FC6, Flexbar) and heated up to 950°C at 1°C/min in H_2 and held at 950°C for 2 h to fire the anode in situ. Then, at 950°C, the *I-V* curves of the cell were measured using a potentiostat/galvanostat (273A, EG&G PAR) in pure H_2 and 5% H_2S balanced by CH_4 (5% H_2S/95% CH_4), respectively. The fuel flow rate was kept at 15 cm^3/min. The effluent gases from the SOFC under different conditions [open circuit, constant current ($i = 160$ mA/cm^2 and $i = 400$ mA/cm^2)] were analyzed using a mass spectrometer (HPR-20, Hiden Analytical). The range of mass/charge ratio detected was 1-80 and the increment was 0.01.

Results and Discussion

Figure 2 shows the performances of the cell operated at 950°C. The peak power density was as high as 280 mW/cm^2 in 5% H_2S/95% CH_4. This performance is the highest ever reported for fuel cells operating on similar fuel mixtures.[2] It is very interesting to note that the cell performance in 5% H_2S/95% CH_4 was almost double that in pure H_2. (The peak power density in pure H_2 fuel was only 155 mW/cm^2.) This result was consistent with the
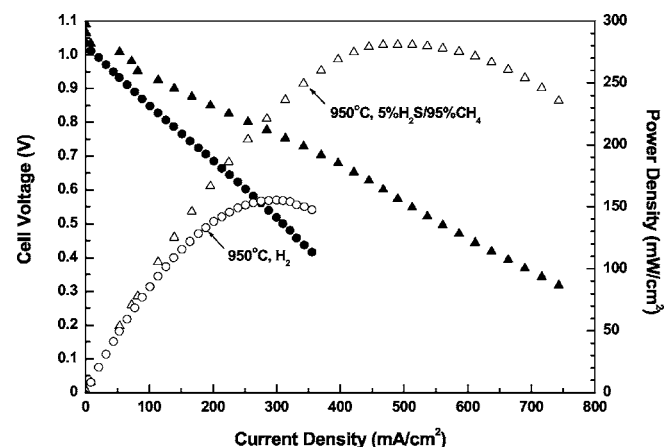

Figure 2. Performances of the SOFC with $La_{0.7}Sr_{0.3}VO_3$ anode at 950°C in pure H_2 and 5% H_2S balanced by CH_4 (5% H_2S/95% CH_4), respectively.

Table I. Compositions of the exhaust gases from the SOFC with $La_{0.7}Sr_{0.3}VO_3$ anode running on 5% H_2S/95% CH_4 fuel mixture at 950°C.

Species	$E = $ OCV $i = 0$	$E = -0.7$ V $i = 160$ mA/cm^2	$E = -0.5$ V $i = 400$ mA/cm^2
H_2	29.61%	20.79%	12.09%
CH_4	57.45%	71.27%	76.87%
H_2O	1.37%	5.67%	6.87%
H_2S	1.23%	1.12%	2.72%
CO_2	0.12%	0.41%	0.79%
SO_2	0.07%	0.22%	0.31%
CS_2	0.27%	0.52%	0.36%

observation that the cell interfacial resistance decreased significantly as H_2S was introduced into the fuel flow.[6-8] The reason for this behavior is not very clear at the moment as it is contrary to the normally expected poisoning effect of sulfur on catalysts. Because it was shown that bulk $La_{0.7}Sr_{0.3}VO_3$ was chemically resistant to fuels containing 10% H_2S at 950°C,[8] one hypothesis for the observed sulfur-enhancement behavior is that the surface of the $La_{0.7}Sr_{0.3}VO_3$ anode material transformed to a certain surface sulfide when a high concentration of H_2S was present and the surface sulfide was a better catalyst for the electrochemical reactions. Another possibility is that the $La_{0.7}Sr_{0.3}VO_3$ anode material does have better activity towards the electrochemical oxidation of H_2S than that for H_2. Further analysis, especially surface characterizations, would be required to clarify this point. The cell performance was maintained for 4 h before degradation was observed. The degradation was attributed to the slow delamination of the anode from the electrolyte since the anode was only heat-treated at fairly low temperature (950°C).

