Removal of Hydrogen Sulfide from Natural Gas through an Electrochemical Membrane Separator

Steven Ray Alexander and Jack Winnick
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332

An advanced process is developed for the separation of H_2S from natural gas through an electrochemical membrane. H_2S is removed from natural gas by reduction to the sulfide ion and H_2 at the cathode. The sulfide ion migrates to the anode through a molten salt electrolyte suspended in an inert ceramic matrix. Once at the anode it is oxidized to elemental sulfur and swept away for condensation in an inert gas stream. The natural gas is enriched with H_2. Order-of-magnitude reductions in H_2S concentration have been repeatedly recorded on a single pass through the cell. This process allows removal of H_2S, while producing H_2 and elemental sulfur directly. No absorbents are used, and there is no need for subsequent treatment of a concentrated H_2S stream as with conventional gas sweetening technology. This makes the process economically attractive, since it is much less equipment-intensive than conventional technology.

Introduction

Use of selective membranes for separating gaseous components from mixtures is experiencing escalating interest. Most rely on a pressure or concentration difference to provide a chemical potential driving force:

$$\Delta\mu_i = \mu_i - \mu_i' = RT \ln\left[\frac{a_i}{a_i'}\right] \tag{1}$$

where the activities of component i in the two phases separated by the membrane are noted as a_i and a_i'. Facilitated transport through chemical or surface reaction can sometimes be employed to aid selectivity and permeability.

In certain instances, an electric field can be employed as an alternative. For species with a net charge, z_i, the driving force across a membrane becomes the electrochemical potential difference, $\Delta\bar{\mu}_i$:

$$\Delta\bar{\mu}_i = \bar{\mu}_i - \bar{\mu}_i' = RT \ln\left[\frac{a_i}{a_i'}\right] + z_i F \Delta\Phi \tag{2}$$

where $\Delta\phi$ is the potential difference across the membrane.

This principle can be and has been applied to a high-temperature process gas mixture. The thrust of this work is the purification of fuel gases (specifically natural gas) of H_2S. Since the membrane is exposed to the same pressure on both sides, there is no theoretical limit to the pressure at which the process operates.

Technical Discussion

Natural gas can have a broad range of compositions depending on the location of the well and the extent to which it has been processed. Some representative compositions are: CO_2, 0.8-20%; H_2S, 4 ppm-42.5%; H_2O, 0-12.0%; N_2, 0.3-26.5%; CH_4, 39.6-95.8%; C_2, 1.1-6.2%; C_3, 0.4-3.6%; C_4, 0.1-1.4%; and IC_4, 0.1-1.1%. Processes to remove the H_2S generally rely on low- to ambient-temperature absorption, followed by sorbent regeneration and Claus treatment for conversion of concentrated H_2S to elemental sulfur.

A hot-gas electrochemical membrane process is shown in Figure 1. The process gas is passed by the cathode. Here, the most easily reduced component, that is, the strongest Lewis acid, will be reduced. Under these conditions, it is H_2S:

$$H_2S + 2e^- \rightarrow H_2 + S^{2-} \tag{3}$$

A membrane that contains sulfide ions in a molten state will

Correspondence concerning this article should be addressed to S. R. Alexander, Hoechst Celanese Corp., Corpus Christi Technical Center, 1901 Clarkwood Rd., P. O. Box 9077, Corpus Christi, TX 78469.

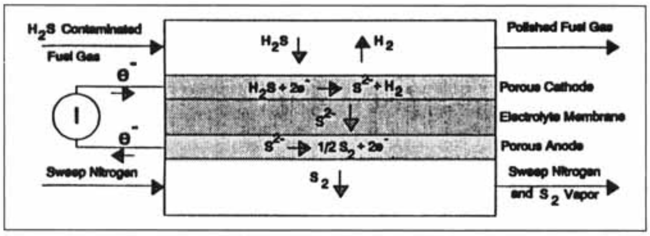

Figure 1. Electrochemical desulfurization cell.

Figure 1. Electrochemical desulfurization cell.

act to transport sulfide across the anode where, in the simplest case, hydrogen can be supplied to form H_2S. If the membrane is capable of preventing the diffusion of hydrogen from the cathode side, an inert sweep gas, such as N_2, can be used at the anode to carry away oxidized sulfide ions as vaporous sulfur, S_2.

This concept has been used with success for gases containing only H_2S in N_2 (Lim and Winnick, 1984), simulated coal gases (Weaver and Winnick, 1987, 1991), and simulated natural gases (Alexander and Winnick, 1990). In this article, H_2S removal for a variety of simulated gas compositions has been examined with application of the process to very sour natural gas (1.5% H_2S), moderately sour natural gas (2,000 ppm H_2S), and slightly sour natural gas (100 ppm H_2S). The cell is shown in Figure 2.

