

High-Activity Mo-Ni-S Anode Catalysts for H₂S-Air Solid Oxide Fuel Cells

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Abstract: A highly active and stable composite anode catalyst for a H₂S-air fuel cell has been developed based on the requirements of three-phase boundary (TPB) theory. The anode material is based on a metal sulfide (Mo-Ni-S) catalyst, admixed with Ag as electronic conductor and yttria-stabilized zirconia (YSZ) as ionic conductor. A fuel cell using a 0.2 mm thick YSZ membrane produced a maximum power density 42 mW cm⁻² at 750°C and over 200 mW cm⁻² at 850°C. Dilution of H₂S with CO₂, which often presents in the H₂S feed from an amine regenerator, reduces the open cell voltage, maximum current density and maximum power density.

Key words : solid oxide fuel cell, hydrogen sulfide, molybdenum sulfide, anode, three-phase boundary.

1. INTRODUCTION

H₂S is one of the most poisonous and abundant air pollutants. Currently, a large quantity of H₂S is converted to elemental sulfur using the Claus process. Fuel cell technology provides a more desirable alternative method of converting H₂S by generating high-grade electric power from the large amount of chemical energy associating with the oxidation of H₂S [1]. The first H₂S-air solid oxide fuel cell (SOFC) was reported in 1987 [1]. Since then, many efforts have been directed toward development of anodes appropriate for the stringent operating environment [2-7]. Metal sulfides have been generally considered as the most promising candidates, such as thiospinels [2], WS₂ [2,3], CoS_{1.035} [3], or Li₂S/CoS_{1.035} [3]. MoS₂-based materials have been tested as anode materials for H₂S-air SOFC and have shown promise for industrial applications [6,7]. However, MoS₂ is a semiconductor that does not have significant ionic conductance.

The present work is directed to development of more efficient anodes for H₂S-air SOFC based on sulfides of a combination of Mo and Ni, using yttria-stabilized zirconia (YSZ) as ionic conductor and Ag as electronic conductor. Sulfide catalysts based on combinations of Mo and other metals are known to be effective for activation of H₂S [8].

According to the three-phase boundary (TPB) theory, a lack of efficient electronic or ionic conduction paths in electrodes would effectively limit the performance of fuel cells. Consequently, the catalyst system described herein has been designed to address this problem by inclusion of both an electron conductor and a porous ion-conducting oxide material.

2. EXPERIMENTAL

Anode catalyst materials were prepared by initially mechanically mixing MoS₂ (Sigma-Aldrich, <2 micron) with NiS (Sigma-Aldrich, 150 mesh) in the weight ratio 1:1, and then drying the mixture at 110°C in an oven under ambient atmosphere. Composite catalysts were prepared by further mixing this material with 5wt% of one or each of Ag powder (Sigma-Aldrich, 2-3.5

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microns) and/or YSZ (Toso TZ-8Y). A paste in α -terpineol of a catalyst mixture was screen-printed onto one side of a YSZ disk (0.2 mm thick, Intertec Southwest ZO-8Y). The assembly was heated in N_2 atmosphere at up to 1050°C for two hours. Pt was used as cathode with an effective area of 1 cm².

The test cell was configured as previously described in [5-7]. Briefly, to install the positive-electrolyte-negative (PEN) unit into the fuel cell test station, the cathode side first was attached to a supporting annular ceramic disk with Aremco 503 sealant and dried in air. The supporting disk and attached PEN assembly were then sealed between two Al₂O₃ peripheral tubes, with the unattached side of the supporting disk facing the cathode chamber. Platinum mesh was used as current collector, and was refreshed in the flame of a gas lamp before each experiment. The sealed cell was heated in a tubular furnace (Thermolyne F79300), with air passing through the cathode chamber and nitrogen through the anode chamber. To cure the sealant, the furnace temperature was increased slowly to 250°C, at which temperature it was kept for 1 hr before being increased to 750°C for further curing. Pure H₂S was used as anode feed and air as the cathode feed. Both feeds were controlled at a flow rate of 25 mL/min with Matheson flow controller.

