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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.

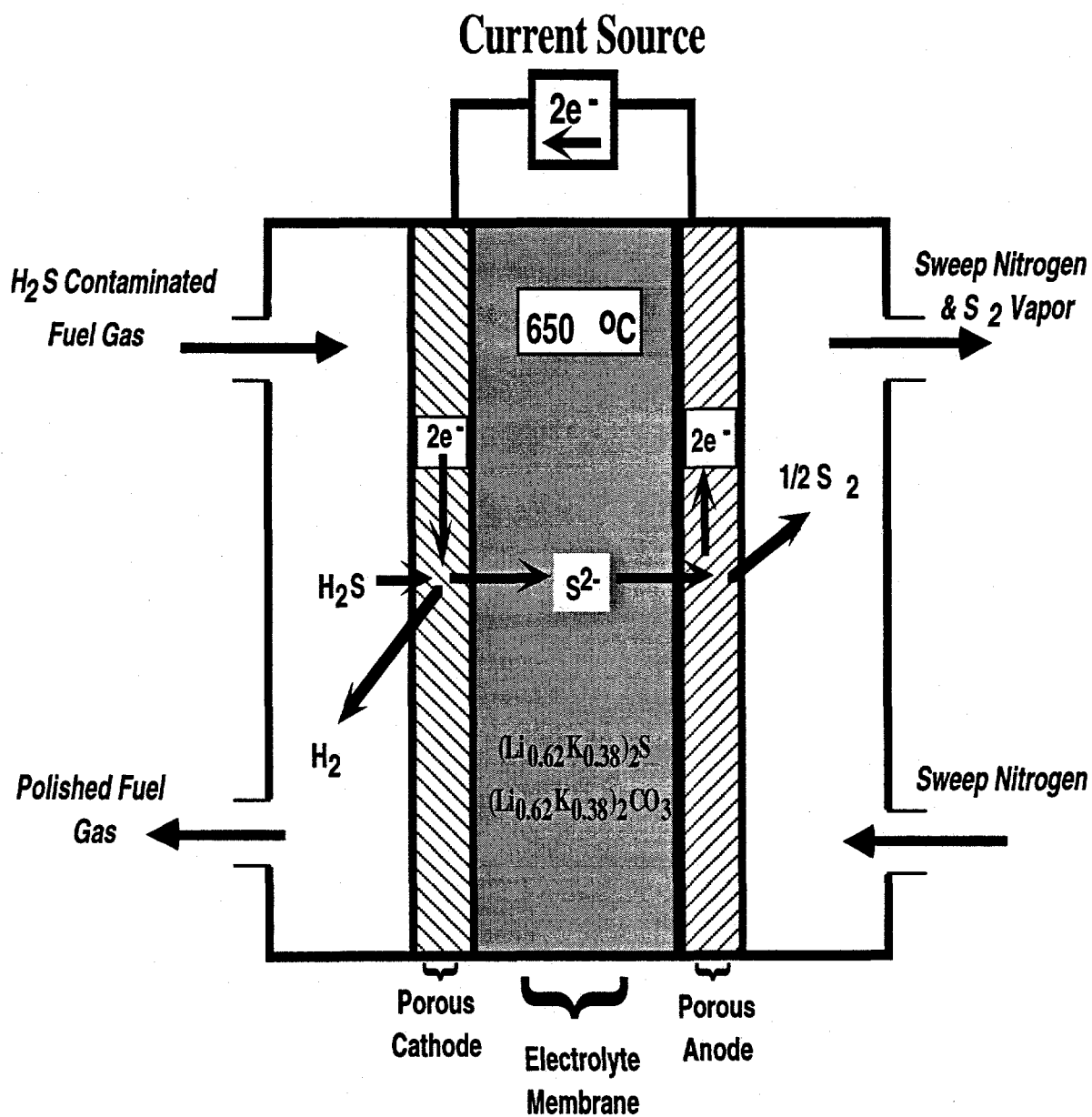


Figure 1. Single-Cell View of the Electrochemical Membrane Separator

Quarterly Research

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 $\text{Ni}_{3+x}\text{S}_2$ when contacting gas with >100 ppm H_2S , requires alternate cathode materials. Co, which converts to Co_9S_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.