The situation can become complicated when realistic gas mixtures are processed. Carbon dioxide and water vapor compete in the reduction reaction by:

$$CO_2 + H_2O + 2e^- \rightarrow CO_3^{2-} + H_2 \tag{4}$$

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

The direct oxidation of carbonate,

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 + 2e^-, \tag{5}$$

occurs at a standard potential some 0.70 V more positive than that for sulfide:

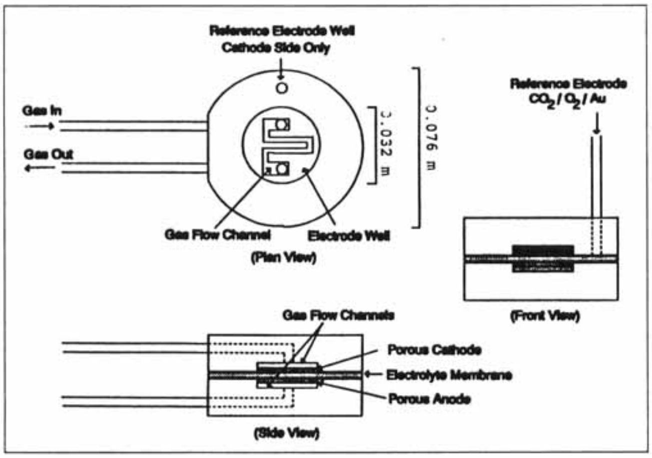

Figure 2. Assembled cell.

$$S^{2-} \rightarrow \frac{1}{2}S_2 + 2e^- \tag{6}$$

When the half-cell reactions (Eqs. 3 and 6) are summed, the resulting cell reaction and standard potential at 900 K is:

$$H_2S \rightarrow H_2 + \frac{1}{2}S_2; \quad E^0 = -0.239\text{V} \tag{7}$$

and when half-cell reactions (Eqs. 4 and 5) are summed, the resulting cell reaction and standard potential are:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2; \quad E^0 = -1.030\text{V} \tag{8}$$

The relative extent of each of these reactions is determined by chemical equilibrium; each will occur at the same potential as predicted by the Nernst relation:

$$E = E^0 - \frac{RT}{2F}\ln\left[\frac{(p_{S_2})^{1/2}}{a_{S^{2-}}}\right]_{\text{anode}} + \ln\left[\frac{p_{H_2}a_{S^{2-}}}{p_{H_2S}}\right]_{\text{cathode}} \tag{9}$$

$$E = E^0 - \frac{RT}{2F}\ln\left[\frac{p_{CO_2}(p_{O_2})^{1/2}}{a_{CO_3^{2-}}}\right]_{\text{anode}} + \ln\left[\frac{a_{CO_3^{2-}}p_{H_2}}{p_{CO_2}p_{H_2O}}\right]_{\text{cathode}} \tag{10}$$

Consider a process gas supplied to the cathode with an H_2S level of 2,000 ppm, a CO_2 level of 1%, and an H_2O level of 12%. If 99% of the H_2S is removed via reaction 3 and the process and sweep gas flow rates are equal, then there will exist an activity ratio $a_{CO_3^{2-}}/a_{S^{2-}}$ of 665 in the anolyte before significant amount (for example, 1%) of the carbonate is oxidized. This assumes equivalent electrode kinetics for the cathodic and anodic reactions. In fact, electrode kinetics for both processes have been found by independent investigations to offer only minor resistance at the current densities involved here (White and Winnick, 1985; Banks and Winnick, 1986).

Comparison of the activity ratio of $a_{CO_3^{2-}}/a_{S^{2-}}$ in the anolyte to the catholyte ratio of 26.9 shows the thermodynamic preference for the oxidation of S^{2-} to elemental sulfur by Eq. 6 in the absence of reductant at the anode. (This mode of operation is preferable for commercial application with direct production of elemental sulfur vapor and eliminates the need for a Claus reactor.) The net effect, under these conditions, is continuous removal of H_2S from the process gas accompanied by enrichment of the process gas with H_2 and the direct generation of elemental sulfur. The only reagent required is electric power at a potentially attractive rate.

The equilibrium potential for a single cell, given by Eq. 9 for the cathodic and anodic reactions (Eqs. 3 and 6), is -0.406 V for a process gas containing 2,000 ppm H_2S and an anode product of pure sulfur vapor (900 K). To this must be added the overpotentials needed for both electrode reactions and ohmic loss. The electrode reactions have been studied in free electrolyte on graphite electrodes (Banks and Winnick, 1986; White and Winnick, 1985). Potential-step experiments showed very rapid kinetics with exchange currents in both cathodic and anodic direction near 400 A/m^2. Cyclic voltammetry verified a 'catalytic' reaction mechanism with disulfide as the electroactive species. At the cathode:

$$H_2S + S^{2-} = H_2 + S_2^{2-} \tag{11}$$

and

$$S_2^{2-} + 2e^- \rightarrow 2S^{2-} \tag{12}$$

At the anode:

$$S_2 + 2S^{2-} = 2S_2^{2-} \tag{13}$$

$$S_2^{2-} \rightarrow S_2 + 2e^- \tag{14}$$

Surprisingly, enhanced cathodic H_2S removal was found with CO_2 and H_2O in the gas, probably due to another 'catalytic' scheme, reaction 4 followed by:

$$CO_3^{2-} + H_2S = CO_2 + H_2O + S^{2-} \tag{15}$$

Another unexpected result was the concurrent removal of COS down to levels below the analytical limit (about 2 ppm). This occurs apparently due to rapid equilibrium between H_2S, CO, CO_2, and COS at these temperatures:

$$H_2S + CO = H_2 + COS \tag{16}$$

$$H_2S + CO_2 = H_2O + COS \tag{17}$$

A study of potential cathode materials (Weaver and Winnick, 1987, 1991) showed several promising alternatives. It was conducted using a configuration similar to anticipated designs (see Figure 2). Since the working membrane will be mostly carbonate at steady state, MCFC (Molten Carbonate Fuel Cell) 'tiles' were used. Several electrode materials were found acceptable, including nickel and cobalt, formed from powders, sulfided *in situ*.

