



Use of Metal Sulfides as Anode Catalysts in H₂S-Air SOFCs

Man Liu, Guolin Wei, Jingli Luo,^{*z} Alan R. Sanger, and Karl T. Chuang

Department of Chemical and Materials Engineering, University of Alberta, Edmonton,
Alberta T6G 2G6, Canada

Anode catalysts comprising MoS₂ and composite metal sulfides have been investigated for electrochemical oxidation of hydrogen sulfide in solid oxide fuel cells (SOFCs) at temperatures up to 850°C. All catalysts exhibited good electrical conductivity and catalytic activity at all temperatures. MoS₂ and composite catalysts were found to be more active than Pt, an established catalyst for high-temperature H₂S-air fuel cells at 650–830°C. However, MoS₂ itself sublimates above 450°C. In contrast, composite catalysts (M-Mo-S) derived from a mixture of sulfides of Mo and other transition metals (Fe, Co, Ni) have been shown to be stable and effective for electrochemical conversion of H₂S in SOFCs up to 850°C. Electrical contact is poor between platinum current collecting layers and metal sulfide anode catalysts. This problem has been overcome by mechanically mixing conductive Ag powder into the anode layer, instead of applying a thin layer of platinum to the anode.

© 2003 The Electrochemical Society. [DOI: 10.1149/1.1583715] All rights reserved.

Manuscript submitted October 4, 2002; revised manuscript received January 31, 2003. Available electronically June 16, 2003.

Hydrogen sulfide is often present in petroleum and natural gas, and is a by-product of processing operations such as hydrotreating. The concentration of H₂S present in natural gas ranges from trace amounts to more than 80%. Disposal and treatment of H₂S is regarded as a worldwide problem. Typically, gas processing plants convert this toxic gas into elemental sulfur and water vapor via the well-established Claus process.¹ The reaction is highly exothermic. Part of the energy can be recovered as low-grade energy in the heat and steam produced. However, it is much more desirable to recover this energy as electricity in a highly efficient manner, from both economic and environmental standpoints.

The feasibility for electrochemically oxidizing H₂S in a fuel cell was first demonstrated in the late 1980s.² This led to the investigation of alternative electrolytes and anode electrocatalysts for H₂S solid oxide fuel cells (SOFC).^{3–10} O^{2–} conducting yttria-stabilized zirconia (YSZ) electrolytes were the most commonly used electrolytes in H₂S SOFC. More recently, ceria-based O^{2–} conducting electrolytes^{4,5} and H⁺ conducting electrolytes^{7,8} have been shown to have some new advantages for H₂S fuel cells operated at temperatures below 700°C. New active anode materials (Li₂S/CoS_{1.035} and WS₂) were found to improve H₂S fuel cell performance greatly.⁶ In order to be a suitable candidate for the electrochemical oxidation of H₂S, an anode material must possess good electrical conductivity and sulfur tolerance at high temperatures, in addition to good catalytic activity. Pt anode catalysts have good catalytic activity, but degrade over time in H₂S streams.^{9,10} Moreover, most metals and metal oxides are severely corroded by H₂S at elevated temperatures. It is therefore intuitive to consider metal sulfides as alternative potentially useful catalysts.

Metal sulfides are inexpensive when compared with precious metals like Pt. Among them, MoS₂, a hexagonal layered n-type semiconductor, is a widely used component in catalysts for a variety of hydrogenation/dehydrogenation and hydrodesulfurization processes in the petroleum industry. Bimetallic sulfides of molybdenum with cobalt, iron, and nickel are each active catalysts for hydrodesulfurization processes.^{11–13} The activity is attributed in part to the presence of MoS₂-like aggregates. An important attribute of these catalysts is sulfur tolerance. MoS₂ also has been shown to be an effective catalyst for reversible decomposition of H₂S above 600°C,¹⁴ which indicates that MoS₂ is chemically stable in a high-temperature H₂S stream and is not poisoned. However, MoS₂ sublimates over 450°C at atmospheric pressure. The electrical conductivity of MoS₂ increases as the temperature approaches 400°C.¹⁵ Molybdenum disulfide supported on a conductive substrate is known

to be an active anode catalyst for H₂S-O₂ fuel cells operating at atmospheric pressure and 20–90°C,¹⁶ and at 120–145°C and 235–510 kPa.¹⁷

The objective of the present work is to examine the effectiveness of several MoS₂-based metal sulfides as anode catalysts in H₂S-air SOFC, by studying the electrochemical behavior of the cell. We show that MoS₂-based anode catalysts exhibit a combination of good electronic conductivity and better catalytic activity than Pt. We also show that composite anode catalysts M-Mo-S, prepared from mixed metal sulfides MS-MoS₂ (M = Fe, Co, Ni), have superior stability and activity up to 850°C. In order to overcome the poor electrical contact between the platinum current collecting layer and the anode layer, Ag powder was mechanically admixed into the anode material as the current collector instead of applying a platinum layer. We show that addition of Ag powder into the anode material Co-Mo-S improves cell performance and that the composite anode is stable over an extended period of time.

