Conf-9406131--49

DOE/PC/91288-94/C0397

HIGH TEMPERATURE ELECTROCHEMICAL SEPARATION OF H_2S FROM COAL GASIFICATION STREAMS

Authors:

E. F. Gleason
J. Winnick

Contractor:

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100

Contract Number:

DE-FG22-91PC91288

Conference Title:

Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC
Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

June 21-23, 1994

Conference Sponsor:

U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy
Technology Center

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

P1 High Temperature Electrochemical Separation of H_2S from Coal Gasification Streams

CONTRACTOR INFORMATION

Contract Number	DE-FG22-91PC91288
Contractor	Georgia Institute of Technology School of Chemical Engineering Atlanta, Georgia 30332-0100 (404) 894-2839
Contractor Project Manager	E. Faith Gleason
Principle Investigator	Jack Winnick
METC Project Manager	Kamalendu Das
Period of Performance	October 1, 1991 - November 30, 1994

OBJECTIVE

A method of polishing coal synthesis gas by an electrochemical membrane operation is being perfected. The operation takes advantage of an electrochemical potential gradient rather than conventional techniques, separating the H_2S from the coal gas stream, leaving only H_2 to enrich the exiting fuel gases. Sulfur is the by-product that is carried away by a separate inert sweep gas and condensed downstream. The technology is attractive due to simplicity as well as economics when compared to alternatives.

An analytical model describing the preferred reduction of H_2S, the transport of S^{2-}, and the competing transport of CO_3^{2-} through the removal cell has continued[11]. The main objective is the relation between cell polarization and current efficiency. This has been realized.

Recent experiments have focused on removing 100 ppm inlet H_2S, utilizing laboratory fabricated cobalt cathodes.

INTRODUCTION

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid, electron acceptor, will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 \tag{1}$$

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\, S_2 + 2e^- \tag{2}$$

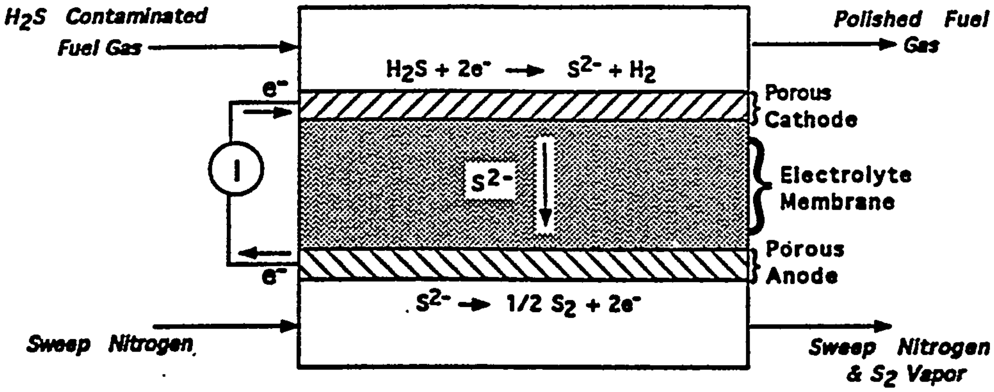


Figure 1. Schematic of Electrochemical Cell

The vaporous sulfur is condensed downstream.

Processes to remove H_2S typically rely on low-to-ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H_2S 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 H_2S levels required by MCFC, there are several disadvantages inherent to these processes[7,8].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[9] or inefficient molten salt sorbent processes[10] negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H_2S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H_2S removal and direct production of elemental sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies. The remaining factor is a thorough economic evaluation asserting the viability of the process.

An initial economic evaluation[11] showed the process noteworthy. Further analysis will require developing an analytical model describing 1) the preferred reduction of H_2S among competing reactants in the gasification stream, 2) the transport of S^{2-} through the electrolyte filled membrane, and 3) competing transport of CO_2 through the removal cell. The model can give the maximum current efficiency for H_2S removal, depending on variables such as flow rate, temperature, current application, and total cell potential. Extended application of the model will predict cell performance under varying cell currents, gas compositions and flow rates. It will also permit economic projection in various applications.

Analytical Model

A theoretical model based on applied current, flow rate, and electrochemical effects has been investigated, relating anode CO_2 production with % H_2S removal. Although the model is not completed, adequate power estimates for percentage removals of H_2S can be computed.

Preferential Reduction of H_2S.

H_2S has been shown to be readily reduced in hot gas mixtures, even at low ppm levels. The situation is complicated when coal gas mixtures are processed. Carbon dioxide and water vapor compete in the reduction reaction at the cathode by:

$$CO_2 + H_2O + 2e^- \Rightarrow CO_3^{2-} + H_2 \quad (3)$$

The ionic flux through the membrane depends on the relative mobility of carbonate and sulfide ions as well as their concentrations.