Studies of 'tile' compositions have also been performed. By analyzing the equilibrium of reaction (Eq. 15), it is possible to know the electrolyte composition which would be in equilibrium with a given process gas at a given process temperature (see Figure 3) (Alexander and Winnick, 1990). Theoretical tile compositions were calculated by thermodynamic analysis of the tile equilibrium reaction (Eq. 18). Since membranes similar to those used in the MCFC were used in this analysis, the cations present were K and Li in a ratio corresponding to the low melting carbonate eutectic ($Li_{0.62}K_{0.38}$):

$$(Li_{0.62}K_{0.38})_2CO_3 + H_2S = (Li_{0.62}K_{0.38})_2S + CO_2 + H_2O \tag{18}$$

This analysis was performed by finding the Gibbs free energy of reaction 18 at the process temperature and relating this to the equilibrium constant, K_a, by the relation:

$$-\ln K_a = \frac{\Delta G^0}{RT} \tag{19}$$

with K_a defined as:

$$K_a \equiv \frac{p_{CO_2} p_{H_2O} a_{S^{2-}}}{p_{H_2S} a_{CO_3^{2-}}} \tag{20}$$

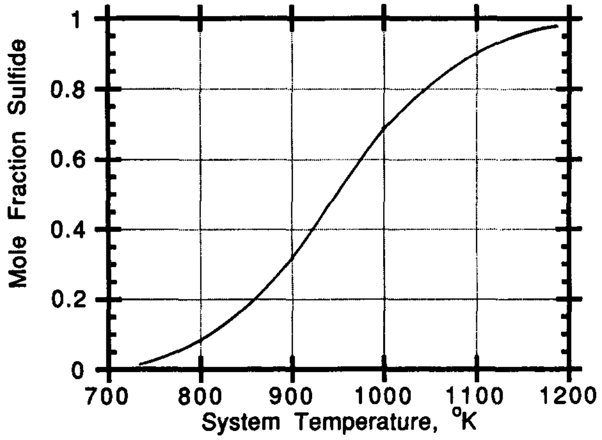

Figure 3. Calculated electrolyte sulfide composition (in carbonate) in equilibrium with gas containing 1.5% H_2S, 20% CO_2, 3% H_2O, balance CH_4 at atmospheric pressure.

By this analysis, a process gas with a composition of 0.88% CO_2, 1,760 ppm H_2S, 12% H_2O, and the balance methane with a run temperature of 883 K will have an equilibrium constant of 6.9. If the activity coefficients of the molten-phase constituents (namely the sulfide and carbonate in the electrolyte) are assumed to be equal, this translates to an electrolyte composition of 19.5% sulfide and 80.5% carbonate.

A 'tile' manufactured to be already in equilibrium with the gas to be treated will not have to undergo the stresses inherent in the density changes associated with 'sulfiding' a carbonate tile or 'carbonating' a sulfide tile. While techniques for manufacturing such a tile are still under study, the concept has been used successfully in both the coal gasification process cell (Weaver and Winnick, 1991) and the natural gas process cell (Alexander and Winnick, 1990).

Several potential anode materials have been identified (Weaver and Winnick, 1987, 1991). Anodes of CoS_2 have been used with some success in the natural gas cell (Alexander and Winnick, 1990). More recently, anodes made of Ni and allowed to go to an equilibrium composition *in situ* have also been used with some success. Anodes constructed of these materials do not have the chemical decomposition problems inherent in the carbon electrodes. With these materials identified, bench-scale experiments were conducted.

Experimental Methods

Cell geometry

The cell housings were machined from MACOR (machinable ceramic) blocks. The housings were 0.076-m-dia. and 0.025-m-deep cylinders. Gas flow channels were machined into the large surface faces, and gas flow tubes were connected to supply process and sweep gases to the cell. Once electrode and membrane materials were ready for testing, the electrodes were set onto gold current collectors placed on top of the gas flow channels on one side and contacting the surface of the membrane on the other (see Figure 4). The full cell was then assembled by placing the membrane between the MACOR blocks and connecting the gas supply lines to the assembly.

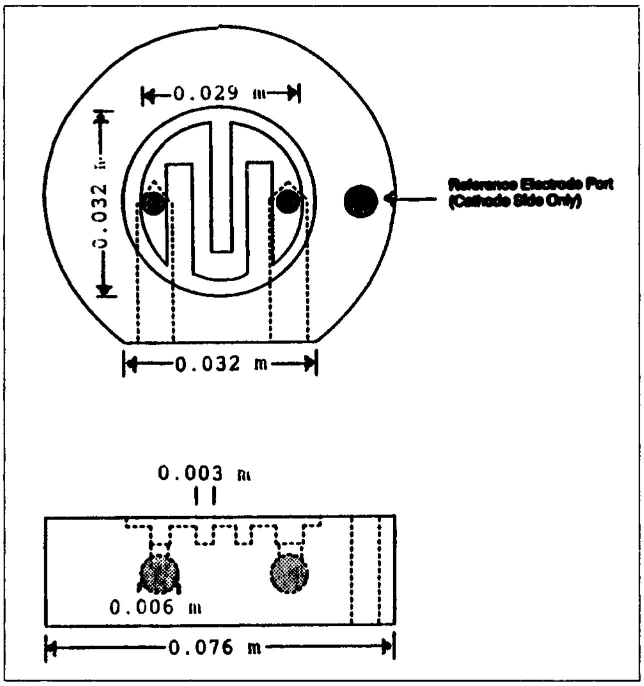

Figure 4. MACOR cell housings.