After the test, the cell assembly was disassembled. No carbon distain was found on the anode by visual observation. There was some carbon deposited on the wall of the effluent gas tube, which was in the intermediate temperature zone of the furnace. The carbon should come from the thermal cracking of methane

$$CH_4(g) \rightarrow C(s) + 2H_2(g) \quad [3]$$
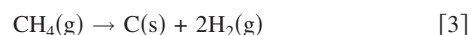
The carbon deposition in the fuel exit is expected to diminish if the operating temperature is lowered. In current research, the use of 250-μm-thick YSZ electrolyte limited the cell operating temperature to above 900°C. It is expected that the operating temperature could be dropped significantly, if the electrolyte thickness is reduced and, as a result, carbon deposition would become less of a concern.

The effluent gases from the SOFC running on 5% H_2S/95% CH_4 fuel mixture were analyzed using mass spectrometry (MS). Table I lists the estimated compositions of the effluent gases from the SOFC under open circuit and cell operating conditions ($E = -0.7$ V, $i = 160$ mA/cm^2 and $E = -0.5$ V, $i = 400$ mA/cm^2). As expected, the majority of the effluent gas was methane and hydrogen. We did identify the presence of CS_2. In fact, CS_2 accounted for ~ 0.3-0.5% of the total effluent gas, which was quite high considering there was only 5% H_2S in the feed. Elemental sulfur was not detected by MS because the equilibrium vapor pressure of sulfur at room temperature is extremely low. Yellow solid condensates, which were identified as sulfur using Raman spectroscopy, were observed in the exhaust fuel line. Table II lists the fractional conversion from H_2S to different sulfur-containing species. [The fractional conversion is defined as the molar ratio of the amount of H_2S transformed to a specific product (e.g., SO_2) to the total amount of H_2S in the feed. This fractional conversion was calculated based on the approximation that all of the H_2 in the effluent gas came from the decomposition of CH_4.] Several observations could be made about the conversion of H_2S. First, significant portions of H_2S transformed to sulfur (15-52%) and CS_2 (14-24%), which is encouraging as preliminary results. Second, the fraction of H_2S oxidized to SO_2 increased with increasing fuel utilization. Future work would be

Table II. Fractional conversion from H_2S to different sulfur-containing species in the SOFC with $La_{0.7}Sr_{0.3}VO_3$ anode running on 5% H_2S/95% CH_4 fuel mixture at 950°C.

Reactant	Product	E = OCV $i = 0$	$E = -0.7$ V $i = 160$ mA/cm^2	$E = -0.5$ V $i = 400$ mA/cm^2
H_2S	H_2S	32.3%	25.8%	61.4%
	CS_2	13.9%	23.7%	16.2%
	Sulfur	52.0%	45.3%	15.4%
	SO_2	1.7%	5.2%	7.0%

required to establish the possible relationships between fractional conversion from H_2S to CS_2 and the cell operating conditions (i.e., current density, temperature, etc.).

Conclusions

A solid oxide fuel cell with a $La_{0.7}Sr_{0.3}VO_3$ anode was operated successfully on 5%H_2S/95%CH_4 fuel mixture. The acceptable cell performance indicates that the anode material has good activity towards H_2S oxidation. In addition, high value chemicals such as elemental sulfur and CS_2 were generated at significant concentrations in the SOFC, indicating that $La_{0.7}Sr_{0.3}VO_3$ anode based SOFC could be a promising alternative for the processing of sour natural gas. The long-term stability of the proposed configuration and the mechanism for electrochemical oxidation of H_2S at the $La_{0.7}Sr_{0.3}VO_3$ electrode need to be investigated in the future.

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