

Quarterly Progress Report

High Temperature Electrochemical Polishing of H₂S

from Coal Gasification Process Streams

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by

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Project Objectives

Coal may be used to generate electrical energy by any of several processes, most of which involve combustion or gasification. Combustion in a coal-fired boiler and power generation using a steam-cycle is the conventional conversion method; however total energy conversion efficiencies for this type of process are only slightly over 30%¹. Integration of a gas-cycle in the process (combined cycle) may increase the total conversion efficiency to 40%¹. Conversion processes based on gasification offer efficiencies above 50%¹.

H₂S is the predominant gaseous contaminant in raw coal gas. Coal depending on the type and area of extraction can contain up to 5 wt% sulfur, which is converted to gaseous H₂S during gasification. Problems arise due to the corrosive nature of H₂S on metal components contained in these cycles. Because of this, H₂S concentrations must be reduced to low levels corresponding to certain power applications. For example, an integrated coal gasification-combined cycle (IGCC) process producing electricity from coal at nearly 50% overall efficiency¹ incorporates gas turbines that cannot tolerate H₂S levels above 100 ppm. Coal gasification/Molten Carbonate Fuel-Cell(MCFC) systems, achieving conversion efficiencies around 60%², function properly only if H₂S is below 1 ppm.

An advanced process for the separation of hydrogen sulfide (H₂S) from coal gasification product streams through an electrochemical membrane is being developed using funds from this grant. H₂S is removed from the syn-gas stream, split into hydrogen, which enriches the exiting syn-gas, and sulfur, which is condensed from an inert sweep gas stream, Figure 1. The process allows removal of H₂S without cooling the gas stream and with negligible pressure loss through the separator. The process is made economically attractive by the lack of need for a Claus process for sulfur recovery. To this extent the project presents a novel concept for improving utilization of coal for more efficient power generation.

Past experiments using this concept dealt with identifying removal of 1-2% H₂S from gases containing only H₂S in N₂³, simulated natural gas^{4,5}, and simulated coal gas⁶. Data

obtained from these experiments resulted in extended studies into electrode kinetics and electrode stability in molten melts^{7,8,9}. The most recent experiments evaluated the polishing application (removal of H₂S below 10 ppm) using the Electrochemical Membrane Separator (EMS). H₂S removal efficiencies over 90% were achieved at these stringent conditions of low H₂S concentrations proving the technologies polishing capabilities.

Other goals include optimization of cell materials capable of improving cell performance. Once cell materials are defined, cell experiments determining maximum removal capabilities and current efficiencies will be conducted.

Also, a model theoretically describing the preferred reduction of H₂S, the transport of S²⁻, and the competing transport of CO₂ will be investigated. The model should identify the maximum current efficiency for H₂S removal, depending on variables such as flow rate, temperature, current application, and the total cell potential.

Introduction

The Electrochemical Membrane Separator (E.M.S.), the focus of experimental work, purges a fuel gas contaminated with H₂S. This is done by reducing the most electro-active species in the gas stream. In this case, H₂S is reduced by the following:



A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H₂ diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.



Processes to remove H₂S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H₂S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H₂S levels required by MCFC, there are several disadvantages inherent to these processes^{10,11}.

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds¹² or inefficient molten salt sorbent processes¹³ negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H₂S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H₂S removal and direct production of elemental

sulfur offered by this process provide several advantages over existing and developmental H₂S removal technologies.