Cell current-voltage curves and morphological characterization were conducted to elucidate the improvement of anode performance. Current-voltage curves were recorded potentiodynamically with a Gamry electrochemical system (PC4-750) in the IR compensation mode at cell temperature 750, 800 or 850 °C, respectively.

Surfaces of fresh and used samples of anode catalyst materials were examined using SEM with a Hitachi S-2700 Scanning Electron Microscope.

The effect of CO₂ in the anode feed stream on the performance of a fuel cell having [90% Mo-Ni-S + 5% Ag + 5% YSZ] anode catalyst was determined by comparing the performance of the fuel cell using pure H₂S with mixtures in which H₂S was diluted with 15, 50 and 85% CO₂, respectively. The compositions of the feed gas mixtures were determined by independently controlling the flow rates (using Matheson mass flow controllers) of CO₂ and H₂S flowing into a single anode feed line in the corresponding ratio and with the total flow rate being controlled at 25 mL/min. Fuel cell performance using H₂S-CO₂ mixtures was determined at 750 and 850°C. In each case, after the operating parameters of the fuel cell had been adjusted, the OCV of the cell was allowed to stabilize under open circuit conditions before performance data were measured.

3. RESULTS AND DISCUSSION

3.1 Catalyst composition

We had shown previously that metal sulfides, and in particular MoS₂, had superior catalytic activity over Pt as anode catalysts in H₂S-air SOFC [6]. Herein we will show that the composite sulfide Mo-Ni-S offers the advantages of higher activity and greater stability than catalysts based on MoS₂ alone when used as anode catalysts for electrochemical conversion of H₂S.

MoS₂ is active as an anode catalyst for H₂S-air fuel cells, both at moderate and higher temperatures [5-7]. However, MoS₂ is volatile and tends to sublime out of the anode compartment of high temperature fuel cells, resulting in an irreversible loss in activity with time on stream. A composite metal sulfide catalyst was prepared by heat treatment of an admixture of MoS₂ with NiS to form a new Mo-Ni-S anode catalyst. This new material was not volatile at the operating temperature of our H₂S-air fuel cell (750-850°C) [5-7]. We have also found that the composite sulfide catalyst has enhanced catalytic activity compared with MoS₂ (see table 1 below). It was known that related composite sulfides are active catalysts for hydrodesulfurization of hydrocarbons [8] and has shown to be active for conversion of H₂S in a low or intermediate-temperature fuel cell [9].

Table 1: Cell maximum current and power at different operating temperature

Temp (°C)	750		850	
	Current (mA/cm ²)	Power (mW/cm ²)	Current (mA/cm ²)	Power (mW/cm ²)
Anode				
MoS ₂	33	6	47	10
MoS ₂ + Ag (10%)	36	4	48	5
MoS ₂ + Ag (5%)	27	5	32	7
+ YSZ				
Mo-Ni-S	60	8	99	14
Mo-Ni-S + Ag	65	7	108	19
Mo-Ni-S + YSZ	52	13	93	26
Mo-Ni-S + Ag	234	42	819	203
+ YSZ			(at 235 mV)	

However, we found that anode catalysts prepared from Mo-Ni-S alone had poor electronic and ionic conductivity. Further, performance of the fuel cell was limited by mass transfer effects at high currents [5]. Consequently, we have now designed and tested a composite catalyst to address these issues. The new composite catalysts comprised Mo-Ni-S admixed with up to 10wt% Ag and up to 10wt% YSZ [7]. Silver was selected because it is a good electronic conductor. Silver sulfide (Ag₂S) was unstable at the operating temperatures for our cell, and so Ag remained in the elemental form during operation of the cell in the presence of H₂S. YSZ was selected because it is an ion conducting oxide that is porous and is stable in the presence of H₂S. We will show that all three components were required

to achieve optimum performance of the catalyst system. To illustrate the effect of each component, we used admixtures of either MoS_2 or Mo-Ni-S with 5wt% of one or both of Ag and YSZ, and we then compared the activities of the composite admixtures of materials with those of the metal sulfide catalysts alone.