Experimental

Preparation of anode catalysts.—The sources of metal sulfides used as starting materials for preparation of anode catalysts were: MoS₂ (Aldrich, 99.9%), CoS (Alfa Aesar, 99.9%), FeS (Alfa Aesar, 99.9%) and NiS (Alfa Aesar, 99.9%). Two-component metal sulfides to be tested were made by initially mixing MoS₂ with one of the metal sulfides FeS, CoS, or NiS in 1:1 molar ratio. To get a uniform mixture, ethanol was added to the combination to make a suspension that was mixed thoroughly for several hours. Then ethanol was allowed to evaporate slowly, to leave the binary metal sulfides as powders. The binary metal sulfides were heat-treated in N₂ atmosphere at 1050°C for 2 h and allowed to cool under N₂ to room temperature. The resulting powders were then used to prepare the anode catalysts.

Measurement of electrical resistivity of anode catalysts.—The electrical resistivity of each anode catalyst was measured as membranes having the structure Pt/anode catalyst/Pt under a flow of N₂ at temperatures between 25 and 850°C.

A wafer of each catalyst was made by pressing the catalyst powder in a die at room temperature and a pressure of 47000 psi. Each catalyst disk so made was about 1 mm thick and 2.54 cm in diameter. Pt paste was painted onto both faces of the wafer, then each face was connected to a Pt lead. The catalyst disk was sealed between two ceramic tubes using ceramic sealant. Both faces were exposed to N₂ streams. The total resistance of the electrochemical apparatus, including that of the connecting wire, was determined using a Keithley 199 digital multimeter.

Cell preparation and construction.—The electrolyte wafers consisted of 8 mol % YSZ with a thickness of 0.2 mm and a diameter of

* Electrochemical Society Active Member.

^z E-mail: jingli.luo@ualberta.ca

Table I. Electrical resistivities of anode catalysts, MoS₂ or M-Mo-S.

Anode catalyst	Resistivity (Ω cm)						
	25°C	100°C	300°C	500°C	750°C	800°C	850°C
MoS ₂	210.17	198.02	178.78	63.31	9.12	8.10	7.60
Fe-Mo-S	96.22	53.68	11.14	8.61	8.61	6.08	4.56
Co-Mo-S	11.14	9.62	11.65	4.56	3.04	4.05	7.60
Ni-Mo-S	73.43	64.32	45.58	0.51	0.51	1.52	1.01

2.54 cm. Platinum paste was screen printed on one side of the electrolyte substrates as the cathode. After drying, the platinum film was fired in air at 1050°C for 30 min. Anode catalysts were applied as viscous pastes formed by mixing the metal sulfide powder with α -terpineol.

When the anode catalyst was MoS₂ or M-Mo-S, a layer of the paste (ca. 0.15 mm) was applied onto the other side of the YSZ membrane using a screen printing technique. Then, the cell was heated to 1050°C and held at that temperature for 30 min. The sintering of the metal sulfides necessarily was performed in an oxygen-free atmosphere to avoid formation of volatile MoO₃.¹² The membrane was cooled under N₂. Then, for anode catalysts containing no Ag powder, platinum paste was also painted on top of the sintered metal sulfides and dried. The porous Pt layer so formed was intended to serve as the current collector and improve electrical contact between the anode and the electrical lead.

When the anode catalyst was MoS₂ or M-Mo-S admixed with Ag, Ag powder (up to 10% by weight) was thoroughly mixed with the metal sulfide powder, and the mixture was mixed with α -terpineol to make the paste. The paste was applied to the anode face of the YSZ membrane and sintered as before. No Pt paste was applied to the anode of these cells.

A sheet of Pt mesh connected to a Pt lead wire was placed across the surface of each electrode. The membrane electrode assembly (MEA) was sealed between two alumina tubes arranged horizontally, using ceramic adhesive (Ceramabond 503, Aremco) placed on both sides of the electrolyte to seal the gas compartments. The cell was placed in a tubular furnace. Air and nitrogen flowed through cathode and anode chamber, respectively. The cell was brought slowly up to the operating temperature. Nitrogen was used as inert feed when the cell was not in use. Pure H₂S was used as the fuel gas, and air was supplied as the oxidant during all tests.