Eventual scale-up of the E.M.S. system will probably incorporate cobalt electrodes; bench-scale experiments have confirmed that consistent inlet H_2S levels are difficult to control.

This would be detrimental in a full-scale operation where a high local H₂S density could result in electrode destruction.

An alternative would allow use of Ni as the cathode material but require a lower run temperature to avoid the liquid NiS_y from forming²¹. This was attempted successfully in Run 30 this quarter.

Quarterly Summary

Utilizing Ni as a cathode material at reduced temperatures (decrease from 650 °C to 580 °C) in full-cell experiments was the primary focus this quarter. A Ni cathode was purchased and utilized in two full-cell experiments (run 29 and run 30); both runs utilized a fabricated membrane purchased from Zircar Corporation. Table III gives an outline of the membrane materials as well as other components used for experiments 29 & 30.

Two full-cell experiments served a three-fold purpose: 1) testing the electrochemical membrane separators ability to concentrate CO₂; 2) testing the electrochemical membrane separators ability to remove H₂S; and 3) testing modifications of the experimental apparatus (i.e. Ni cathode performance at 580 °C).

Table I. Experimental Components

Run	Temp. °C	Cathode	Anode	Membrane	Housings	Electrolyte
29	580	Ni	Lithiated NiO	Fabricated (ZrO ₂)	Stainless Steel (316)	(Li _{0.62} K _{0.38}) ₂ CO ₃
30	580	Ni	Ni	Fabricated (ZrO ₂)	MACOR machineable ceramic	(Li _{0.62} K _{0.38}) ₂ CO ₃

Run #29

A ZrO₂ membrane purchased from Zircar Corporation provided a barrier to process gases and entrained the molten-salt electrolyte for ionic transportation between electrodes. The 2.0 grams of electrolyte needed to saturate the 64% porous ceramic membrane was inserted in-situ after process components reached run temperature (580 °C). 85% porous Ni electrodes were purchased from Energy Research Corporation. Housing materials consisted of 316 stainless steel with two pressed aluminum disk as process-gas sealants; adherence of process seals to the housings was aided by application of aluminum paint(29 wt% Al).

Several power outages, due to Olympics preparation in the surrounding area, prevented collection of data.

Run #30

A fabricated zirconia membrane was utilized in run 30. Housings were MACOR, a machineable ceramic. Electrodes consisted of two 85% porous nickel matrices purchased from Energy Research Corporation.

Upon full-cell start-up the initial temperature was set at 300 °C and increased to 550 °C in 50 °C increments. Cathode and anode gas flow rates were 150 cc/min N₂ and 100 cc/min N₂ respectively. Once the cell temperature reached 580 °C, 2.0 grams of electrolyte were added; cathodic flow was adjusted to 225 cc/min; 61 cc/min was comprised of fuel gas (6% CO₂, 18% CO, and 13% H₂) and the remaining 164 cc/min of N₂. The anodic inlet gas consisted of 133 cc/min N₂, 17 cc/min CO₂. Both cathode and anode seals were excellent.

Evaluation of theoretical CO₂ removal from the process-gas (cathode-gas) and anode CO₂ evolution with applied current was the first test conducted on the Electrochemical Membrane Separator (E.M.S.) full-cell run; percentage of CO₂ removal/evolution compared to the theoretical value determines system performance. Application of 100 mA to the cell caused process-gas CO₂ levels to decrease by 100% of the theoretical value, which is necessary before H₂S application. Internal resistance was measured by current interrupt and found to be ~ 3Ω; an

acceptable value is 1Ω (0.5 grams of electrolyte were added to the cell). A current step method was performed in order to determine CO_2 removal, Figure 2 and CO_2 evolution, Figure 3. H_2S addition occurred after cell stability was proven.