Electrode preparation

Several potential electrode materials have been identified. Of these, carbon, CoS_2, and Ni were used in the experiments.

Carbon. While useful for free-electrolyte kinetic studies and bench-scale removal cell testing, graphite will not be acceptable for commercial electrodes in a removal cell. At the cathode it will eventually be eroded by the steam or CO_2:

$$C + H_2O = CO + H_2 \tag{21}$$

$$C + CO_2 = 2CO \tag{22}$$

And at the anode it can act as a reductant for carbonate:

$$CO_3^{2-} + C \rightarrow CO + CO_2 + 2e^- \tag{23}$$

Carbon electrodes were obtained for use as cathode material from Stackpole/Ultra Carbon.

CoS_2. High-purity materials were obtained from Alfa Chemicals and mixed with hydroxyethyl cellulose (HEC) from Union Carbide Corp. Void percentages as high as 60% were obtained using a mixture of 10 wt. %. HEC and 90 wt. % CoS_2 powder. This mixture was loaded into a 0.032-m stainless steel die and pressed at 550×10^5 N/m^2 using a hydraulic ram. The resulting electrode wafer was then heated at 623 K for 30 min to burn out the HEC. This final electrode was then cooled, weighed, and stored for use in the electrochemical cell.

Ni. Porous Ni electrodes similar to those used in the MCFC were obtained from Energy Research Corp. (ERC). Due to the proprietary nature of these materials, however, no physical data on their structure may be released. These materials were allowed to go to equilibrium nickel sulfides and nickel oxides *in situ*.

Membrane preparation

Two techniques have been used for the manufacture of the membranes utilized in the experiments discussed here. The first technique involved manufacturing a sintered ceramic matrix of MgO without electrolyte present and then 'wicking' the molten electrolyte into the matrix by capillary action.

The inert ceramic matrix which holds the electrolyte in place between the cathode and anode serves two purposes: it holds the electrolyte by capillary action and prevents the molten salts from completely flooding the porous electrodes; the membrane acts to prevent the bulk diffusion of gases between the cathode and the anode side of the cell. If the electrolyte were not in chemical equilibrium with the process gas, localized density changes in the electrolyte caused by reaction 18 would cause the membrane to crack and allow bulk mixing of the process and sweep gas streams.

The second technique for membrane manufacture involved making a composite structure consisting of woven zirconia cloths which had been densified with MgO powder. The structure consisted of three mats of ZYW-30A zirconia cloth (purchased from ZIRCAR Inc.) layered with three tapes of MgO ceramic powder suspended within acrylic binder K565-4 (purchased from Metoramic Sciences, Inc.). The electrolyte was layered into the structure as pressed powder disks during setup. Due to the amount of handling outside the cell run conditions involved during setup, the electrolyte used in this membrane manufacture technique was initially all eutectic Li/K carbonate which is stable (though hygroscopic) in normal room air.

A nitrogen sweep was applied to both the process and sweep sides of the cell, which was loaded into the furnace for heatup. The binder from the MgO tapes was volatilized out at 648 K overnight. The temperature was then ramped up to run temperature and the electrolyte wicked into the MgO powders and zirconia cloth upon melting. Process gas was then supplied to the cell, and the electrolyte was allowed to reach the equilibrium composition described by reaction 18. Since the ceramic matrix was no longer a rigid sintered structure, localized density changes in the electrolyte did not cause the cracks seen with the more rigid structures.

Cell assembly and heating

The electrodes were arranged on either side of the membrane as shown in Figure 2. Current was carried to the electrode surfaces by 2.29×10^{-4}-m-dia. gold wire. The electrodes themselves were separated from the MACOR housing surfaces by resting atop gold current collectors. Gas channels were cut into the MACOR above the electrodes to allow process gas to pass (see Figure 4).

Once assembled, the cell was loaded into a custom-made furnace and connected to the process and sweep gas supply lines. The exit gas from the cathode was routed to a Beckman IR scanner for reading CO_2 levels. A Hewlett/Packard gas chromatograph fitted with a thermal conductivity detector was used for reading H_2S levels greater than 100 ppm, and a flame photometric detector was used for H_2S levels less than 100 ppm. A gold reference electrode was placed on the surface of the membrane away from either process electrode and supplied with a low flow rate of a 15% CO_2/3% O_2/balance N_2 mixture to maintain a stable thermodynamic reference potential by reaction 24:

$$CO_2+\frac{1}{2}O_2+2e^-=CO_3^{2-} \tag{24}$$

Initially, dry nitrogen was blown through both sides of the cell as the assembly was heated at a rate of 100 K/h. Melting of the electrolyte was verified by a sudden improvement in the seals formed by the contact of the membrane with the MACOR surfaces and observed electrical conductivity through the cell. Process gas, consisting of specified levels of H_2S, CO_2, H_2O, and the balance CH_4, was then supplied to the cathode side, and the cell was heated to the run temperature.

Test procedure

Once the cell had reached run temperature, conductivity across the cell was estimated by the current interrupt method. The equilibrium potentials at the cathode and anode were measured with respect to the reference electrode. Base-line exit cathode gas compositions were also measured at this point. Current was then applied to the cell in a stepwise fashion, and the cell was allowed to equilibrate for 15 min after each current step. Once stabilized, potentials with respect to the reference electrode and the exit gas compositions were measured.