Preventing the oxidation of carbonate at the anode is necessary for prohibiting its transport through the membrane, the desired anodic reaction being:

$$S^{2-} \Rightarrow 1/2\ S_2 + 2e^- \quad (2)$$

This occurs at a standard potential some 700 mV lower than the oxidation of carbonate:

$$CO_3^{2-} \Rightarrow CO_2 + 1/2\ O_2 + 2e^- \quad (4)$$

Summing the half-cell reactions (1) and (2) results in the following overall reaction at 923K:

$$H_2S \Leftrightarrow H_2 + 1/2\ S \quad (5)$$
$$E_a^o = -\ 0.239\ V$$

and when the half-cell reactions (3) and (4) are summed:

$$H_2O \Leftrightarrow H_2 + 1/2\ O_2 \quad (6)$$
$$E_b^o = -\ 1.030\ V$$

The relative extent of each of these reactions is determined by chemical equilibrium. Each will occur at the *same cell potential*; but as expressed by the Nernst relation, the concentration terms will be greatly affected by the large difference in the standard cell potentials, E^o, values.

$$E = E_a^o \cdot \left(\frac{RT}{nF}\right) \ln \left\{ \frac{a_{S^{2-}_{cath}} P_{H_2\,cath} P_{S_2\,an}^{\frac{1}{2}}}{a_{S^{2-}_{an}} P_{H_2S_{cath}}} \right\} \quad (7)$$

$$E = E_b^o - \left(\frac{RT}{nF}\right) \ln \left\{ \frac{a_{CO^{2-}_{3\,cath}} P_{H_2\,cath} P_{CO_2\,an} P_{O_2\,an}^{\frac{1}{2}}}{a_{CO^{2-}_{3\,an}} P_{CO_2\,cath} P_{H_2O_{cath}}} \right\} \quad (8)$$

We here assume a process gas is supplied to the cathode with an H_2S level of 100 ppmv, a CO_2 level of 14.2%, and an H_2O level of 5.7%, and that 90% of the H_2S is to be removed via reaction (1). There exists an activity ratio of $\frac{a_{CO_3^{2-}}}{a_{S^{2-}}}$ on the order of 10^5 in the anolyte, assuming equivalent electrode kinetics[5,6] for the two reactions, before a significant amount (e.g. 1%) of the carbonate is oxidized. When compared to the activity ratio of $\frac{a_{CO_3^{2-}}}{a_{S^{2-}}}$ in the catholyte of 3000, this shows the huge thermodynamic preference for the oxidation of S^{2-} to elemental sulfur by equation (2).

The net effect, under these conditions, is continuous and selective removal of H_2S from the process gas accompanied by enrichment of the process gas with H_2 and direct generation of elemental sulfur at the anode.

Electrical Power Requirements.

The power to drive the electrochemical membrane separator is a direct function of the potential required to drive the removal cell multiplied by the current carried by the sulfide ions across the membrane.

Power=(CellPotential) *(Cell Current) **(9a)**

Estimation of the current carried by the removal cell is straight-forward since two faradays of charge are carried by each mole of sulfide transported (or each mole of H_2S removed). Calculation of the cell potential is outlined below.

Along with the Nernst relation, additional energy is required to operate the separation cell due to irreversible losses. These losses occur by internal resistance, concentration effects in the process gases, and the activation barrier for electron transfer. The result is the total cell potential increasing over the reversible potential[1].

Ohmic Polarization:

Ohmic losses occur due to resistance in ionic and electronic transfer of current through the separation system. The ohmic losses can be expressed by:

$$\eta_{ohm} = IR \tag{9}$$

with **I** representing current and **R** the total cell resistance.

Concentration Polarization:

Concentration polarization originates from developing concentration gradients due to consumption of electro-active species at the electrode surface. Transport of these species is composed of four steps, occurring in series: 1) the H_2S must diffuse through the gas-phase boundary layer to the cathode interface, 2) it must diffuse through the pores of the electrode to the electrolyte film, 3) the sulfide ion must migrate to the anode, and 4) the oxidized species must diffuse out into the sweep gas at the anode. The effect of step 3 has been minimized due to proper membrane design and steps 2 and 4 have been found to be of no consequence[2]. The limiting process for removal is thus diffusion of electro-active species to the electrode pores from the bulk gas. Since the gas-phase concentration of H_2S changes along the length of the channels, a log-mean average is used in the calculation of limiting current density by:

$$i_L = nFk_m\rho\frac{\left(y_{inlet} - y_{exit}\right)}{\ln\left(\frac{y_{inlet}}{y_{exit}}\right)} \tag{10}$$

where **n** is the number of electrons transferred per mole of species removed, **F** is Faraday's constant, $\mathbf{k_m}$ is mass transfer coefficient, ρ is the molar density of the bulk gas, and $\mathbf{y_x}$ is the inlet and exit mole fraction of H_2S. The average mass transfer coefficient was derived from an estimated Sherwood number dependent on channel dimension and constant H_2S surface concentration[3] given by:

$$N_{Sh} = \frac{k_m D_{eq}}{D_{ab}} \tag{11}$$

with $\mathbf{D_{eq}}$ defined as the equivalent channel diameter above the electrode surface:

$$D_{eq} = 4r_h = \frac{4(\text{cross-sectional area})}{(\text{wetted perimeter})} \tag{12}$$

and $\mathbf{D_{ab}}$ the diffusion coefficient of H_2S through the predominant species by volume in the bulk according to[4]:

$$D_{ab} = \frac{0.0018583T^{\frac{3}{2}}}{P\sigma_{ab}\Omega_{D_{ab}}}\sqrt{\frac{1}{M_a}+\frac{1}{M_b}} \tag{13}$$

therefore, concentration overpotential is expressed in terms of applied current by:

$$\eta_{conc} = \frac{RT}{nF}\ln\left(1-\frac{i}{i_l}\right) \tag{14}$$

Activation Polarization:

The activation polarization at both cathode and anode is related to the rates of electrochemical reactions occurring at these electrodes. The expression relating the kinetics of these electrode reactions is the Butler-Volmer equation:

$$i = i_o\left[\exp\left(\frac{\alpha_a F\eta_{act,a}}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta_{act,c}}{RT}\right)\right] \quad (15)$$

which holds for specified temperature, pressure, and concentration of reacting species. The transfer coefficients α_a and α_c sum to the number of electrons transferred in the reaction:

$$\alpha_a + \alpha_c = n \quad (16)$$

Cell Voltage:

Total cell voltage incorporating *ohmic*, *concentration*, and *activation* overpotentials along with the Nernstian effects (7) sums to:

$$V_{cell} = \Delta E_{c-a} - |\eta_{conc}| - |\eta_{act}| - \eta_{ohmic} \quad (17)$$

where $\Delta E_{c\text{-}a}$ is the total cathode-to-anode cell voltage.

The results exhibited in Figure 2, 3, and 4 were generated using this analytical approach. The run conditions assumed equal cathodic and anodic flow rates of (200 cc/min) (the calculated results are independent of anode sweep gas flow rate), atmospheric system pressure, a run temperature of 650 °C, and three order of magnitude changes in H_2S removal (1000 ppm to 1 ppm). The cathodic and anodic exchange current densities were estimated at 40 mA/cm^2 after the results of the free electrolyte studies[5,6]. The exchange coefficients, α_a and α_c, were assumed to be unity. Ohmic resistance across the cell was conservatively estimated to be 1 Ω, based on Molten Carbonate Fuel Cell (MCFC) results[1]