Electrochemical characterization of MEA.—Impedance measurements were carried out in the frequency range 0.5 Hz to 100 kHz using a Gamry EIS300 system. Potentiodynamic current-potential measurements were performed using a Gamry electrochemical measurement system (PC4-750) at a scan rate of 1 mV/s. Current-potential curves were corrected for ohmic voltage losses in

the system by subtracting ohmic drop (IR) from the measured potential, where the ohmic resistances (R) were calculated from the impedance spectra.

Volatility of catalyst materials.—The volatility of anode catalysts was determined by the formation of a mirror comprising sublimed material downstream from the anode. When MoS₂ alone was used as the anode catalyst, a MoS₂ mirror formed on the cell walls downstream from the anode. In contrast, when composite sulfides M-Mo-S were used, no mirror was formed. Similarly, when M-Mo-S admixed with Ag was used as the anode catalyst, no mirror was formed.

Results and Discussion

Resistivity of MoS₂ and M-Mo-S.—The electrical resistivities of anode catalyst samples with the structure Pt/anode catalyst/Pt are listed in Table I. The resistivity of MoS₂ wafer decreased rapidly as the temperature increased to 750°C, and was then approximately constant to 850°C. The data are consistent with the decrease of the electronic resistance of MoS₂ with increasing temperature.^{15,18} Above 750°C, the resistivity of MoS₂ wafer decreased to less than 10 Ω cm.

As shown in Table I, the electrical resistivities of the composite catalyst pellets Pt/M-Mo-S/Pt (M = Fe, Co, Ni) at the temperature range of 25–500°C were much lower than that of MoS₂. At a fuel cell operating temperature of 750–850°C, the resistivities of the composite anode catalysts were in the range 0.51–8.61 Ω cm. Thus the present anode catalysts have good electrical conductivity for use as anode catalysts under high temperature operations.

Electrochemical characteristics of metal sulfide anode catalysts MoS₂.—Figure 1 and 2 compare the performances of MoS₂ and Pt anode catalysts in H₂S-air SOFC at 800°C. The polarization characteristics with and without IR correction are shown in Fig. 1. In the low-current region, the MoS₂ anode showed a higher current output when compared with that of the Pt anode at the same voltage, which indicated that MoS₂ had a greater catalytic activity.¹⁹ However, it would be more desirable to have a good reference electrode,²⁰ which

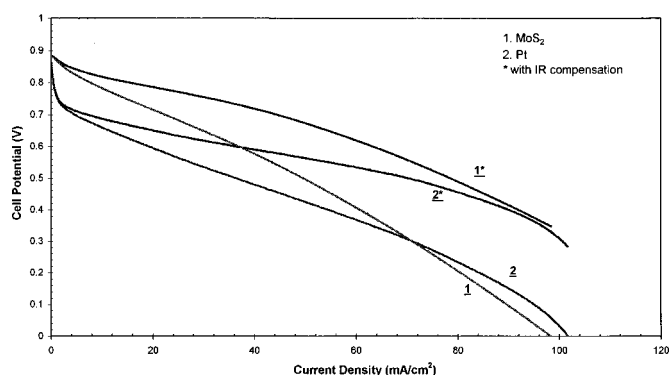


Figure 1. Comparison of potential-current relations obtained for MoS₂ and Pt at 800°C with and without IR correction.

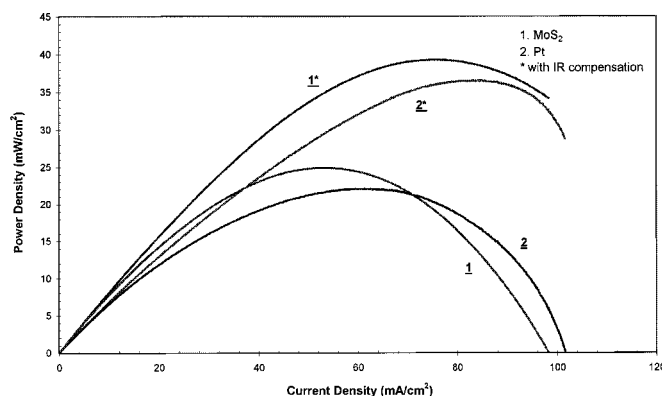


Figure 2. Relationship of current density to power density for H₂S-air fuel cell using MoS₂ and Pt as anodes at 800°C.