Current-voltage curves were obtained with H_2S -air SOFC using different anode materials: MoS_2 alone, [MoS_2 + Ag (10%)], [MoS_2 + Ag (5%) + YSZ], Mo-Ni-S alone, [Mo-Ni-S + Ag], [Mo-Ni-S + YSZ], and [Mo-Ni-S + YSZ + Ag]. Table 1 lists the values for maximum current and power for each catalyst.

The anodes having Mo-Ni-S as catalyst were superior to those based on MoS_2 . However, addition of either Ag alone or both Ag and YSZ had no strongly beneficial effect on performance of fuel cells with MoS_2 anode catalysts. Comparison of the data for MoS_2 alone and Mo-Ni-S alone showed that the performance of the composite sulfide catalyst was better than performance of MoS_2 . Further, the composite Mo-Ni-S catalyst was not volatile, in contrast to MoS_2 . MoS_2 sublimed from the anode compartment, but no material sublimed when the anode catalyst was Mo-Ni-S. Thus the Mo-Ni-S catalyst was not simply an admixture of MoS_2 and NiS; all Mo was incorporated into an involatile compound of all three elements.

At 750 °C, addition of Ag had little influence on Mo-Ni-S anode performance, indicating that the conductivity of Mo-Ni-S was not the limiting factor at 750 °C. The maximum current for [Mo-Ni-S + Ag] was 65 mA/cm². At 850 °C, addition of Ag improved the current and power densities. The maximum current density was 108 mA/cm² and power density was 19 mW/cm².

The addition of oxide ion conductor YSZ, but not Ag, caused a small decrease in the maximum current density of the Mo-Ni-S anode catalyst. This effect was attributed to the agglomeration of anode catalyst particles and consequent reduction in anode porosity, as shown by SEM (Fig. 1). However, when compared with the performance of fuel cells using anode catalysts without YSZ, the fuel cell using [Mo-Ni-S + YSZ] as anode catalyst showed higher voltage in both the reaction-controlling region and the mixing reaction kinetics/mass transport-controlling region. Consequently, there was an increase in maximum power density. These effects are attributed to improved ionic conductivity, resulting from YSZ providing an oxide-conducting path and thereby reducing resistance to ion transport and extending the reaction zone.

The greatest improvement in performance was observed using a composite anode comprising an intimately contacted mixture of finely divided materials having the approximate composition Mo-Ni-S (90wt%), Ag (5wt%) and YSZ (5wt%). In contrast to [Mo-Ni-S + YSZ], the three-component catalyst system [Mo-Ni-S + Ag + YSZ] did not agglomerate significantly (SEM, Fig. 2) and therefore remained porous. SEM showed

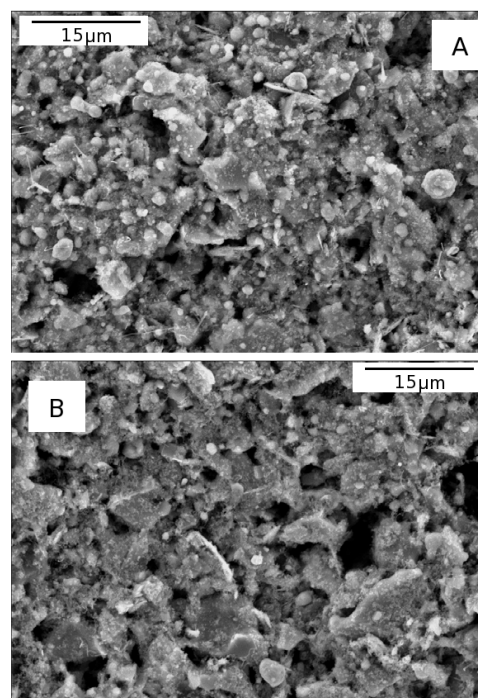


Figure 1: SEM of (a) [Mo-Ni-S] and (b) [Mo-Ni-S + YSZ] anode catalysts.