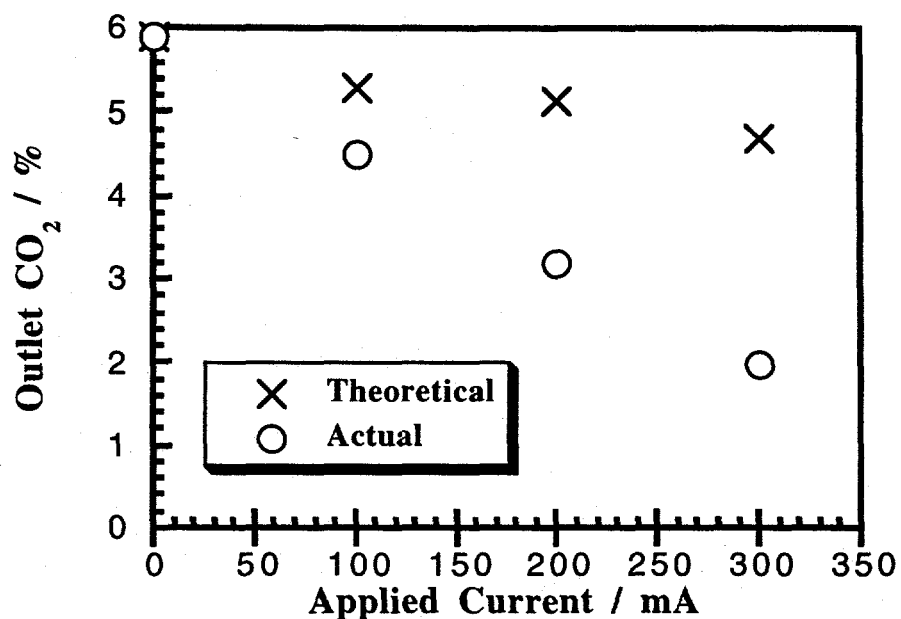


Figure 2. CO_2 Removal with Applied Current

Upon addition of H_2S , process gas equilibrated to 8.74% CO_2 , 6.96% CO , 6.15% H_2O , 15.9% H_2 , 4006 ppmv H_2S , 105 ppmv COS . The molten-electrolyte - process-gas equilibrium given by:



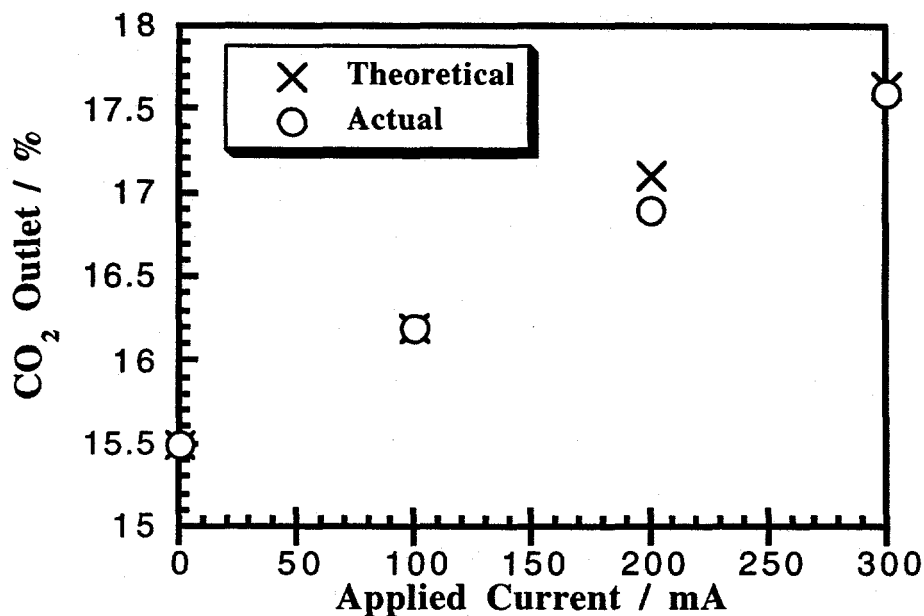


Figure 3. CO₂ Addition with Applied Current

creates a conversion of carbonate ions to sulfide ions dependent on the partial pressure of H₂S above the electrolyte; equilibrium electrolyte content consisted of 93.5 mol% (Li_{0.68}K_{0.32})₂CO₃, 6.5 mol% (Li_{0.68}K_{0.32})₂S.