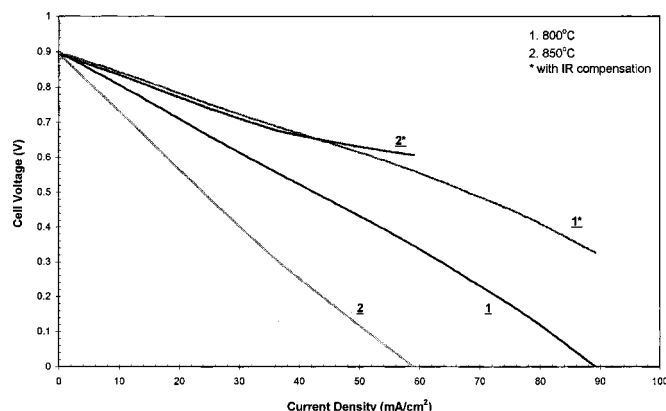
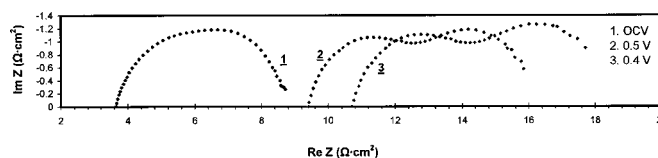
Table II. Cell area specific ohmic resistance (RA) using different anode catalysts under different operating temperatures.

Temperature (°C)	RA ($\Omega \text{ cm}^2$)				
	Pt	MoS ₂	Co-Mo-S	Fe-Mo-S	Ni-Mo-S
800	2.77	3.54	3.10	3.65	
850			4.01	10.28	8.85

will enable identification of anode effects more accurately. The maximum current density measured for Pt was 101 mA/cm², which was slightly higher than 98.3 mA/cm² for MoS₂, because of the lower ohmic resistance of the cell using Pt as anode. The ohmic resistance determined from impedance measurements (Table II) was 2.77 $\Omega \text{ cm}^2$ for Pt and 3.54 $\Omega \text{ cm}^2$ for MoS₂, from which the IR compensated I - V curves were derived. By comparing the actual I - V curves with those after IR correction, it was seen that the potential was reduced by as much as 384 mV for MoS₂. Thus it was necessary to reduce the internal ohmic resistance of the cell to improve cell performance.

In contrast to the I - V relations, the maximum power densities obtained for MoS₂ were higher than those for Pt, with and without IR correction (Fig. 2). After IR compensation, power densities as high as 40 mW/cm² are achieved for MoS₂ at 800°C. Although the IR-corrected curves do not exhibit the real cell performance, they show the potential value of MoS₂ as active anode catalysts. However, MoS₂ is volatile above 450°C. Thus there was continuous loss of MoS₂ in the anode stream, resulting in limited cell lifetime. Consequently, we have investigated M-Mo-S composite anode catalysts, as these materials are not volatile in the same temperature range.

Fe-Mo-S.—Figure 3 shows the current density vs. voltage behavior with Fe-Mo-S as the anode catalyst. In contrast to MoS₂ and the Co and Ni analogues, the maximum current density measured at 800°C was considerably higher than that at 850°C. The cause of this phenomenon was the large increase in the ohmic resistance of the cell from 3.65 $\Omega \text{ cm}^2$ at 800°C to 10.3 $\Omega \text{ cm}^2$ at 850°C (Table II), which exceeded the decrease in electrolyte resistance at higher temperature. The large increase in cell-area-specific ohmic resistance was mainly ascribed to detachment and/or poisoning of Pt thin film in H₂S gas, caused by electrochemical polarization at 800°C. Previously, we have shown that PtS was easily formed on the surfaces of Pt electrodes in high-temperature H₂S streams, and that electrochemical oxidation of H₂S on Pt/YSZ interface severely accelerated the formation of PtS and led to rapid detachment of the Pt anode from the YSZ.^{9,10} Although herein Pt served as the current collector and not as the catalyst, the large current flow had the same damaging effect. The failure of the contact between the Pt current collector and

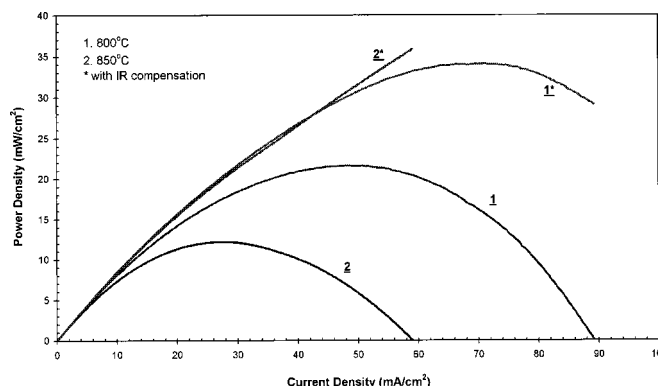
**Figure 3.** Relationship between current density and voltage using Fe-Mo-S as the anode.**Figure 4.** Impedance spectra for the cell using Fe-Mo-S as the anode catalyst at 800°C.