improved anode morphology with smaller particle size and consequently higher surface area. The average particle size was 4.3 microns, as compared with 8.5 microns for [Mo-Ni-S+YSZ] and 4.4 microns for Mo-Ni-S. The maximum current density was 234 mA cm⁻² at 750 °C and over 820 mA cm⁻² at 850 °C. This corresponded to the maximum power density of 42 mW cm⁻² at 750 °C and 203 mW cm⁻² at 850 °C (Fig. 3). A highly expanded reaction zone was developed in this anode. YSZ provided ionic conduction paths and Ag provided electronic conduction paths.

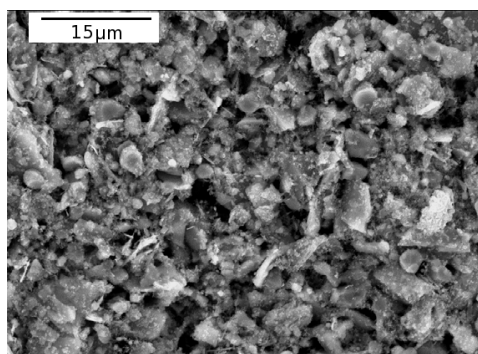


Figure 2: SEM of [Mo-Ni-S + Ag + YSZ] anode catalyst.

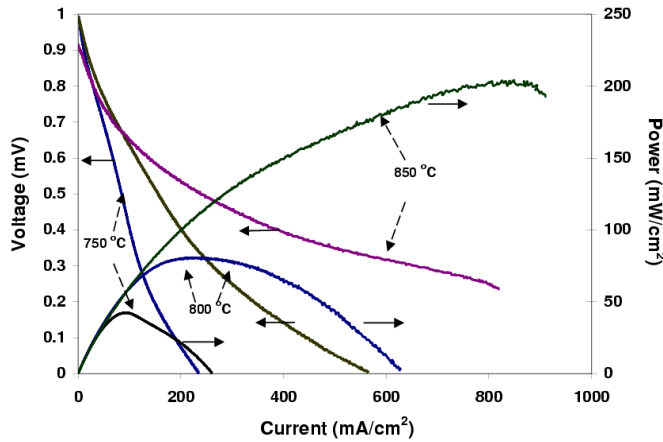
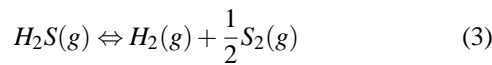
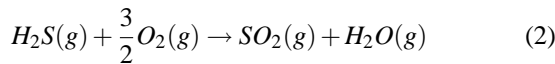
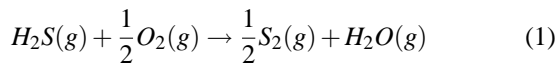


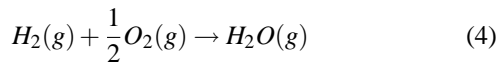
Figure 3: Performance of H₂S-air SOFC with 90wt% (Mo-Ni-S) + 5wt% Ag + 5wt% YSZ anode at 750°C, 800°C and 850°C.

3.2 Effect of dilution with CO₂

There are several possible overall cell reactions [5]. H₂S can be converted directly to SO₂ (Eq. 1) or to elemental sulfur (Eq. 2). Alternatively, H₂ may be formed by internal reforming of H₂S at temperatures in excess of 700°C according to Eq. 3.