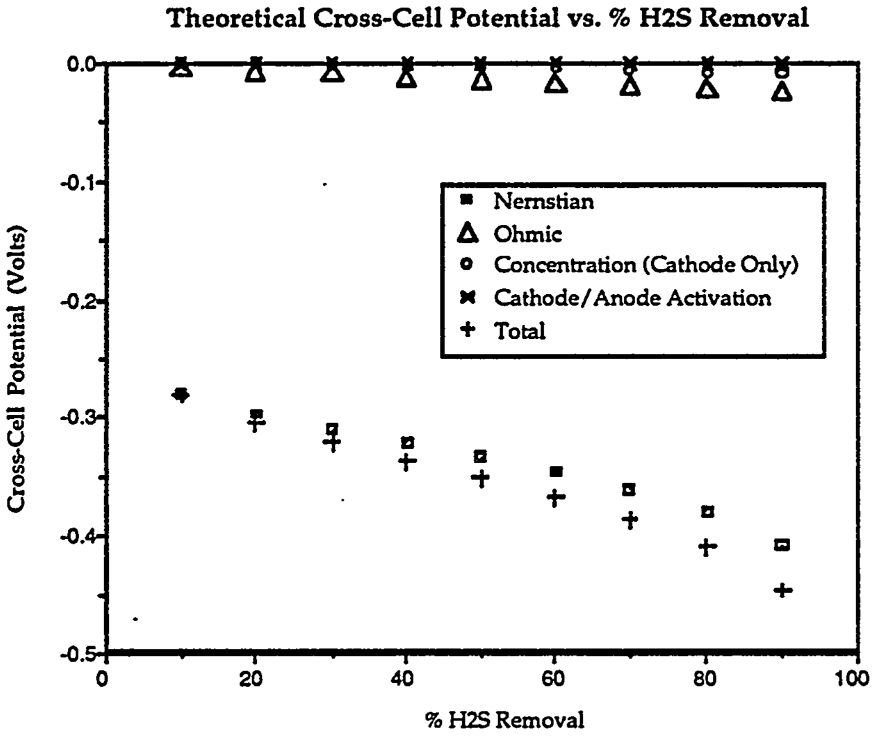


Figure 2. Theoretical Cross-Cell Potential vs. % H_2S Removal; 1000 ppm inlet

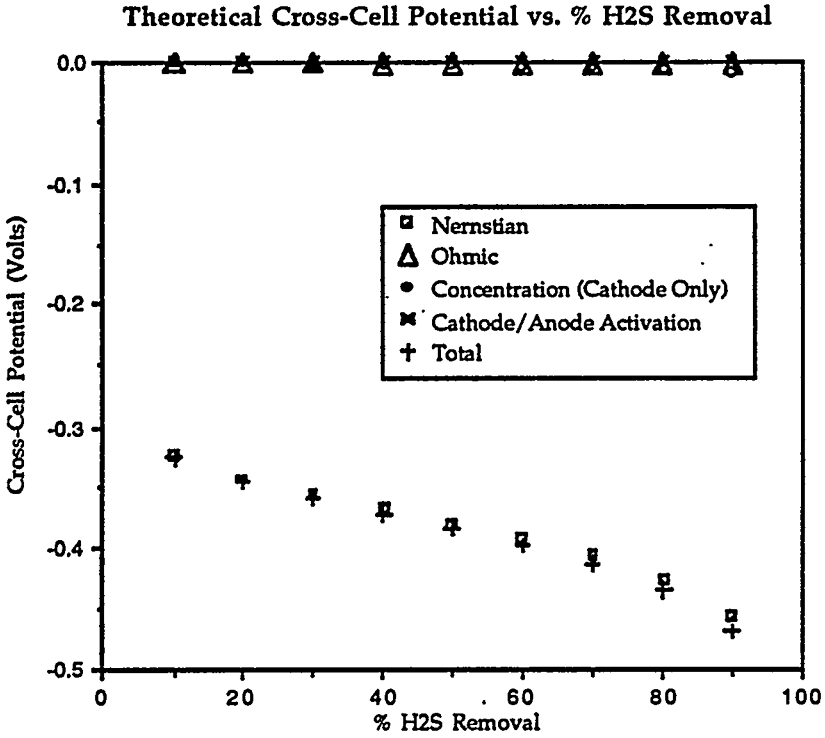


Figure 3. Theoretical Cross-Cell Potential vs. % H_2S Removal; 100 ppm inlet

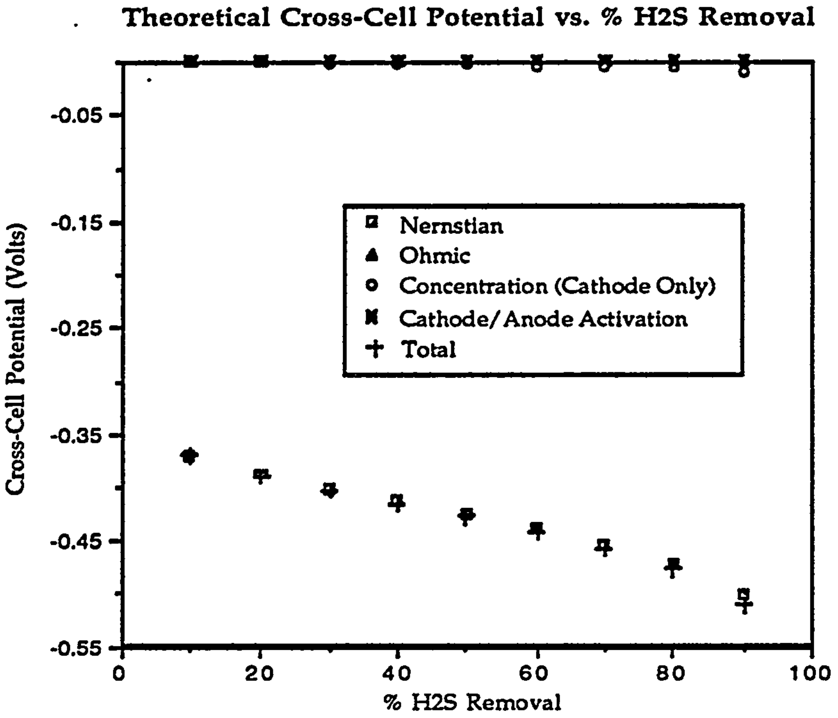


Figure 4. Theoretical Cross-Cell Potential vs. % H_2S Removal; 10 ppm inlet

These results show the activation overpotentials at both cathode and anode are negligible. This shows extremely rapid electrochemical kinetics as compared to diffusion effects from the bulk gas phase and through the electrolyte filled membrane. Cross-cell potentials are shown as the sum of the Nernstian, concentration, and ohmic polarization effects. Therefore, at 90% removal H_2S (1000 ppm - 100 ppm; 100 ppm - 10 ppm; 10 ppm to 1 ppm), the data of Figure 2, 3, and 4 show total cross-cell potentials of -0.4474 V, -0.4675 V, and -0.5107 V, which agree well with experimental cross-cell potentials. Total power requirements for these removals from (9a) are 10.5 W, 1.09 W, and 0.12 W (not considering current loss from anodic CO_2 production).

Parallel Sulfide, Carbonate Transport.

Since the carbonate transport of reaction (6) parallels the sulfide transport of reaction (5), the same current is available for transport of both species. Therefore, only a certain amount of current will act to transport either constituent giving a finite maximum current efficiency with respect to H_2S removal for any percentage of H_2S removed. This is dependent on gas composition and total cross-cell potential required for the desired separation of H_2S. Once the total cross-cell potential is calculated for the desired H_2S removal, the Nernst expression for transport of carbonate (8) can be equated to this value, since the relative extent of each occur at the same potential. The extent of parasitic CO_2 current from the removal cell associated with %H_2S removal is shown in Figure 5, 6, and 7.