Post-run electrolyte analysis

At the conclusion of each run, the membrane was removed for analysis. A sample of membrane material was weighed and then dissolved in water. The insoluble matrix materials were filtered and the filtrate treated with excess hydrogen peroxide, which oxidizes all sulfur species to sulfate. It was assumed that only sulfur in the form of sulfide was present in the membrane under run conditions. This solution was then acidified with hydrochloric acid to decompose the carbonate to carbon dioxide and water. The solution was then boiled to degas the mixture and barium chloride was added, causing the sulfate to precipitate as barium sulfate. The solution was then filtered, and the precipitate was rinsed, ignited, and weighed. The moles of barium sulfate precipitated are equal to those of sulfide in the electrolyte.

The mass of the soluble electrolyte present in the sample was known by difference. It was assumed that carbonate and sulfide species were the only components of the electrolyte; since the mass of sulfide present was determined by the above analysis, the mass of carbonate present in the sample was also known by difference.

Results

Among 19 runs successfully completed, three representative runs are presented here: run A (representative of very sour natural gas, 1.33% H_2S); run B (representative of moderately sour natural gas, 2,000 ppm H_2S); and run C (representative of polishing application, 100 ppm H_2S). Reproducibility of removal trends has been observed with all 19 runs.

Run A: scrubbing application with 1.33% H_2S natural gas

This experimental run used a membrane manufactured by wicking an equilibrium composition electrolyte into a partially sintered MgO matrix. The cathode in this cell was carbon and the anode was CoS_2. The process gas supplied to the cathode had an H_2S concentration of 1.33% and a CO_2 concentration of 19.3%. H_2S concentrations were driven as low as 2,000 ppm as shown in Figure 5 (corresponding to 84.9% removal). Condensed sulfur was recovered from the anode sweep lines.

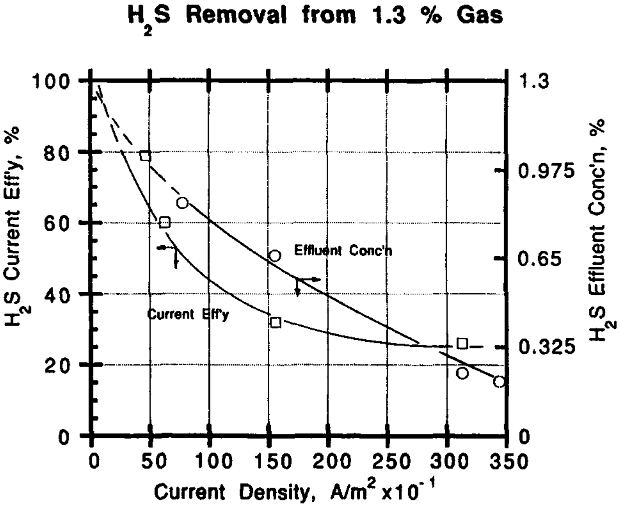

Figure 5. H_2S removal vs. applied current density, run A.

While H_2S removal at the cathode with sulfur production at the anode was shown, the process was not yet completely selective since cocurrent removal of CO_2 was also observed. This was due to hydrogen diffusion through the membrane which caused reactions 6 and 5 to simply become the reverse of reactions 3 and 4. In this situation, there is no net cell reaction for species transport, and H_2S, CO_2, and H_2O would simply be concentrated on the anode side of the cell as a function of applied current.

Typical cell polarization data are presented in Figure 6. Total cell polarizations of around 1 V (or less) were observed for most of the run duration.

Selectivity is defined by the following equation:

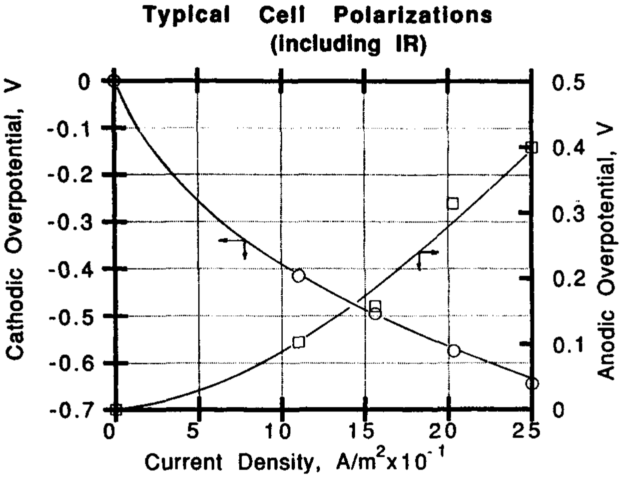

Figure 6. Typical cell polarization (including IR) vs. applied current density.

$$\text{Selectivity} \equiv \left[\frac{\%\ \text{Removal}_{H_2S}}{\%\ \text{Removal}_{CO_2}}\right]\left[\frac{\%\ CO_{2_{\text{inlet}}}}{\%\ H_2S_{\text{inlet}}}\right] \tag{25}$$

If selectivity is equal to one, removal of H_2S and CO_2 is equivalent. If the selectivity is greater than one, H_2S is preferentially removed. For this run selectivity is found to be 21.1 at the highest applied current. Thus, H_2S is removed preferentially to CO_2, even with the parasitic effect of hydrogen diffusion.

The current efficiency for H_2S removal is defined as:

$$\eta \equiv \frac{\text{Removal}_{\text{actual}}}{\text{Removal}_{\text{theoretical}}} = \frac{\text{Current}_{\text{stoich.}}}{\text{Current}_{\text{actual}}} \tag{26}$$

at any applied current. At applied current densities less than 200 A/m^2, current efficiency is nearly 100%. At 2,500 A/m^2, current efficiency dropped to 25%. This was likely due to gas-phase diffusion limitations in addition to hydrogen crossover.