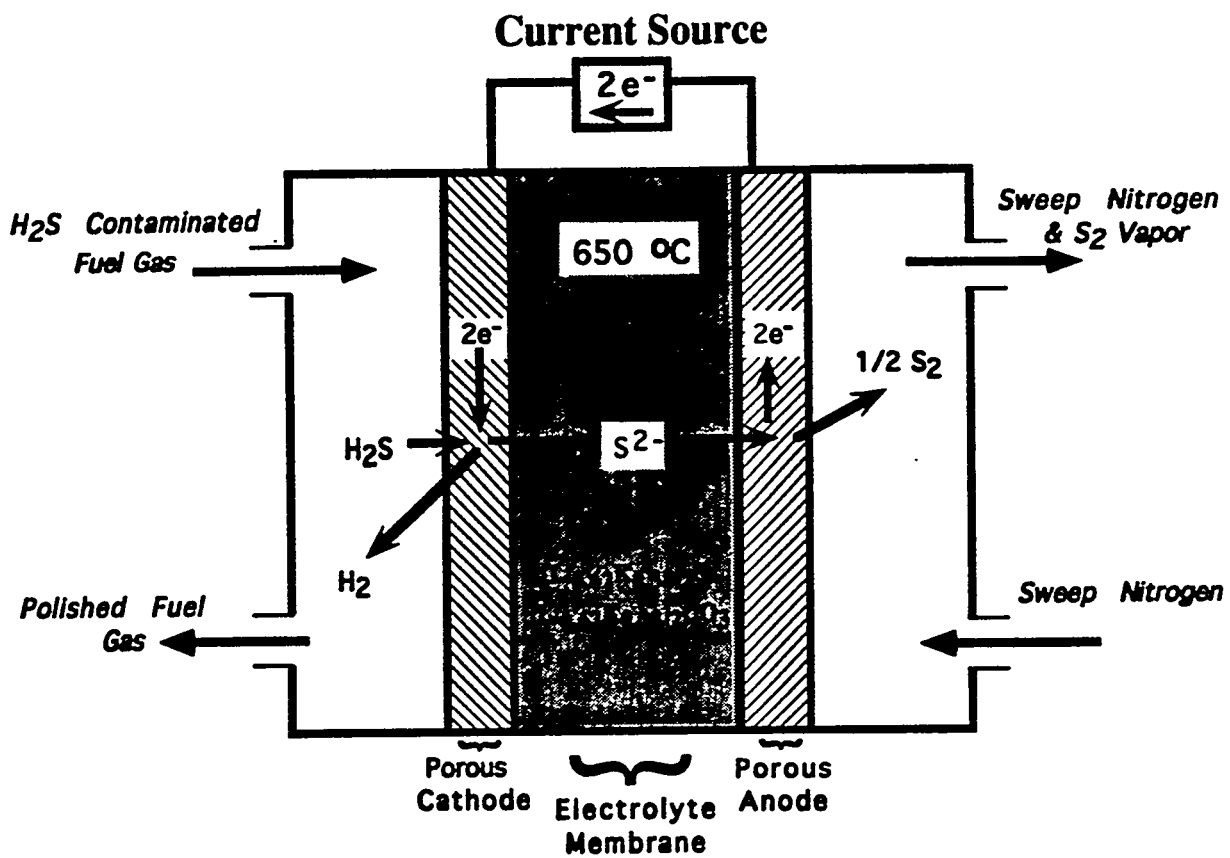


Figure 1. Single-Cell View of the Electrochemical Membrane Separator

Quarterly Research

Electrolyte Management

Electrolyte losses associated with molten carbonate salts is a consistent problem; the mechanism of such losses is not fully understood with CO₂ evolution and reactions with system materials comprising possible mechanisms.

Proposed mechanisms for the loss of electrolyte in the E.M.S. are:

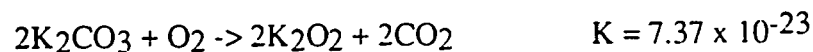
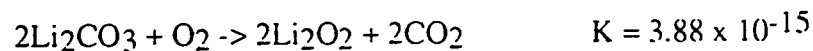
1) Material reactions upon process-gas seal formation:



2) Evaporation at the anode due to a deficiency of CO₂:



3) Evaporation into the surroundings:



with lithium carbonate, comprising 62 mole% electrolyte, being the least stable (larger K).