the catalyst may also have been affected by another cause, weak bonding of the Pt film to the anode Fe-Mo-S. The adverse effect of polarization on cell resistance can also be seen in Fig. 4, which shows how the cell resistance changed with polarization conditions at 800°C. The impedance spectra were measured under these conditions, open circuit, polarization at 0.5 V, and polarization at 0.4 V. The cell-area-specific ohmic resistance increased from 3.65 $\Omega \text{ cm}^2$ under open-circuit conditions to 9.39 $\Omega \text{ cm}^2$ at 0.5 V, then kept rising up to 10.7 $\Omega \text{ cm}^2$ at 0.4 V. However, when the temperature was increased to 850°C, the ohmic resistance dropped back to 10.3 $\Omega \text{ cm}^2$, which was consistent with the decrease in the YSZ electrolyte resistance at higher temperature. This indicated that the increase in operating temperature did not further deteriorate the electrical contact between the Pt current collector and the anode.

Figure 5 shows current density as a function of power density for the use of Fe-Mo-S as anode catalyst. The IR-corrected power density obtained at 800°C increased to 34 mW/cm². However, it was not possible to determine a maximum value for the IR-compensated power density for this system due to the large internal resistance.

Ni-Mo-S.—A bimetallic Ni-Mo-S anode catalyst has been tested at 850°C only. Figure 6 shows the cell voltage and power density as a function of current density, with and without IR correction. The maximum current density was 67.6 mA/cm². The ohmic resistance was 8.85 $\Omega \text{ cm}^2$, as determined by impedance spectroscopy (Table II). Consequently, IR corrections as high as 600 mV potential were calculated at maximum current density. The large resistance found for fresh samples indicates that the original electrical contact between the screen-printed Pt layer and this anode material was poor, even before any effects resulting from polarization. Thus, as was found for Fe-Mo-S, the maximum IR-corrected value for power density at 850°C cannot be determined. Postmortem inspection of the materials showed that the Pt film had become detached from the anode during testing. Thus Pt film alone cannot be used as the current collector on Ni-Mo-S anode catalysts.

Co-Mo-S.—Use of Co-Mo-S as the anode catalyst in H₂S-air fuel cell gave better cell performance than either Fe-Mo-S or Ni-Mo-S. Figure 7 shows the relationship of current density to cell voltage for Co-Mo-S anode at 800 and 850°C. The maximum current density

**Figure 5.** Relationship between power density and current density for the cell using Fe-Mo-S as the anode at 800 and 850°C.

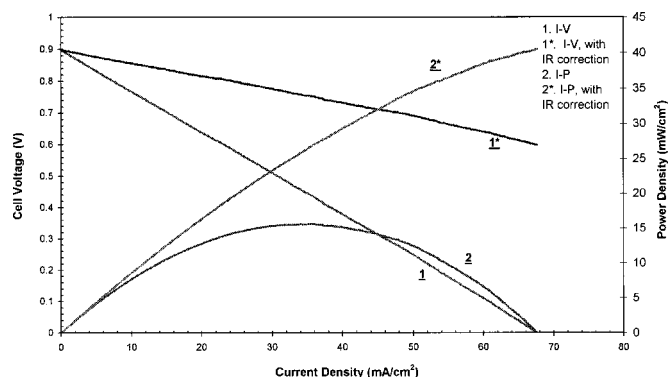


Figure 6. Current-voltage and current-power relationships of H_2S -air fuel cell using Ni-Mo-S anode at 850°C .

was 83.3 mA/cm^2 at 800°C , and was 142 mA/cm^2 at 850°C . At 800°C , the current-voltage curve showed a steep drop in cell potential in the high current range, which was characteristic of mass-transport limitation.¹⁹ However, this effect was greatly reduced when the temperature was increased to 850°C . These observations were consistent with a mechanism in which sulfur was generated more rapidly at active sites than it was removed by desorption and transport at 800°C , which limited the ability of H_2S fuel to access the triple-phase boundary, the reaction area. At 850°C , the rate of desorption and transport of sulfur from the vicinity of the active sites was increased, which thereby enhanced mass transport of H_2S to the active sites.