Run B: scrubbing application with 2,000 ppm H_2S natural gas

The membrane used in this run also used a membrane manufactured by wetting an equilibrium composition electrolyte into a partially sintered MgO matrix. As in run A, the cathode was carbon and the anode was CoS_2. The process gas supplied to the cathode had an H_2S concentration of 1,927 ppm and a CO_2 level of 0.874%. H_2S concentrations were driven as low as 94 ppm (corresponding to 95.7% removal) as shown in Figure 7. CO_2 was driven to 0.089% with the same applied current level (84.5% removal). As before, hydrogen crossover limited the current efficiency. Sulfur was recovered from the sweep lines on the anode side of the cell. Electrolyte analysis showed a final composition of 20.4% sulfide and 79.6% carbonate. This compares with a theoretical composition of 18% sulfide and 82% carbonate.

Selectivity in this experiment was 4.9. Current efficiency went from nearly 100% at low applied currents to 10% at 200 A/m^2. This is a more dramatic example of gas-phase diffusion limitations and hydrogen diffusion on cell removal performance. In this case, the limitation is pronounced due to the order of magnitude drop in current-carrying species in the gas mixture from that used in run A. This limitation is inherent in the design of the gas flow channels and could be overcome by careful design of flow channels to maximize gas-phase mass transport to the surface of the electrode.

Run C: polishing application with 100 ppm H_2S natural gas

This experimental run used the layered membrane structure described earlier. Aluminum foil gaskets were also cut and laid into the wet seal area between the membrane and the MACOR housings. This was done to improve the wet seal of the cell by intimately binding the membrane structure to the MACOR housings with a layer of $LiAlO_2$ formed *in situ*. During heat-up to run temperature, the aluminum was converted to Al_2O_3 and then to $LiAlO_2$ through a subsequent reaction with Li_2CO_3 (Swaroop et al., 1978).

$$Li_2CO_3 + Al_2O_3 = 2LiAlO_2 + CO_2 \tag{27}$$

This run used carbon at the cathode and Ni (converted to NiO *in situ*) at the anode. The process gas for this run had a composition of 98 ppm H_2S, 1.45% CO_2, and 3.9% H_2O. H_2S levels in the process gas were brought as low as 2 ppm (below GC analytical limits, H_2S level corresponds to 98.0% removal) over the course of the run with application of as little as 0.8 mA/cm^2 (cathode flow rate $= 4.50 \times 10^{-4}$ m^3/min) with total cell potentials of only around 0.8 V and no detectable CO_2 removal. H_2S levels with applied current are presented in Figure 8. Selectivity in this run was infinite, signifying completely selective removal of H_2S from the process gas stream. Current efficiency was 55.9%, this value was higher than the other runs due to a more H_2 impermeable membrane.

After 135 hours of continuous operation, the cell was shut down for post-mortem analysis. The carbon cathode, while still operational, had degraded and was showing obvious signs of erosion. An analysis of the membrane showed an actual sulfide level of 7.5 mol % and a carbonate level of 92.3 mol %. Theoretical analysis predicted a sulfide level of 3.7 mol % and a carbonate level of 96.3 mol %.

An analysis of the anode showed that the structure was

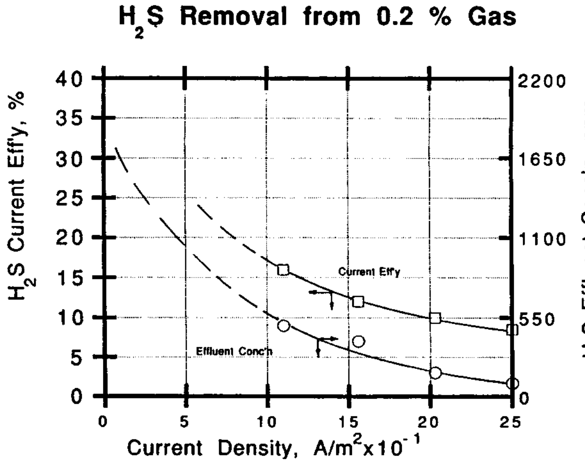

Figure 7. H_2S removal vs. applied current density, run B.

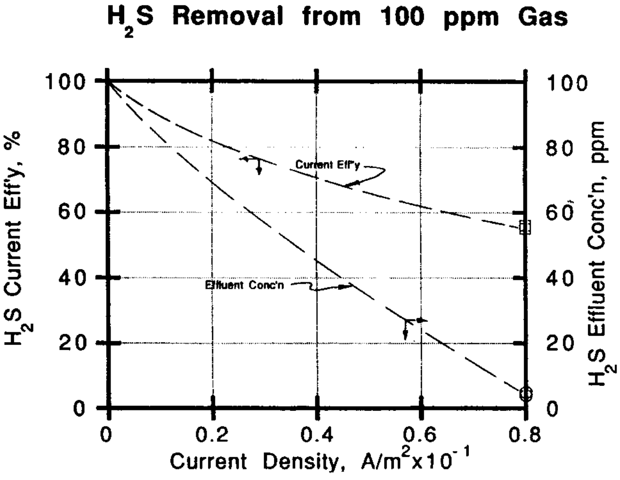

Figure 8. H_2S removal vs. applied current density, run C.

62.9% flooded. The electrolyte wetting the pores of the electrode had an approximate composition of 4.8 mol % sulfide and 95.2 mol % carbonate. Examination of the electrode material by X-ray diffraction showed that the primary species were Ni and NiO, with a small amount of Ni_3S_2 present.