The cell reactions will then include



The open circuit voltage generated by a fuel cell is a function of the concentration of the feed at each electrode, as described by the Nernst equation [10]. According to Nernst Equation, the theoretical cell voltages, V_1 , V_2 , or V_4 , for reaction 1, 2 and 4 are:

$$V_1 = V_1^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2S} P_{O_2}^{1/2}}{P_{S_2}^{1/2} P_{H_2O}} \right) \quad (5)$$

$$V_2 = V_2^o + \frac{RT}{6F} \ln \left(\frac{P_{H_2S} P_{O_2}^{3/2}}{P_{SO_2} P_{H_2O}} \right) \quad (6)$$

$$V_4 = V_4^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) \quad (7)$$

where V^o is the standard cell voltage, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and P is the partial pressure of the specified species.

Diluting H₂S with CO₂ resulted in lower partial pressure of H₂S (and therefore the lower partial pressure of H₂ in reaction 4), which resulted in decreased open cell voltage. In addition, the current density depends on the rate of reaction attainable at each electrode, and this too is a function of concentration. We have performed a series of experiments to examine the effects of diluting H₂S anode feed with CO₂ in the temperature range 750-850°C. The system was tested first with the stream having the highest CO₂ concentration (85%), and then the amount of CO₂ was reduced to 50% and then 15%, and finally the catalysts were tested using pure H₂S.

Dilution of H₂S anode feed with CO₂ reduced both the current density and the power density in the present cell (Figures 4,5). At 750°C, the OCV was reduced from 0.992 V to about 0.973 V, and at 850°C the OCV was reduced from 0.957 V to 0.934 V, as the concentration of H₂S was reduced from 100% to 15%. At 750°C, the current density at 50 mV decreased from over 280 mA/cm² for pure H₂S to about 256 mA/cm² for a 50:50 mixture of H₂S and CO₂, and then dropped to 226 mA/cm² for the mixture containing only 15% H₂S. The maximum power density for pure H₂S was 40 mW/cm² at 135 mA/cm², and was reduced to 26 mW/cm² at 121 mA/cm² for the mixture containing 15% H₂S.

At 850°C, the corresponding current densities and power densities were each higher. The current density at 160 mV decreased from over 800 mA/cm² for pure H₂S to about 652 mA/cm² for a 50:50 mixture of H₂S and CO₂, and then dropped to 548 mA/cm² for the mixture containing only 15% H₂S. The maximum power density was close to 200 mW/cm² at 540 mA/cm² for pure H₂S, was over 130 mW/cm² at 455 mA/cm² for the 50:50 mixture, and then dropped to 100 mW/cm² at 400 mA/cm² for the mixture having 15% H₂S.

There was no evidence for poisoning of the anode catalyst by CO₂. The data show that the new composite anode materials comprising metal sulfide catalysts admixed with Ag and YSZ have potential value as sulfur-tolerant catalysts for use in fuel cells.