Limiting current density analysis within the E.M.S. system shows that the gas-phase limiting current density was 46.6 mA/cm² while the membrane limiting current density was 59.5 mA/cm². This reveals the expedience of ionic transport through the membrane. Cathode and anode electrode areas were both 7.91 cm²; therefore the maximum applicable current to the cell for H₂S removal was 369 mA before exceeding the limiting current based on bulk-gas diffusion of H₂S. Stoichiometric current needed to remove 4100 ppmv H₂S down to 410 ppmv H₂S was 79.1 mA.

Upon equilibration of the electrolyte and process-gas species (H₂S inlet ~ H₂S outlet at varying flow rates) current was applied to the cell to test H₂S removal capabilities; some electrolytic polishing of gaseous species remained evident. Figure 4 shows H₂S removal and current efficiency versus current density. Effective H₂S removal did occur; close to 90% H₂S removal was evidenced at 98% current efficiencies. Potential values above those expected did not interfere with the removal, however constant electrolytic dissolution did influence the internal resistance (IR ~ 6Ω) creating the superfluous cross-cell values of over 2 Volts.

Application of 4950 ppmv H₂S to the cell ensued after adequate removals were recorded at the previous values; flow rate remained constant 165 cc/min. 3 grams of electrolyte was added to the system to improve the internal resistance (~3Ω) and thereby reducing cell potentials (1.5 volts) . Anode flow involved 17 cc/min CO₂ and 90 cc/min N₂. Cathode gases equilibrated to 8.74% CO₂, 6.96% CO, 6.16% H₂, 15.92% H₂O, 4828 ppmv H₂S, and 126.7 ppmv COS. Electrolyte composition consisted of 92.3 % M₂CO₃ and 7.7% M₂S. 90% H₂S removal required 96.5 mA at 165 cc/min. Gas-phase & membrane limiting current densities were 56.16 mA/cm² and 70.7 mA/cm², respectively. Figure 5 illustrates 100% current efficiency was achieved at 90% removal efficiency.

Inlet concentration and flow rate were changed to 1630 ppmv H₂S and 560 cc/min respectively. Cathode gases equilibrated to 7.6% CO₂, 5.8% CO, 6.6% H₂O, 16.4% H₂, 1596 ppmv H₂S, and 33.8 ppmv COS; electrolyte species consisted of 97.2% M₂CO₃, 2.8% M₂S at process gas composition. Over 90% current efficiencies were seen at 80% removal efficiency shown in Figure 6.