Quantitative evaporation studies were performed duplicating full-cell conditions¹⁴. Mechanism (2) & (3) were investigated with evaporation by mechanism (3) entailing the predominant amount of electrolytic losses; 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li₂O₂ & Li₂O by:



Cathode Materials

From results obtained in previous studies, the path to a commercial process is now clear. The primary unresolved components are the cathode and membrane. The cathode must be chemically and mechanically stable in the sulfide/carbonate/hydrogen sulfide environment, and

be electronically conductive at 650°C. Lithium-doped NiO has already proven effective in polishing applications; however, the Ni phase transition to liquid $Ni_{3+x}S_2$ when contacting gas with >100 ppm H_2S , requires alternate cathode materials. Co, which converts to Co_8S_9 in-situ, has recently been shown¹⁵, using Scanning Electron Microscopy (S.E.M.), to be morphologically stable in full cell testing with 100 ppm H_2S . The microscopic view revealed adequate porosity and pore size were maintained in the harsh cell environment. Production of cobalt electrodes in the laboratory is ongoing; consistently manufacturing these electrodes with a pore size and arrangement comparable to the Ni electrodes has been accomplished although current attempts have been less successful. Dry pressing the cobalt powder ($d_p = 2$ microns) with ~ 40 wt% binder (methylethylcellulose) stabilized the metal in disk form to accomplish the burnout and sintering steps. Stress fractures often occur due to the non-uniform release of binder and apparent temperature inequality within the furnace. These concerns involve the physical aspects of dry pressed powders. Non-uniform distribution of binder material incorporated within the cobalt particles creates particle segregation in certain regions; local density gradients due to disproportionate binder distribution effects the final electrode morphology (i.e. pore size, pore distribution, tortuosity, and crystallographic stability). Adjustments dealing with binder content and temperature cycling will be the impetus of future membrane production as well as improvements in dry-pressing of the cobalt-binder system.

Membrane Materials

Several membranes have been utilized in the EMS since its genesis. MCFC tiles used by Weaver¹⁶, sulfided in-situ, resulted in micro-crack development; however MCFC tile technology will be used in scale-up applications of electrochemical separations, due to success in real-time MCFC. The technology has been refined, but replication in our laboratory is expensive and inefficient for bench-scale testing. Tape-cast membranes of MgO were somewhat more efficient but inconsistent laboratory replication proved detrimental¹⁷; however, tape casting with zirconia particles still remains a viable option. The most promising membranes for bench-scale

experiments have been manufactured zirconia membranes purchased from Zircar Corporation. Polishing of the gasification streams with these membranes confirms their usefulness; however micro-cracks are still evident from S.E.M. analysis ¹⁵, Figure 2, and must be controlled. Alternative laboratory-densified membranes with fiber mats replicating the preprocessed membranes from Zircar Corporation are also being investigated. Positive removal results (over 90% H₂S removal) have been obtained from full-cell testing with these membranes¹⁸; however, more work is needed to improve the manufacturing techniques. Dry pressing zirconia particles admixed with binder has been the most recent attempt to produce a viable membrane material.



Figure 2. S.E.M. View of a Purchased Zirconia Membrane

Zirconia Cloth-Stabilized Matrices

Continued cell testing will be done utilizing the purchased zirconia membranes along with laboratory-densified zirconia membranes containing zirconia fibers. Laboratory-densified membranes which have proven successful in the past¹⁸ will be tested further. One reason for this is financial. Conventional purchased zirconia membranes cost approximately \$ 150.00 per membrane (7.62 cm (3 in) x 7.62 cm (3 in) x 0.063 cm (0.025 in)), compared to \$ 10.00 per membrane (7.62 cm (3 in) x 7.62 cm (3 in) x 0.092 cm (0.036 in)) for self-produced membranes.

Laboratory-densified membranes consist of two knit zirconia mats (7.62 cm (3 in) x 7.62 cm (3 in) x 0.0762 cm (0.030 in)) purchased from Zircar Corporation. The initial porosity of the mats is approximately 85%. The objective is to fill (rigidize) the knit to a porosity of approximately 65%, which is essential, according to past experiments, in order to operate efficiently¹⁹. The material used to rigidize the membrane is an aqueous suspension of sub-micron zirconia particles. The combination of mats are submerged in a container of rigidizer, then placed under a vacuum to evacuate the pores. Once pores are relieved of gaseous fillers, the rigidizer infiltrates the pores.