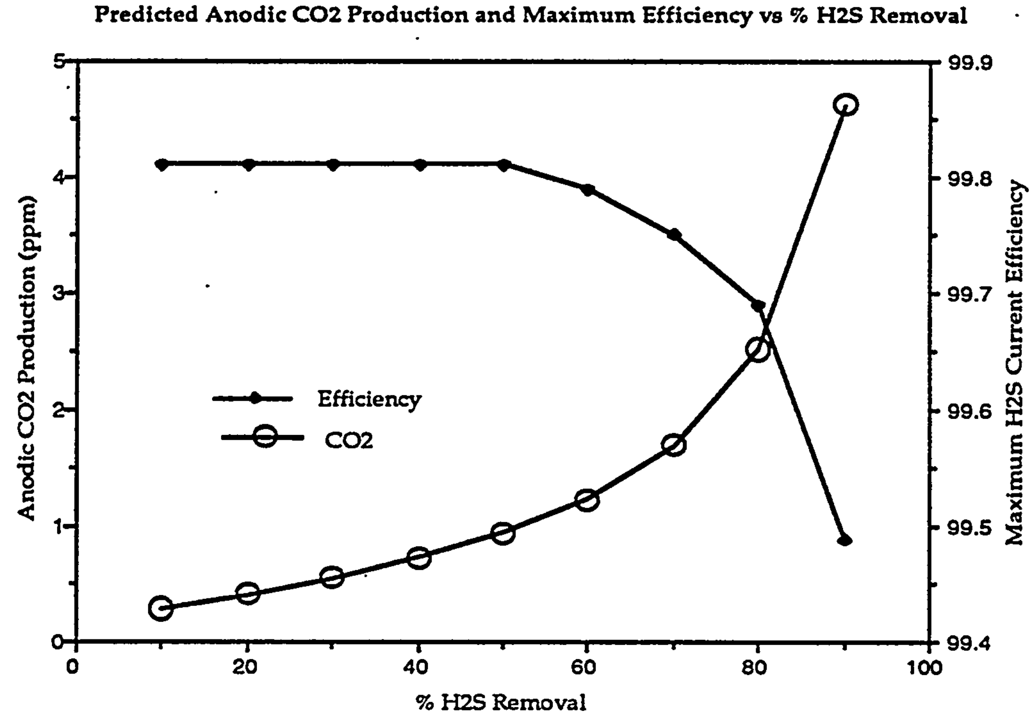


Figure 5. 1000 ppm inlet H_2S

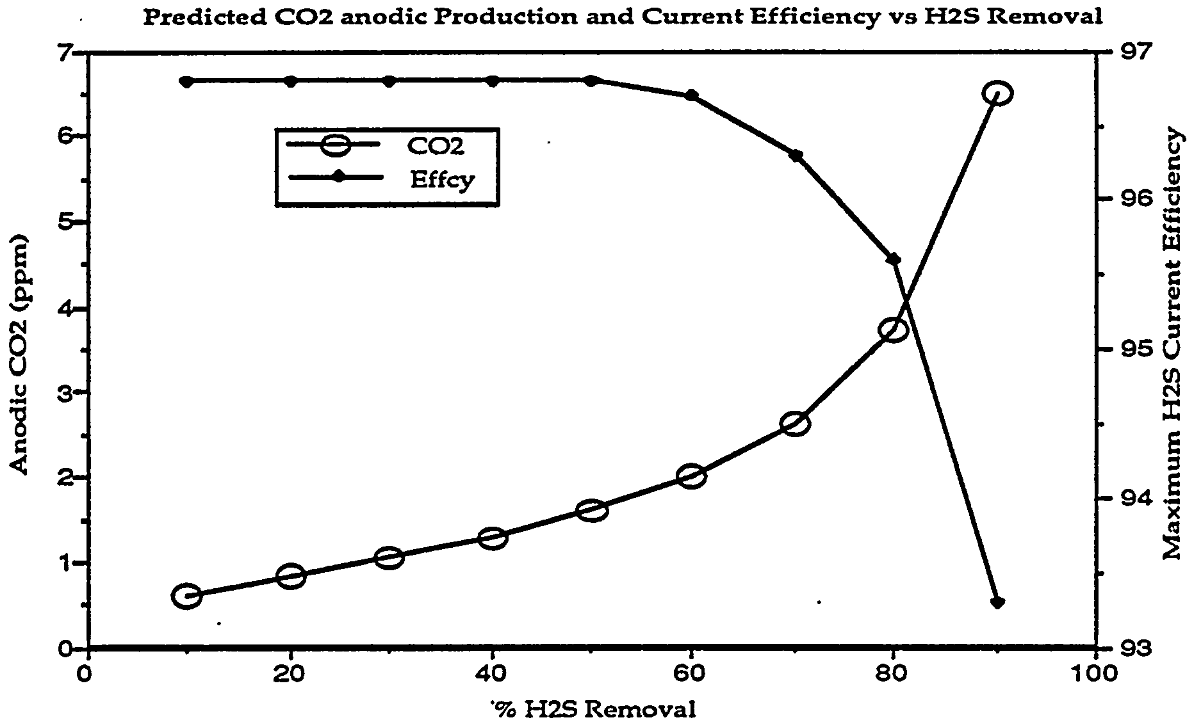


Figure 6. 100 ppm inlet H_2S

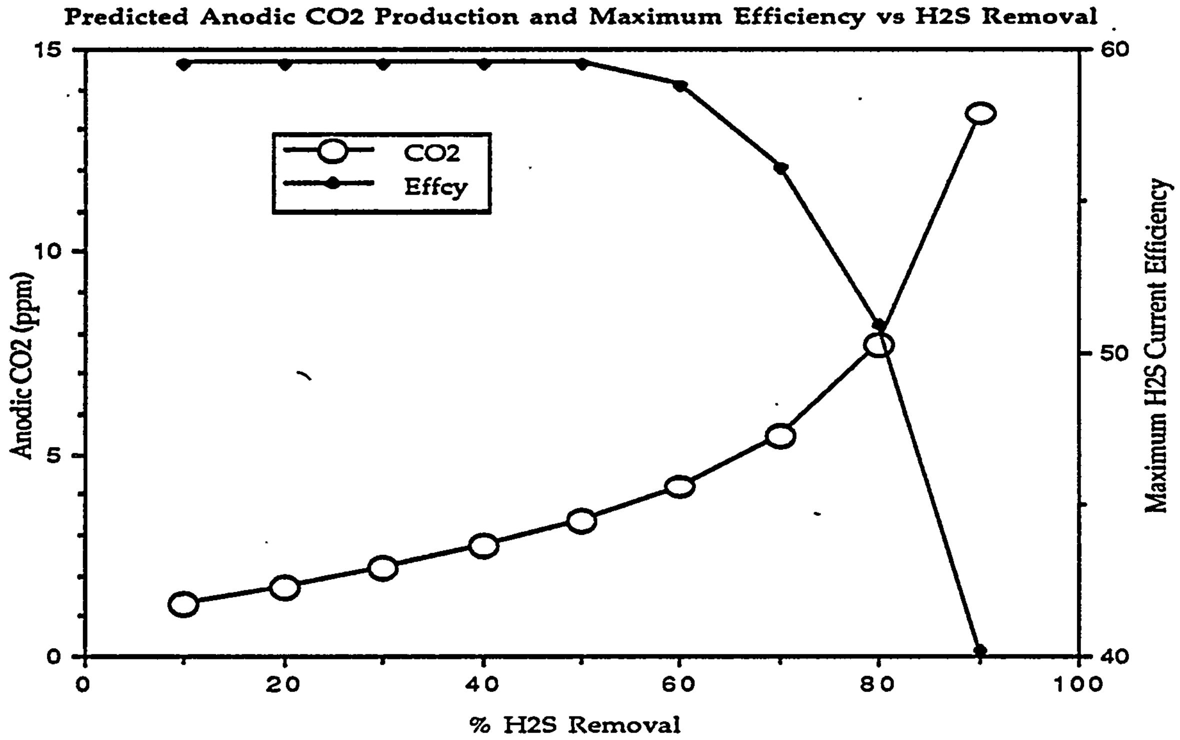


Figure 7. 10 ppm inlet H_2S

Examination of the results shows that H_2S current efficiency drops only to 99.5% at 90% H_2S removal (1000 ppm to 100 ppm H_2S), 93.2% at 90% H_2S removal (100 ppm to 10 ppm H_2S), and 40.2% at 90% H_2S removal (10 ppm to 1 ppm H_2S). The excess current goes to produce anodic CO_2.

This is a favorable result considering the power requirement at higher inlet H_2S concentrations is considerably greater than at lower concentrations, Figure 8 (10.52 W at 1000 ppm inlet H_2S, 0.29 W at 10 ppm inlet H_2S); a high efficiency is a must in the higher H_2S concentrations if the process is to be economically viable. Energy requirements for the 10 ppm H_2S removal are negligible, shown in Figure 8, alleviating concern due to lower current efficiencies.