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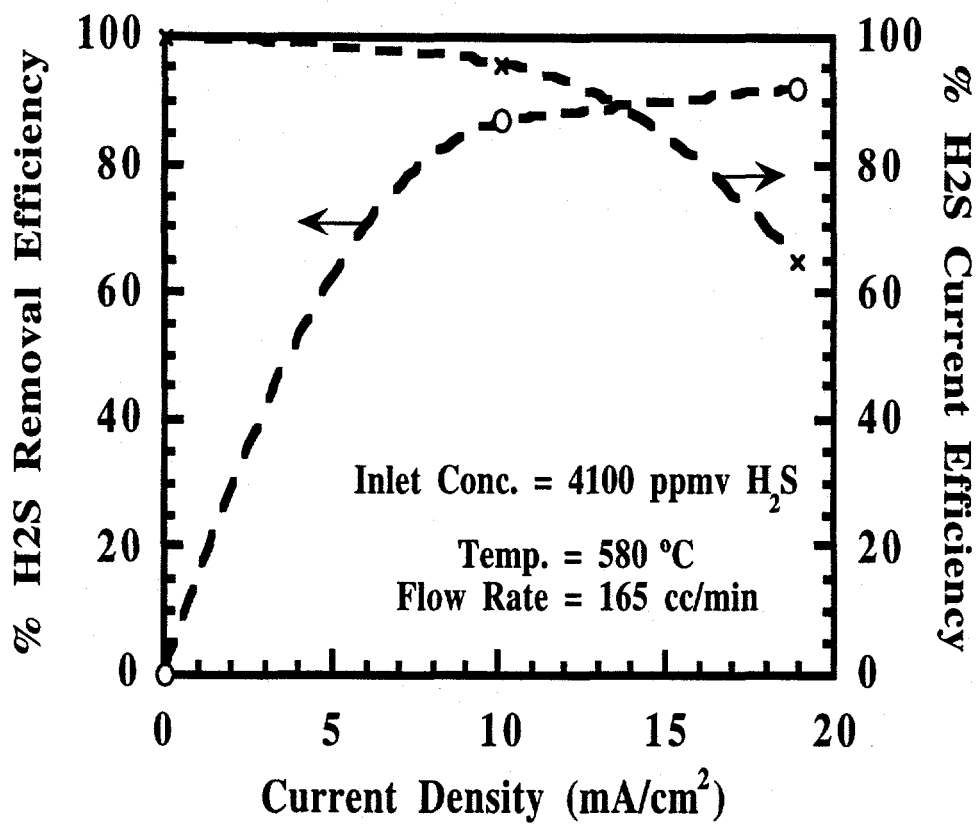


Figure 4. H₂S Current Efficiencies and Removal Efficiencies versus Current Density
 4100 ppmv H₂S Inlet / 165 cc/min flow rate