In previous manufacturing, after the infiltration step, the membrane(cloth plus aqueous suspension of sub-micron zirconia particles) was placed on a flat Teflon surface, covered with weighing paper, and constrained from curling by a metal mesh. More recent techniques relied on the wet matrices being placed atop a thin wire bent into a square configuration and attached to a speed controlled rotor; the rotating of the free body should allow a faster more uniformly dry body(matrices) compared to previous techniques.

Once dry, the membrane is analyzed for void fraction and reprocessed if found unacceptable. In the cell, the 65% porous membrane with infiltrated electrolyte prevents cross-over of harmful amounts of hydrogen and allows a low-resistance path for sulfide diffusion and migration. In order to reach such porosity, the method of rigidization must be performed several times, each reducing the porosity by approximately 10%. Every cycle requires drying, placing

mechanical stress on the membrane. The fabricated membrane meeting the 65 % porosity performed adequately in full- cell testing¹⁸.

Thus far improvements in laboratory-densified manufacturing techniques consist of: i) Adding zirconia rigidizer into a knit-zirconia matrix under an extended vacuum (>5 min.). This drastically decreases porosity , reducing the number of steps required to fabricate the membrane. ii) Suspending the mat during drying to increase diffusion since both faces of the mat are exposed, decreasing solvent diffusion distance and iii) vertically rotating the suspended body to uniformly distribute the suspension of zirconia particles throughout the membrane.

Preliminary manufacturing using the rotary dryer failed due to handling problems; Figure 3 reveals an S.E.M. view of membrane cracks connected to these problems. Improvements in the process between steps i and ii are being handled with a more efficient rotor frame, stabilizing the cloth mat prior to the infiltration of the zirconia particles therefore creating a more desirable transition from the vacuum chamber to the rotary drying stage. Processing of membranes with this technique will continue.



Figure 3. S.E.M. View of a Self-Fabricated Zirconia-Cloth Membrane

Dry Pressing

Dry pressing of sub-micron zirconia particles with a percentage of binding material corresponding to a desired porosity has been attempted. Stages in dry pressing include i) the filling of a circular 3 inch diameter carbon steel die with the zirconia particle binder mixture, ii) compacting and shaping of the zirconia binder admixture, and iii) ejection of the pressed disk. Pressing can be accomplished by uniaxial pressing Figure 4a or isostatic pressing Figure 4b. Uniaxial pressing was the technique of choice for initial compression experiments due to ease and availability.

In dry-pressing, pressure produced by moving the die punches compacts the zirconia-binder powder mixture into a cohesive disk with a certain shape and micro-structure according to the extent of applied pressure and binder content. Generally pressures range from 10 - 200 MPa although above 10 MPa rate of densification decreases rapidly; binder content is between 2 and 12 vol%²⁰. Dry-pressing of the zirconia-methocel system was accomplished with a pressure of 20 MPa and a binder content of ~ 50 vol%. A high membrane porosity necessitates a higher than normal binder content although inherent problems in binder burnout are inevitable.

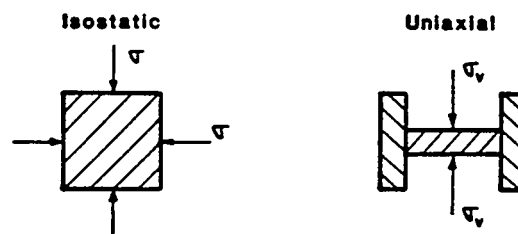


Figure 4. Dry-Pressing with an a) Isostatic Stress Loading and b) Uniaxial Stress Loading

Initial attempts at membrane manufacture by dry-pressing showed promise. Figure 5, an S.E.M. view of the sintered dry-pressed zirconia membrane, reveals an acceptable membrane surface and pore distribution: membrane porosity was ~60 % with an average pore size of 1 micron. Work must continue on obtaining a more uniform membrane surface creating parallelism between the membrane and electrode, housing materials as well as alleviating stress fractures during binder burnout and sintering which leads to cracks. Also reduction in membrane thickness must be addressed in order for the dry-pressed membranes to be a viable options for E.M.S. bench-scale experiments; three experiments yielded a membrane of thickness ~.2 cm. Previous membranes utilized successfully in the E.M.S. removal system had a thickness of ~.5 mm.