As can be seen in Fig. 8, the ohmic resistance of the cell with Co-Mo-S as the anode catalyst increased with polarization at 800°C . However, the adherence of Pt current collecting film to Co-Mo-S anode surface deteriorated less rapidly than for either Fe-Mo-S or Ni-Mo-S. Compared to the data acquired under open-circuit conditions, the cell-area-specific ohmic resistance increased only $1.38 \Omega \text{ cm}^2$ for the condition of polarization at 0 V. In a similar manner to Fe-Mo-S, the resistance of Co-Mo-S decreased with increasing temperature, which suggested that the temperature change alone had no deleterious effects on the interface between the Pt film and the anode.

The power density characteristics at cell operating temperatures of 800 and 850°C are shown in Fig. 9. The values of maximum power density at 800 and 850°C were similar, 29.7 and 34.6 mW/cm^2 , respectively. However, the maximum IR-compensated value at 850°C was over 80 mW/cm^2 , approximately double that at 800°C .

The excellent cell performance after IR compensation using each of Fe-Mo-S, Ni-Mo-S, and Co-Mo-S as anodes indicated that the

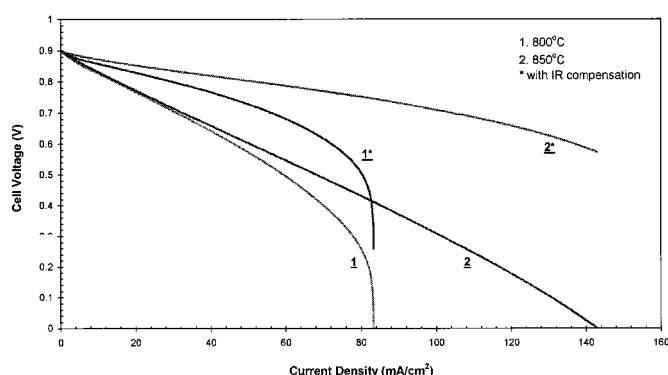


Figure 7. The relationship between cell voltage and current density for the Co-Mo-S anode at 800 and 850°C .

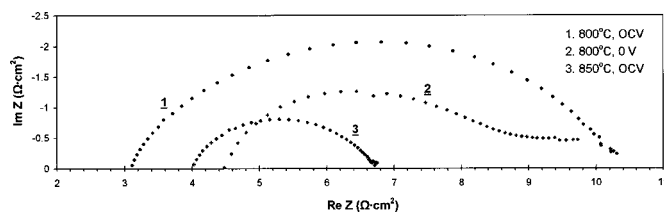


Figure 8. Impedance spectra for the cell using Co-Mo-S as the anode catalyst at different temperature and polarization conditions.

above binary metal sulfides were active catalysts for the electrochemical oxidation of H_2S , but that improved contact was required.

The high activity of these catalysts is attributed to the properties of the M-Mo-S structure ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$), a general feature previously recognized for MoS_2 -based HDS catalysts.¹¹⁻¹³ This type of structure is regarded as a MoS_2 -like phase with the promoter atoms (Fe, Co, or Ni) located at the edges.²¹ These materials appear to have been stable throughout the whole tests. No sublimation of the binary anode catalysts was detected. The IR-corrected data show that it is necessary to improve electrical contact in order to realize the full potential for these anode catalysts. The major source of the large ohmic resistance in the cell was the poor electrical contact between the Pt film and the anode. Consequently, we have also examined alternative compositions of the anode, with the objective of improving electrical contact and reducing ohmic resistance.

Admixing Ag powder into Co-Mo-S anode catalyst.—In order to overcome the weak bonding and poor electrical contact of the Pt current-collecting film with the anode, we have investigated alternative anode compositions, in particular, composite anodes having up to 10% Ag powder admixed with Co-Mo-S, with the objective of improving anode electrical conductance. It was found that, when Ag powder was well distributed in the anode, the anode and mesh current collector were in good electrical contact. Thus there was no need to apply a Pt film, thereby avoiding the presence of an unstable interface between the Pt film and the anode, and also increasing the intimate contact area.

Ag powder easily reacts with sulfur to form Ag_2S . However, Ag_2S thermally decomposes to its elements above 200°C .²² As a result, whereas formation of PtS increased resistance and caused detachment of the current collector, there were no similar adverse effects resulting from use of Ag powder. Pt mesh spot-welded with a Pt lead made good electrical contact when placed directly across the surface of the anode.