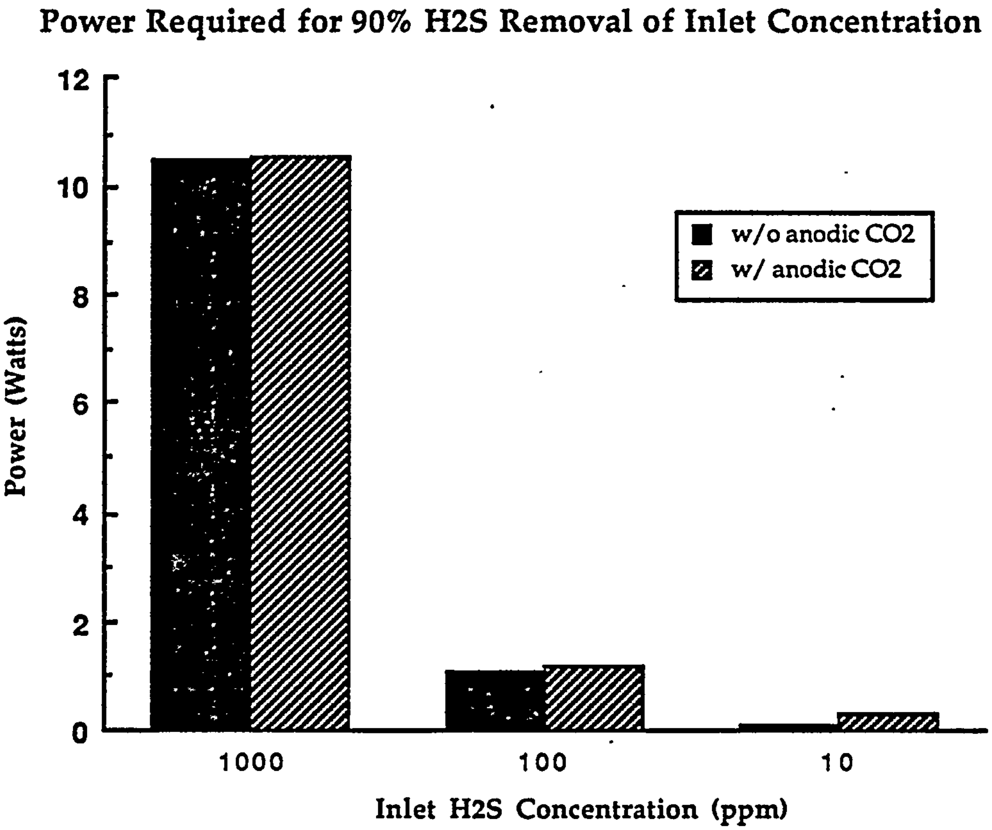


Figure 8. Power Estimates

Table I. Percentage Removal with Applied Current

I_{app} (mA)	% of Total H_2S Removed	% of Total CO_2 Removed
200	0	10
500	28	30
1000	50	50
1500	70	75

EXPERIMENTAL RESULTS

An experiment (Run#16) examining the removal capability of the EMS with cobalt cathode was recently performed The focus dealt with H_2S removal as well as containing hydrogen cross-over from the process gas side (cathode) of the membrane to the sweep gas side (anode).

Run #16

Cell materials consisted of a cobalt cathode (80% porous), the anode material remained Ni (85% porous), a stabilized zirconia membrane (66% porous), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(Li/K)_2CO_3$ (8 grams) corresponding to the void volume in the zirconia membrane. Electrode materials were verified by x-ray diffraction, Figure 9.

Examination of the cobalt-cathode electrochemical membrane separator (EMS), produced stoichiometric CO_2 removal and addition at both cathode and anode, respectively, before addition of H_2S. After introducing H_2S to the EMS, system gases equilibrated to 10% CO_2, 18% CO, 10% H_2O, 36% H_2, 26% N_2 and 90 ppmv H_2S after the water-gas shift reaction. H_2S removal at varying currents was attempted, starting with stoichiometric current (2 mA for a flow of 158 cc/min), and increasing to 200 mA. H_2S removal did not appear significant (< 10 ppmv), with continued stoichiometric CO_2 removal at the cathode and production at the anode. Further application of current in steps from 200 mA to 1.5 A revealed percentage of total H_2S removal coincided with percentage of total CO_2 removal, shown in Table I. This trend was evidenced in past experiments with hydrogen cross-over present. Micro-cracks in the membrane that would enable hydrogen to cross from the process gas side (cathode side) to the sweep side (anode side) seem to be evident from Scanning Electron Microscopy (SEM) in pre-run analysis, Figure 11.

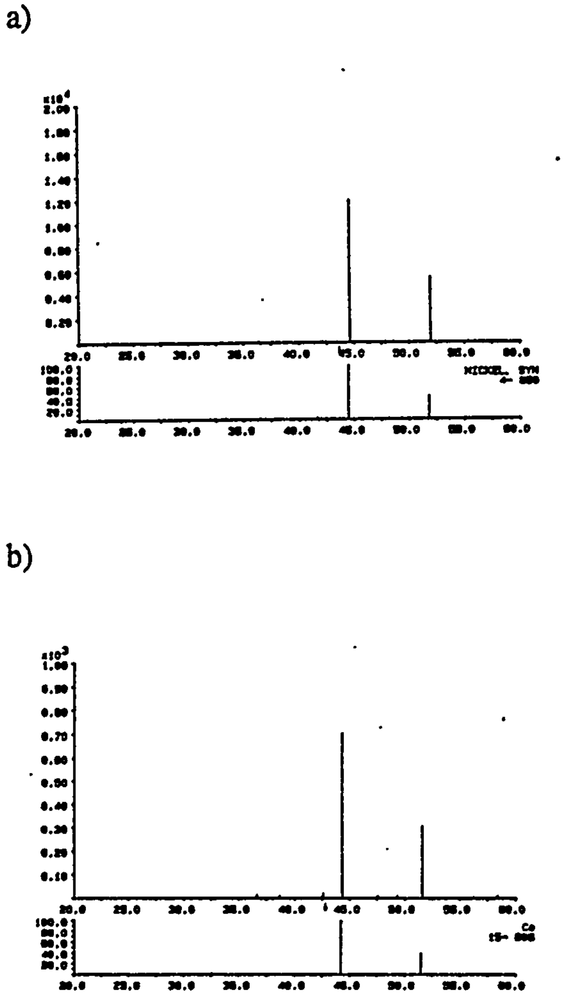
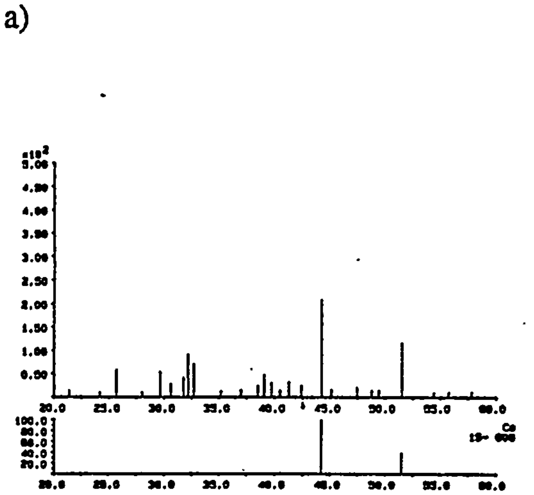