Figure 5. S.E.M view of a Dry-Pressed Membrane

Tape casting

Tape casting is the process of forming a film of controlled thickness under a blade onto a supported substrate. Tape-casting provides a smooth membrane surface as well as a thin (0.01 - 1 mm), flat, uniform, and somewhat compressible membrane²⁰. Membranes produced by dry-pressing and extrusion have a less smooth surface below 2 mm in thickness, consist of breakage, non-uniform density, and a non-parallelism between surfaces can be a problem; therefore tape cast membranes if manufactured properly could produce the most viable membranes to date.

Future work will focus on this technique as a possible membrane manufacturing process. S.E.M analysis as well as crystal structure given by X-ray Diffraction will identify the morphology of these membranes, illuminating this technique for future use.

Borosilicate membranes

Alternate matrix materials also have been investigated including microporous glass membranes with porosities of .2 and .02 microns, shown in figure 6 and a thickness of 60 microns exceeding the probable limit of the bench-scale E.M.S. set-up provisions; thus far, these membranes have shown chemical instabilities with the electrolytic melt. Several experiments to illuminate the chemical stability of these membranes in the molten salt electrolytic melt showed a trend of membrane dispersion throughout the melt. Without a stable matrices to entrain the electrolyte, leakage will occur reducing the ionic pathway between electrodes which is detrimental to E.M.S. performance. Future tests with these membranes are not scheduled.

Membrane Thickness

Once effective membranes have been developed, other variables such as thickness of the membrane will be investigated in high-flow rate experiments in order to lower the resistance to sulfide migration. The rate of mass transport corresponding to sulfide migration through the membrane is given by:

$$i = \frac{nFD (C_c - C_a)}{\delta} \quad (3)$$

where n is the charge number, F is Faraday's constant, D is diffusion coefficient, δ is the membrane thickness, and C is the concentration of sulfide species at the cathode and anode. At high process-gas flow rates, mass transfer from the gas is equivalent to the limit of diffusion through the membrane, given by:

$$i_1 = \frac{nFD C_c}{\delta} \quad (4)$$

The limiting current is a measure of the maximum rate at which sulfide can be transported through the membrane, and occurs when $C_a = 0$. Equation (4) reveals that a thinner membrane creates a higher limiting current for the transport of sulfide. This is extremely important at high flow rates to insure diffusion from the bulk process-gas is the only limiting factor.

Optimization of membrane thickness and porosity will be investigated at high flow rates during full-cell testing using a singular laboratory-densified membrane, thickness ~ 0.38 mm (0.015 in) as well as tape cast and dry-pressed membranes discussed earlier.

Quarterly Summary

Work continued this quarter to improve experimental conditions (laboratory & equipment enhancement). The oven containing the Electrochemical Membrane Separator (E.M.S.) is the main focus of improvement readjusting spatial requirements conforming to the controlled environmental emissions equipment while creating a controlled atmosphere gauntlet to unfavorable reactions with electrolytic species.

Manufacturing of yttria-stabilized zirconia matrices was the primary focus of laboratory experimentation while full-cell testing is not possible. Dry-pressing and particle infiltration have

been utilized thus far with moderate success with future experiments scheduled to enhance present knowledge of these techniques. Tape-casting attempted previously with MgO particles will be attempted with zirconia particles, hopefully obtaining a better production efficiency.

Project Conclusion

The Fossil Energy Advanced Research Program requires high temperature separations to remove environmental contaminants from post-combustion flue gases as well as pre-combustion process gases. This project is aimed at the latter: the removal of hydrogen sulfide from coal gas at gasifier temperatures. This development would enable a simplification of the entire gasification scheme by permitting a one-step removal of hydrogen sulfide and production of elemental sulfur. Energy savings accrue due to the high temperature processing.

The DOE programs relating to gasification for power production have as their goal the more efficient, clean paths toward affordable energy from coal. Gas clean-up accounts for nearly one-third of the cost of this conversion. Simplification and economization will benefit the entire effort.

Project Output

Current experiments are based on improving selective removal from low initial H₂S concentrations (100 ppm and 20 ppm H₂S). High flow rate effects, membrane stability and selectivity, and electrode morphology characterizes present studies, with recent results showing over 90% H₂S removal with applied current.