The cell was operated at 750 – 850°C and at atmospheric pressure (Fig. 10). Curve 1, 2, and 3 were measured without IR compensation, while curve 1*, 2* and 3* were determined using the IR compensation function of the Gamry system. The maximum current density increased with temperature, both with and without IR cor-

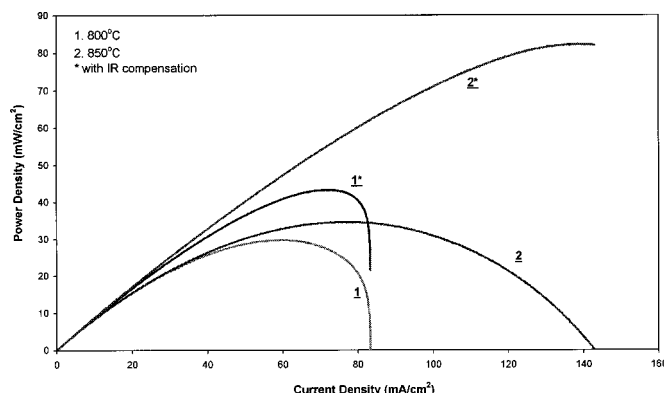


Figure 9. The relationship between current density and power density for the cell using Co-Mo-S as the anode at 800°C and 850°C .

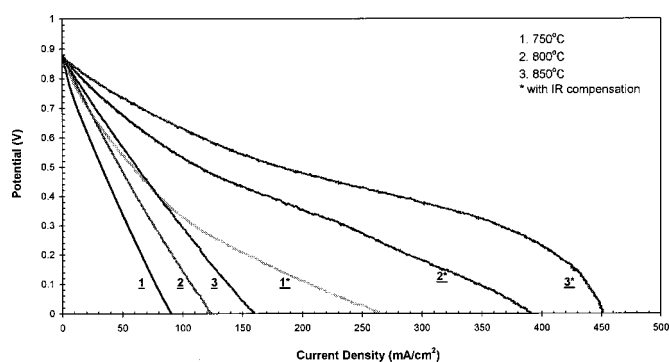


Figure 10. The relationship between current and potential at 750, 800, and 850°C using (Co-Mo-S) + 5% Ag as the anode.

rection. The values without IR compensation were 90.5, 124, 159 mA/cm² at 750, 800, and 850°C, respectively. With IR compensation, the highest maximum current density of 450 mA/cm² was achieved at 850°C. The *I*-*V* curve 3* in Fig. 10 indicated a slight mass-transfer limitation in the high-current region. However, this characteristic was not observed at 750°C (curve 1*) or 800°C (curve 2*), probably because sulfur produced at high reaction rate at 850°C occupied the active sites and therefore limited the further reaction of H₂S gas. The current-power density curves are presented in Fig. 11. The maximum power density increased with increasing temperature. The initial parts of these curves overlapped, suggesting that the electrocatalytic activity of the anode was independent of temperature at low-current density. The maximum value for IR compensated power density was 115 mW/cm² at 850°C. This value was higher than the maximum value for a Pt film/Co-Mo-S anode system, and the performance was sustainable for a much longer time, showing that the system had higher performance and integrity.

The cell was tested for a period of 5 days. The maximum current densities and power densities with IR compensation at 850°C for each day are presented in Fig. 12. The current and power values were stable. Thus an anode catalyst comprising Co-Mo-S catalyst admixed with Ag powder has superior activity, superior longevity, and improved electrical contact characteristics when compared with the same catalyst having an overlayer of Pt.

Conclusions

Four different metal sulfide catalysts have been shown to be active H₂S-air fuel cell anode catalysts in the range 750-850°C.

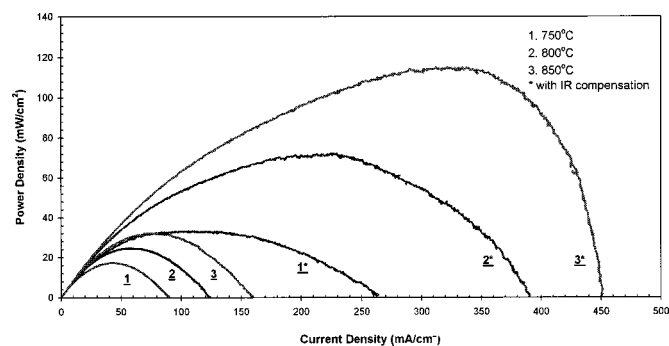


Figure 11. The relationship between current and power at 750, 800, and 850°C using (Co-Mo-S) + 5% Ag as the anode.