Economic Projection

Accurate cost figures for processes early in development are impossible to project. However, it is possible to roughly estimate the power and capital requirements to assess viability. The power consumption is overwhelmingly due to the cell current, which will be stoichiometric for well constructed membranes. Cell voltage, as shown earlier, can be estimated with reasonable accuracy. Capital costs can be estimated by analogy with MCFC stacks, whose design these membrane cells will mimic.

The electrochemical membrane separator (EMS) technology being developed is here compared to a 'wet' removal process with subsequent Claus plant processing to elemental sulfur and SCOT tail gas treatment of flue gases. This 'wet' process utilizes aqueous methyldiethanolamine (MDEA) as an absorbent in a scrubbing operation to bring the H_2S level from 1.7% to 4 ppm. The flow rate to these processes is 1.4×10^6 std m^3/d and the process pressure is 49×10^5 N/m^2. The process gas in this study has a CO_2 content of 18.2% (Borio, 1990). Marshall-Swift equipment cost indexes were used to estimate the expenses for the EMS facility in 1987 dollars. On-stream time is 360 days in both cases. Table 1 breaks out the direct and indirect costs of the present and proposed technologies for comparison.

Table 1. Operation Costs: Current Technology vs. ERC*

Fixed Capital Investment ($\times 10^{-6}$):	Conventional 11.158	EMS 5.368
Direct Operations Costs		
Utilities ($\times 10^{-6}$)		
Steam ($5.38/1,000 kg)	0.518	0.000
Electricity ($0.0524/kWh)	0.392	1.110
Raw H_2O ($198/1,000 m^3)	0.000	0.006
Gas Losses ($70.6/1,000 std m^3)	0.000	0.420
Chemical Losses	0.021	0.000
	0.931	1.536
Operating Labor ($10.30/h)	0.180	0.089
Maintenance (4% FCI)	0.446	0.215
Plant General (40% Labor)	0.072	0.036
	0.698	0.340
Total Direct Costs	1.629	1.876
Indirect Operating Costs		
Depreciation (10% FCI)	1.116	0.537
Tax & Insurance (2.5% FCI)	0.279	0.107
Total Indirect Cost	1.395	0.644
Total Operating Costs	3.024	2.520
Cost of Profit (25% FCI) (Includes income tax, interest on investment, and reasonable profit)	2.790	1.342
Grand Total Treating Cost	5.814	3.862
Sulfur Credit ($110/1,000 kg)	1.152	1.152
Net Treating Cost (Grand Total-Credit)	4.662	2.710
Treating Cost/1,000 std m^3	$9.25	$5.38

*1987 dollars.

The capital cost is more difficult to estimate than the power consumption. In the MCFC, current densities greater than 1,600 A/m^2 are routinely achieved. There are, however, two major differences between the MCFC and the EMS (electrochemical membrane separator). In the MCFC, the gases are relatively richer than the dilute reactants treated in the EMS. Further, there is no competing reaction to dilute the current-carrying anion. Thus, gas-phase diffusion of H_2S or sulfide migration in the membrane may limit the current density and define the needed active membrane area for a given duty.

Gas-phase transport can be controlled through proper design of the gas channels (Townley and Winnick, 1991); pore diffusion in the electrodes has been found not limiting in similar designs for CO_2 removal to very low levels (Kang and Winnick, 1985).

The limiting step for removal in this analysis is gas diffusion of H_2S to the cathode of the cell. This is assuming that the process gas has been dehydrated to the point that the equilibrium of Eq. 18 provides a sulfide-rich tile. The operating temperature of the EMS thus must be high enough to insure that the sulfide-rich electrolyte is molten. The current density is based on 2 F of charge transferred for each mole of H_2S diffusing to the surface of the cathode.

The capital cost estimation assumes that the tiles are available as 1.2 m × 1.2 m (as used in MCFC units) and are arranged in 'stacks' of parallel removal cells with the process gas equally divided to each cell (Appleby and Foulkes, 1989). Each 'stack' removes approximately 90% of the H_2S fed to it. In this analysis, there are four 'stacks' in series; the first bringing the H_2S composition from 1.7% to 2,000 ppm, the second from 2,000 ppm to 200 ppm, the third from 200 ppm to 20 ppm, and the fourth from 20 ppm to 4 ppm. There is assumed to be a 0.03-m-deep and 1.2-m-wide gas flow path above each cathode. This analysis also assumes the use of a regenerative heat exchanger and a furnace fueled by polished natural gas to heat the process gas to the cell temperature (see Figure 9). The heat-exchanger system was priced using standard costing figures (Peters and Timmerhaus, 1982). Costs associated with the EMS

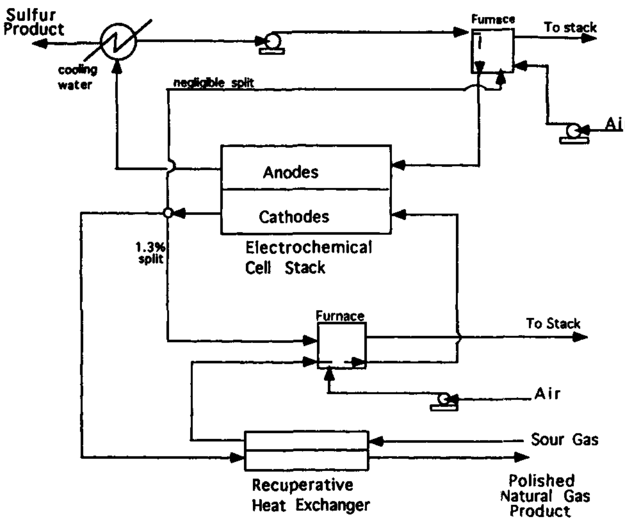

Figure 9. Proposed electrochemical membrane separator plant.