Experimental results presented are based on two experiments with initial H₂S concentrations of 100 ppm and 20 ppm. To represent probable industrial conditions, variables such as flow rates, selectivity of the membranes, and process-gas seals, were of primary concern in these experiments. Maximum removals of H₂S are reported on a zero current basis, thus compensating for any chemical scrubbing effects of the non-equilibrium electrolyte species in the

membrane. Percent H₂S removal with applied current exceeded 80% and in some cases reached 90%, given by:

$$\%H_2S \text{ Removal} = \frac{(\text{Outlet } H_2S_{\text{zero current}} - \text{Outlet } H_2S_{\text{I applied}})}{(\text{Outlet } H_2S_{\text{zero current}})} \times 100 \quad (5)$$

Cell housing materials used for both experiments were a machineable ceramic (MACOR). Cathode and anode electrodes consisted of Ni, oxidized in situ to form NiO. Process-gas seals developed, in-situ, by placing aluminum foil gaskets on both sides of the electrolyte filled membrane. Al oxidation initially forms Al₂O₃ which on reaction with Li, contained in the electrolyte, forms LiAlO₂.

The membrane for the 100 ppm experiment, used two tapes of MgO and one mat of zirconia cloth. Acrylic binders used in the MgO tapes (Metoramics K565-4 binder system) were burned out under an O₂ atmosphere at 350°C and the (Li_{0.62}K_{0.38})₂CO₃ eutectic-composition electrolyte was added with the cell at run temperature. Inlet gases were passed through a stainless steel shift reactor, allowing them to equilibrate before passing through the cell. Gas compositions at 973K after the shift reactor were 14.3% CO₂, 50.8% CO, 4.8% H₂O, 30.1% H₂, and 100 ppm H₂S.

H₂S removal vs. applied current, with a cathodic flow rate of 88 cc/min., is presented in Figure 6. H₂S removals of 90% were achieved with H₂S current efficiencies of 5%.

The membrane for 20 ppm experiments was purchased from Zircar Corporation, consisting of yttria-stabilized zirconia in a rigid form at 66% porosity. The advantages of these membranes are consistently uniform porosities and no warping. A cold pressed disk of the Li/K eutectic carbonate electrolyte, placed between the cathode housing and the Zircar membrane, provided a stable start-up configuration. Inlet gases equilibrated to 5.8% CO₂, 25.6% CO, 6.7% H₂O, and 65.3% H₂, after the water-gas shift reactor. The electrolyte sulfide concentration equilibrated in-situ to 0.11 mole%.

Temperature remained constant (650°C) while flow rates varied from 170 cc/min. to 814 cc/min. H₂S removal at all flow rates exceeded 80% with applied current as shown in Figure 7; Current efficiencies were ~ 35%.