Figure 9. a) Pre-run Ni anode and b) Pre-run Co cathode



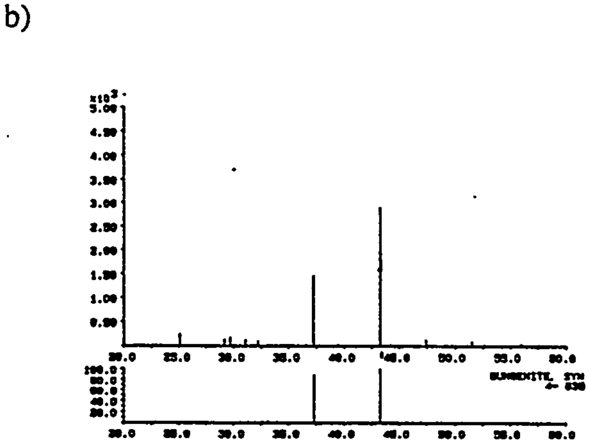


Figure 10. a.) Post-run Co cathode and b.) Post-run NiO anode

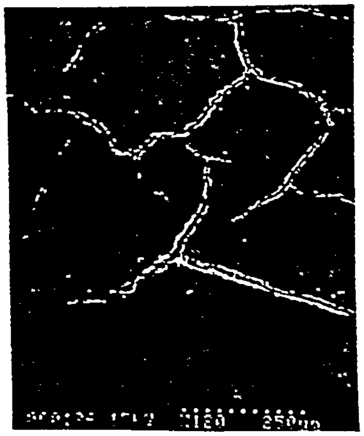


Figure 11. Scanning Electron Microscopic view of zirconia membrane.

If hydrogen cross-over occurs, two reactions are possible at the anode. One reaction is the oxidation of hydrogen and the sulfide ion to hydrogen sulfide.

$$H_2 + S^{2-} \rightarrow H_2S + 2e^-$$

Anode exit gases checked by gas chromatography showed no evidence of H_2S. The other possible reaction is the oxidation of hydrogen and carbonate to water and carbon dioxide.

$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

Gas chromatography did reveal minute amounts of water vapor on the anode side substantiating hydrogen cross-over. This creates loss of carbonate from the electrolyte, induces the favorability of carbonate reduction at the cathode over H_2S due in part to the higher pressure of CO_2 and H_2O available at the cathode (order of 10^5 higher than H_2S) promoting the parasitic reaction.

Favored:
$H_2S + 2e^- \rightarrow H_2 + S^{2-}$

Competing:
$H_2O + CO_2 + 2e^- \rightarrow CO_3^{2-} + H_2$

Internal resistance remained ~1 ohm.

Ineffective removal due to hydrogen cross-over forced shut-down of the cell after 76 hours of operation. Post-mortem X-ray diffraction of electrode materials revealed a conversion of the Ni cathode to NiO (bunsenite), with the cathode remaining Co, Figure 10.

SUMMARY

Initial results from the analytical model show favorable H_2S current efficiencies. Upper H_2S concentration removal resulted in a minuscule loss in current to the parasitic reaction (6) at 90% H_2S removal. Although the lower concentrations showed less efficiency, the amount of current needed for these removals are negligible.

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by the possibility of hydrogen cross-over from process gases creating alternate reactions unfavorable to the removal system. Application of back-pressure from the anode side of the cell was attempted to resolve H_2 cross-over, but proved ineffective. Examination of water vapor in the anode exit gases provided proof of the H_2 cross-over reactions parasitizing applied current.

FUTURE WORK

The main focus will be on H_2S current efficiency using a fabricated zirconia membrane with 100 ppmv H_2S fuel gas; hopefully, preventing alternate reactions due to hydrogen cross-over.

Work will continue with the analytical model; a complete economic analysis based on the completed model is the ultimate goal, if a match with real-time data exists.

REFERENCES

1. U.S. Dept. of Energy, Fuel Cell: A Handbook, DOE/METC-88/6090, Morgantown, West Virginia, 1988.

2. Kang, M. and Winnick, J., *J. Appl. Electrochem.*, **15**, 431-39 (1985).

3. Incropera, F.P., and DeWitt, D.P., Fundamentals of Heat and Mass Transfer, 2nd ed., John Wiley and Sons, New York, 1985.

4. Reid, R., Prausnitz, J., and Poling, B., The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

5. Banks, E., and Winnick, J., *J. Appl. Electrochem.*, **16**, 1986.

6. White, K.A., and Winnick, J., *Electrochem. Acta.*, **30**, 1985.

7. EPRIEM-1333, *Assessment of Sulfur Removal Processes for Advanced Fuel Cell Systems, Final Report,* C.F. Braun and Co., Alhambra, CA, Jan., 1980.

8. Vidt, E.J., DOE/METC DE-AC-21-81MC16220, DE82013942, Westinghouse, Dec., 1981.

9. Focht, G.D. et. al., DOE/MC/121166-2163, DE86016041, July, 1986.

10. Lyke, S.E., DOE/MC/19077-1803, DE8500961, Battelle Pacific Northwestern Laboratories, Jan. 1985.

11. Alexander, S., *PhD Thesis*, Georgia Institute of Technology, Atlanta, GA, 1992.