Table 2. Breakdown of Capital Investment for EMS*

Electrochemical Removal Cell Stacks ($\$ \times 10^{-6}$)				
	Stack 1	Stack 2	Stack 3	Stack 4
Ion Exchange Area (m^2)	917	988	988	690
Tiles in Stack	617	664	664	464
Anodes	0.085	0.091	0.091	0.064
Cathodes	0.035	0.037	0.037	0.026
Bipolar Hardware	0.064	0.068	0.068	0.048
Tiles	0.004	0.005	0.005	0.003
Auxiliaries	0.020	0.021	0.021	0.015
Assembly	0.077	0.083	0.083	0.058
Stack Cost	0.285	0.305	0.305	0.214
Rectifier	0.155	0.166	0.166	0.117
Controls & Misc.	0.216	0.233	0.233	0.163
Assembly	0.170	0.183	0.183	0.128
Total Stack Cost	0.826	0.887	0.887	0.622
Total EMS Cost			3.222	
Blowers			0.101	
Heat Exchanger			1.345	
Plant Cost			4.668	
Project Contingency (15%)			0.700	
Fixed Capital Investment			5.368	

* 1987 dollars.

stacks are provided in Table 2. Under these assumptions, the stacks show gas-phase limiting current densities of 2,340 A/m^2 for the first, 261 A/m^2 for the second, 26.1 A/m^2 for the third, and 3.32 A/m^2 for the fourth. Once the limiting current density of the stack is known, the total stack area is calculated by dividing the required stack current by the stack-limiting current density. The total stack current was found by assuming a stoichiometric amount of electricity for the moles of H_2S removed. In other words, 2 F of charge is required for each mole removed. Stack power requirements assume that a potential of 1 V drives the removal cells. With these assumptions in mind, the first stack requires 2,150 kW, the second stack requires 258 kW, the third stack requires 25.8 kW, and the fourth stack requires 2.29 kW. This sums to a total of 2,436 kW for the EMS system. Under these conditions, the EMS plant can perform the scrubbing operation for \$5.38/1,000 std m^3 of gas treated. This favorably compares to \$9.25/1,000 std m^3 for conventional removal technology. The cost of operation for the EMS plant could be further reduced by optimizing the design of the regenerative heat exchanger to cut back the fuel requirements of the gas-heating furnace. The cell stack size could also be reduced by optimizing the gas flow channel design thereby increasing the gas-phase mass transport of H_2S and thus increasing the cell-limiting current density.

Conclusions

Selective removal of H_2S from simulated natural gas streams has been demonstrated for three representative gas compositions representative of a very sour natural gas (1.5% H_2S), a moderately sour natural gas (2,000 ppm H_2S), and a slightly sour natural gas (100 ppm H_2S). These results support the design specifications for the first three removal cell stacks of the economic study presented in this article. Even with current efficiencies well below 100%, the process is still economically favorable. Hydrogen crossover, which lowers the current efficiency, can be eliminated with better membrane construction as shown by the results of run C. Gas-phase diffusion limitations can be overcome by designing the gas flow channels for optimum gas species mass transport to the electrode surface.

Acknowledgment

Economic support and additional expertise are provided by Gas Research Institute, Chicago and ABB/Combustion Engineering in Windsor, CT.

Literature Cited

Alexander, S., and J. Winnick, "Electrochemical Separation of Hydrogen Sulfide from Natural Gas," *Symp. Sep. Sci. and Tech.*, **25**, 2057 (1990).

Appleby, A., and F. Foulkes, *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, p. 574 (1989).

Banks, E., and J. Winnick, "Electrochemical Reactions of Hydrogen Sulfide in Molten Sulfide," *J. Appl. Electrochem.*, **16**, 583 (1986).

Borio, D., ABB/Combustion Engineering, personal communication (1990).

Kang, M., and J. Winnick, "Concentration of CO_2 by a High-Temperature Electrochemical Membrane Cell," *J. Appl. Electrochem.*, **15**, 431 (1985).

Lim, H., and J. Winnick, "Electrochemical Removal and Concentration of H_2S from Coal Gas," *J. Electrochem. Soc.*, **131**, 562 (1984).

Peters, M., and K. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 3rd ed., McGraw-Hill, New York (1982).

Swaroop, R., et al., "Corrosion Protection of Molten Carbonate Fuel Cell Gas Seals," *J. Electrochem. Soc.*, **125**, 1799 (1978).

Townley, D., and J. Winnick, "Flue Gas Desulfurization Using an Electrochemical Sulfur Oxide Concentrator," *I.E.C. Proc. Des.*, **20**, 435 (1991).

Weaver, D., and J. Winnick, "Electrochemical Removal of H_2S from Hot Gas Streams: Ni/NiS Cathode Performance," *J. Electrochem. Soc.*, **134**, 2451 (1987).

Weaver, D., and J. Winnick, "Evaluation of Cathode Materials for the Electrochemical Membrane H_2S Separator," *J. Electrochem. Soc.*, **138**, 1626 (1991).

White, K., and J. Winnick, "Electrochemical Removal of H_2S from Hot Coal Gas," *Electrochem. Acta*, **30**, 511 (1985).

Manuscript received Nov. 18, 1992, and revision received July 15, 1993.