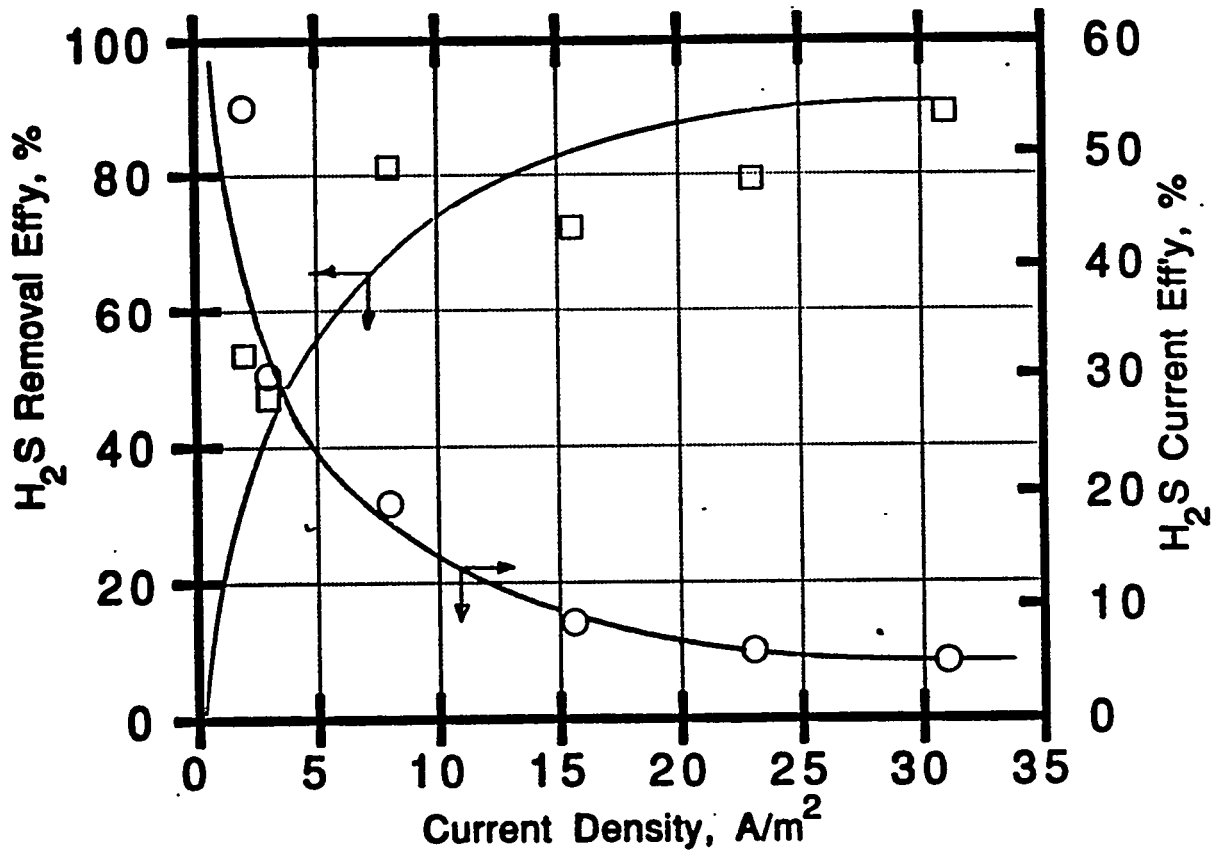


Figure 6. H₂S Current and Removal Efficiency vs. Current Density; 100 ppm inlet H₂S