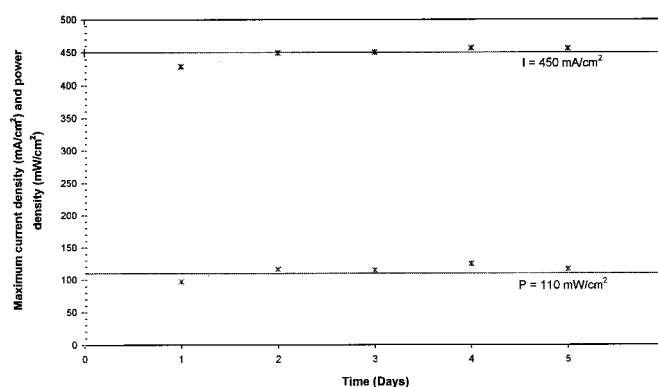


Figure 12. Maximum current density and power density of H₂S-air fuel cell as a function of time on stream at 850°C.

MoS₂ has a superior activity to Pt for oxidation of H₂S to sulfur. Binary metal sulfides M-Mo-S (M=Fe, Co, Ni) are not volatile, in contrast to MoS₂ alone, and have high activity. However, Pt film deposited as a current collector across the metal sulfides does not have good adherence to the anode surface, and its performance is compromised by PtS reversibly formed by reaction with H₂S or sulfur. Detachment of the Pt film from the anode resulted in a large increase in contact resistance and reduction in cell performance. Anode catalyst comprising Co-Mo-S admixed with up to 10% Ag powder were found to have superior performance and longevity, and improved electrical contact when compared with Pt/M-Mo-S anode systems.

Acknowledgments

We thank Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

University of Alberta assisted in meeting the publication costs of this article.

References

1. J. Zaman and A. Chakma, *Fuel Process. Technol.*, **41**, 159 (1995).
2. N. U. Pujare, K. W. Semkow, and A. F. Sammells, *J. Electrochem. Soc.*, **134**, 2639 (1987).
3. N. U. Pujare, K. J. Tsai, and A. F. Sammells, *J. Electrochem. Soc.*, **136**, 3662 (1989).
4. T. J. Kirk and J. Winnick, *J. Electrochem. Soc.*, **140**, 3494 (1993).
5. D. Peterson and J. Winnick, *J. Electrochem. Soc.*, **145**, 1449 (1998).
6. C. Yates and J. Winnick, *J. Electrochem. Soc.*, **146**, 2841 (1999).
7. B. Zhu, *Fuel Cell Bull.*, **4**, 9 (1999).
8. B. Zhu and S. W. Tao, *Solid State Ionics*, **127**, 83 (2000).
9. M. Liu, P. He, J. L. Luo, A. R. Sanger, and K. T. Chuang, *J. Power Sources*, **94**, 20 (2001).
10. P. He, M. Liu, J. L. Luo, A. R. Sanger, and K. T. Chuang, *J. Electrochem. Soc.*, **149**, A808 (2002).
11. D. A. Agievskii, M. V. Landau, and A. A. Slinkin, *Kinet. Katal.*, **29**, 792 (1989).
12. E. I. Stiefel, *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 16, (Molybdenum Compounds), John Wiley & Sons, New York (2001).
13. J. A. Rodriguez and M. Kuhn, *J. Vac. Sci. Technol. A*, **14**, 1609 (1996).
14. T. Chivers, J. B. Hyne, and C. Lau, *Int. J. Hydrogen Energy*, **5**, 499 (1980).
15. M. Breyse, R. Frety, and M. Vrinat, *Appl. Catal.*, **12**, 165 (1984).
16. S. V. Slavov, K. T. Chuang, A. R. Sanger, J. C. Donini, J. Kot, and S. Petrovic, *Int. J. Hydrogen Energy*, **23**, 1203 (1998).
17. K. T. Chuang, J. C. Donini, A. R. Sanger, and S. V. Slavov, **25**, 887 (2000).
18. O. E. Beqqali, I. Zorkani, F. Rogemond, H. Chermette, R. B. Chaabane, M. Gamoudi, and G. Guilaud, *Synth. Met.*, **90**, 165 (1997).
19. J. O'M. Bockris and S. Srinivasan, *Fuel Cells: Their Electrochemistry*, Chap. 4, McGraw-Hill, New York (1969).
20. M. Gödickemeier, K. Sasaki, and L. J. Gauckler, *J. Electrochem. Soc.*, **144**, 1635 (1997).
21. H. Topsøe and B. S. Clausen, *Catal. Rev. Sci. Eng.*, **26**, 395 (1984).
22. *Dictionary of Inorganic Compounds*, 1st ed., Vol. 1, p. 14, Chapman & Hall, London (1992).