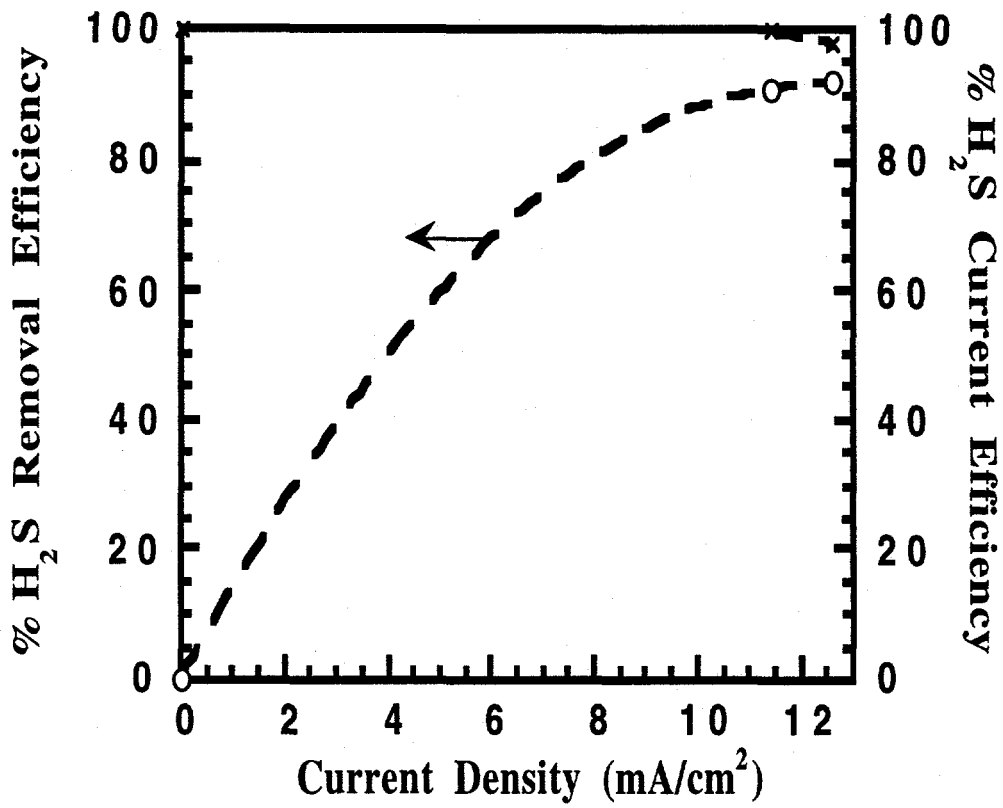
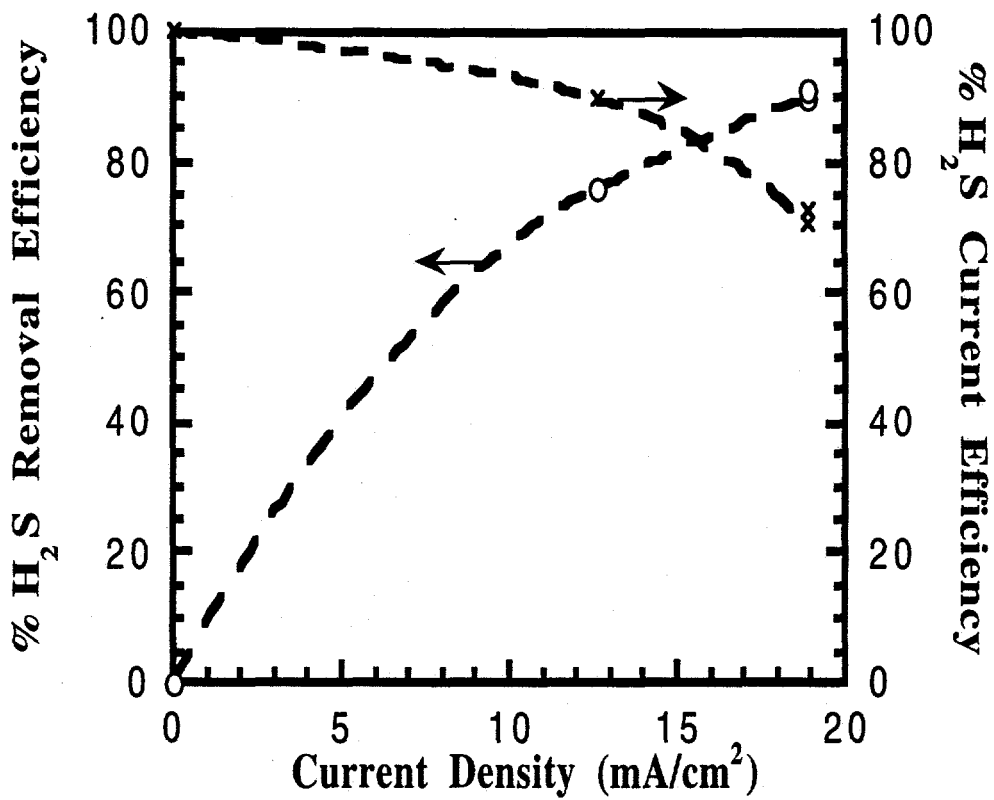


Figure 5. H₂S Current Efficiencies and Removal Efficiencies versus Current Density
4950 ppmv H₂S Inlet / 165 cc/min flow rate



**Figure 6. H₂S Current Efficiencies and Removal Efficiencies versus Current Density
1630 ppmv H₂S Inlet / 560 cc/min flow rate**

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.

Lower temperature experiments utilizing Ni as a cathode material in order to avoid the NiS_y state is also a primary focus. Run 30 showed tremendous promise with this idea which will continue in future experiments.

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:

$$\%H_2S \text{ Removal} = \frac{(\text{Outlet } H_2S_{\text{zero current}} - \text{Outlet } H_2S_{\text{I}_{\text{applied}}})}{(\text{Outlet } H_2S_{\text{zero current}})} \times 100 \quad (4)$$

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 7. 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 8; Current efficiencies were ~ 35%.