Cathodic Flow Rate = 88 cc/min

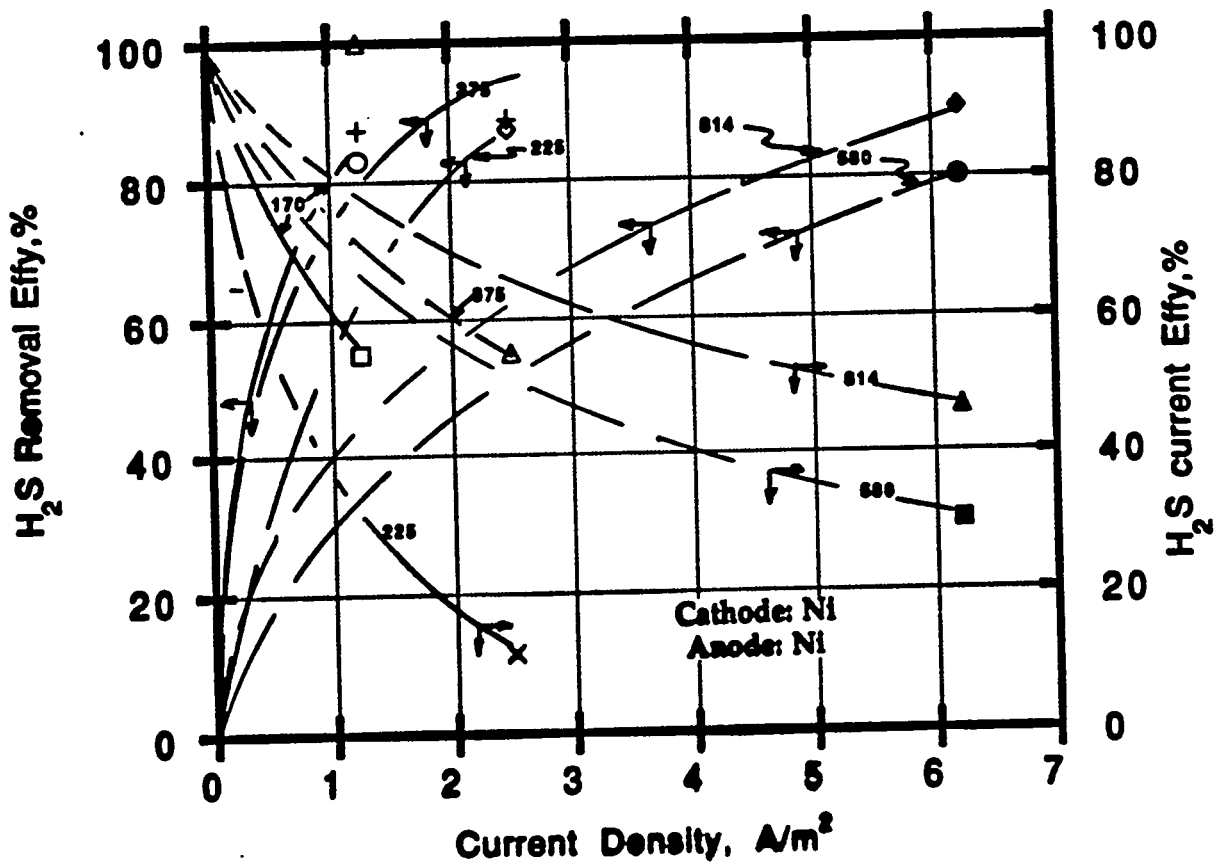


Figure 7. H₂S Current and Removal Efficiency vs. Current Density: 20 ppm inlet H₂S

Parametric values are in cc/min

References

1. U.S. Dept of Energy, DOE/METC 87/0255, DE87006493, Oct., 1987.
2. Skerret, P.J., "Fuel Cell Update", *Popular Science*, 89-91, 120-1, June, 1993.
3. Lim, H.S. and Winnick, J., *J. Electrochem. Soc.*, **131**, 562-8 (1984).
4. Alexander, S., and Winnick, J., *1990 AlChE Annual Meeting*, Chicago, IL., 1990.
5. Alexander, S., and Winnick, J., *Sep'n Sci. and Tech.*, **25**, 2057-72 (1990).
6. Weaver, D., and Winnick, J., *J. Electrochem. Soc.*, **134**, 2451-58 (1987).
7. Weaver, D., and Winnick, J., *J. Electrochem. Soc.*, **138**, 1626-37 (1991).
8. Banks, E., and Winnick, J., *J. Appl. Electrochem.*, **16**, 583-90 (1986).
9. White, K.A., and Winnick, J., *Electrochim. Acta*, **30**, 511-516 (1985).
10. EPRIEM-1333, *Assessment of Sulfur Removal Processes for Advanced Fuel Cell Systems, Final Report*, C.F. Braun and Co., Alhambra, CA, Jan., 1980.
11. Vidt, E.J., DOE/METC DE-AC-21-81MC16220, DE82013942, Westinghouse, Dec., 1981.
12. Focht, G.D. et. al.. DOE/MC/121166-2163. DE86016041, July, 1986.
13. Lyke, S.E., DOE/MC/19077-1803, DE8500961, Battelle Pacific Northwestern Laboratories, Jan. 1985.
14. Winnick, J., Quarterly Progress Report #13, DOE grant DE-FG-91PC91288.
15. Winnick, J., Quarterly Progress Report #11, DOE grant DE-FG-91PC91288.
16. Weaver, D., and Winnick, J., *J. Electrochem. Soc.*, **139**, 492-498 (1992).
17. Alexander, S., *Ph.D. Thesis*, Georgia Institute of Technology, Atlanta, GA, 1992.
18. Winnick, J., Quarterly Progress Report #6, DOE grant DE-FG-91PC91288.
19. Winnick, J., Quarterly Progress Report #8, DOE grant DE-FG-91PC91288.
20. Reed, James S., Introduction to the Principles of Ceramic Processing, John Wiley & Sons, New York, 1988.