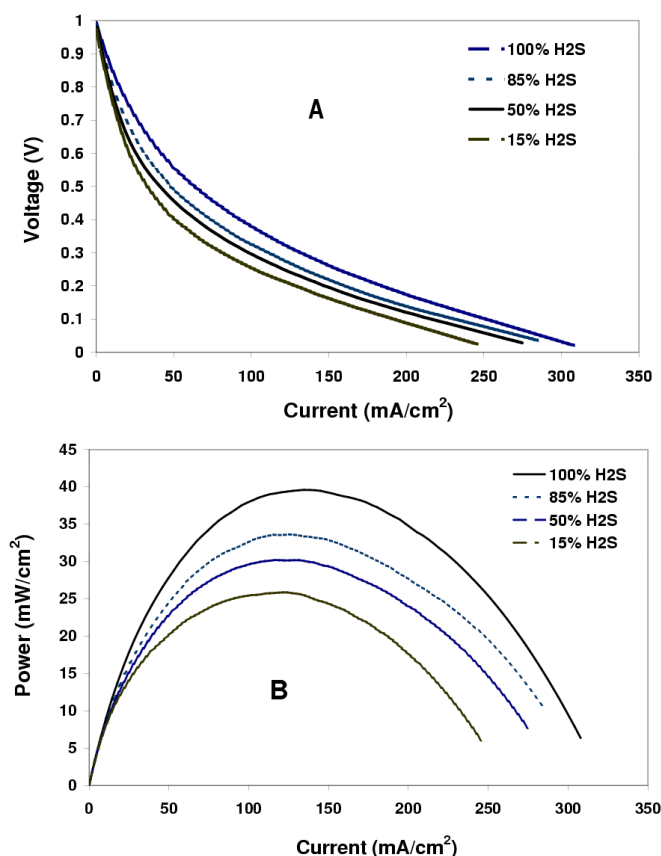


Figure 4: Effect of diluting H₂S feed in a (H₂S/CO₂)-air SOFC with [90wt%(Ni-Mo-S) + 5wt%Ag + 5wt% YSZ] anode at 750°C.

4. CONCLUSIONS

A highly active and stable composite anode catalyst for a H₂S-air fuel cell has been developed. The design of the catalyst is based on the requirements of three-phase boundary (TPB) theory. The anode material is prepared from a mixture comprising approximately 90wt% composite metal sulfide (Mo-Ni-S) catalyst prepared from MoS₂ and NiS (1:1 weight ratio), admixed with 5wt% Ag as electronic conductor and 5wt% yttria-stabilized zirconia (YSZ) as ionic conductor. A fuel cell using a 0.2 mm thick YSZ membrane produced a maximum sustainable current density over 234 mA/cm² at 750°C and over 800 mA/cm² at 850°C, and maximum power densities 42 mW/cm² at 750°C and over 200 mW/cm² at 850°C.

5. ACKNOWLEDGMENTS

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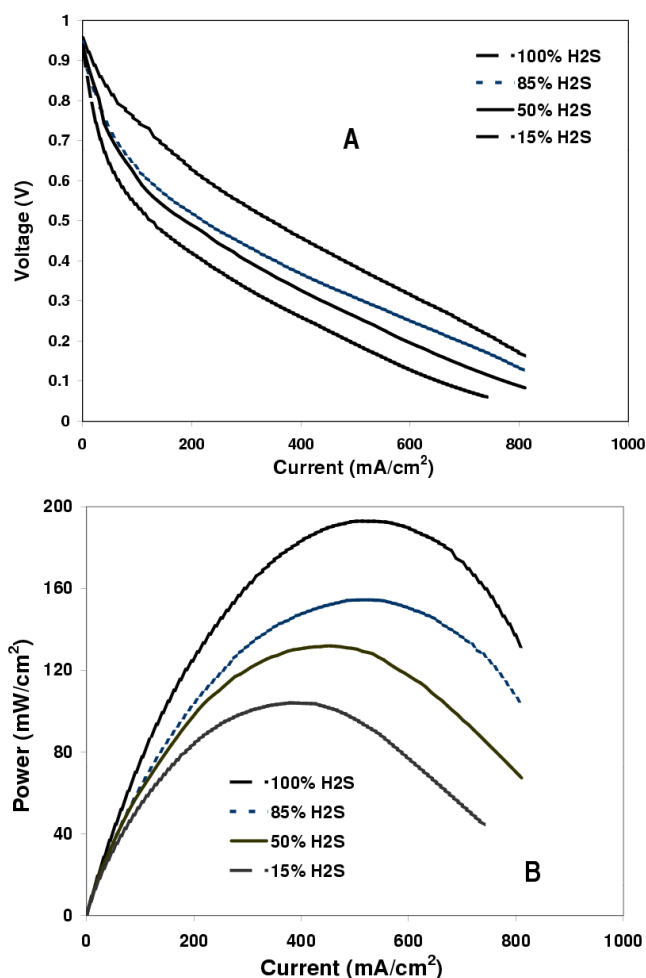


Figure 5: Effect of diluting H₂S feed in a (H₂S/CO₂)-air SOFC with [90wt%(Ni-Mo-S) + 5wt%Ag + 5wt% YSZ] anode at 850°C.

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