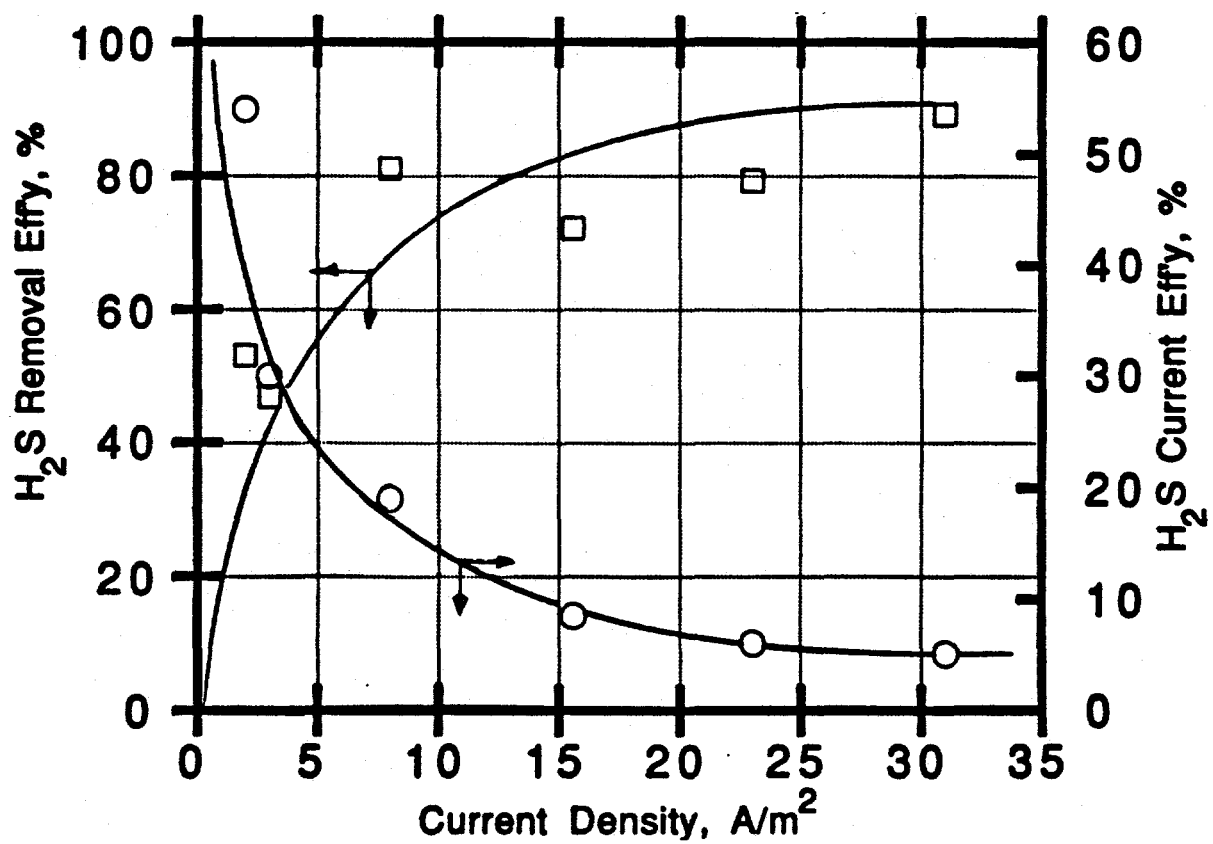


Figure 7. H₂S Current and Removal Efficiency vs. Current Density; 100 ppm inlet H₂S

Cathodic Flow Rate = 88 cc/min

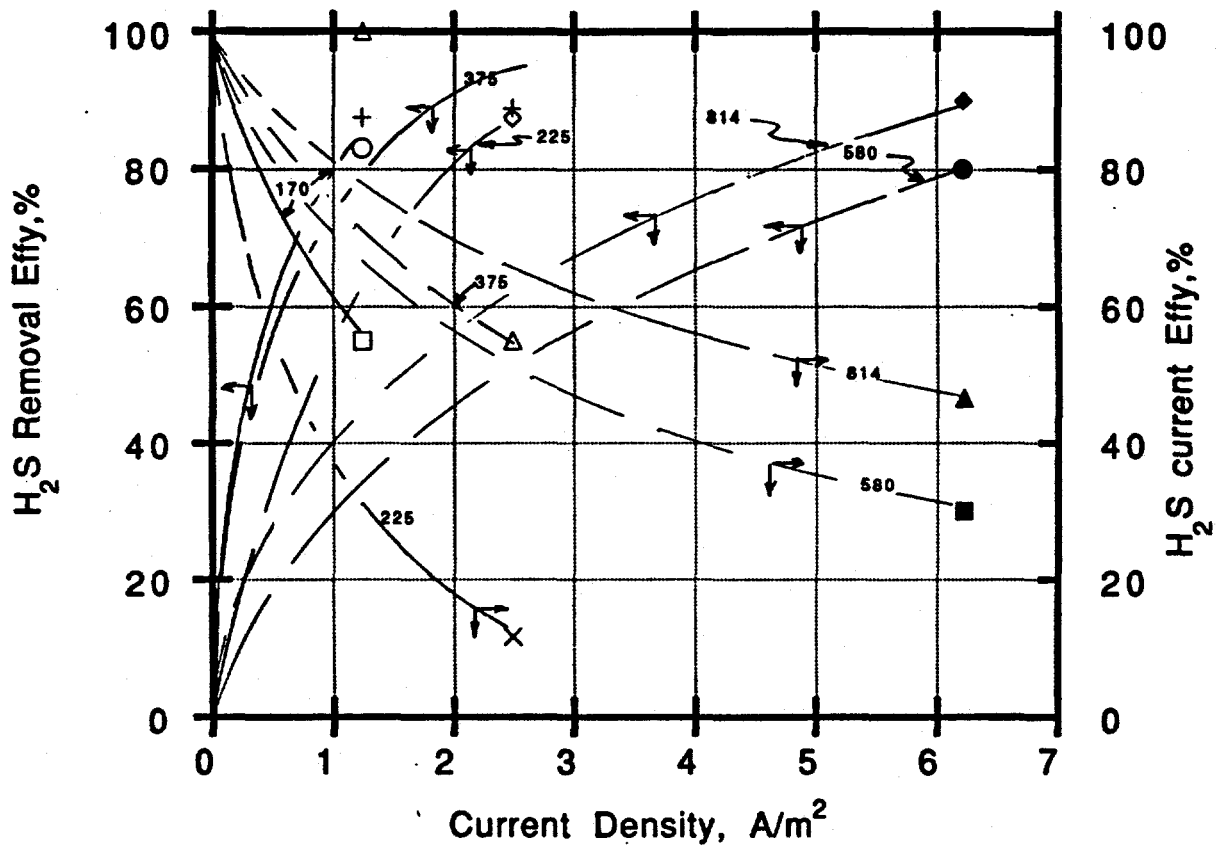


Figure 8. H₂S Current and Removal Efficiency vs. Current Density; 20 ppm inlet H₂S

Parametric values are in cc/min

Next Quarter Goals

A continual problem with the E.M.S. system is an appropriate cathode material with chemical and electrochemical stability in the high temperature corrosive environment. At high levels of H_2S , the Ni cathode converts to a molten NiS_y creating adverse effects mentioned previously. A review of the literature²¹ revealed that maintaining a temperature below $635\text{ }^\circ\text{C}$, usual experiments are performed at $650\text{ }^\circ\text{C}$, prevents the liquid NiS_y from forming. Next quarters experiments will be performed at $580\text{ }^\circ\text{C}$ with the E.R.C. Ni electrodes at the anode and the cathode, hopefully continuing the success of run 30. Co electrodes will continue to be investigated as well; however, persistent oxidation of the material during binder-burn-out has created adverse reactions schemes upon applications of current exposing permanent damage to E.M.S. system.

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