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ELECTROCHEMICAL SEPARATION OF HYDROGEN SULFIDE FROM NATURAL GAS

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ABSTRACT

An electrochemical process has been developed for the removal of H_2S from contaminated natural gas. Removals as high as 80.7% have been achieved from a simulated process gas (2000 ppm H_2S). H_2S is removed by reduction to the sulfide ion and hydrogen gas at the cathode. The sulfide ion migrates to the anode through a molten 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. No materials are required beyond initial electrolyte membrane installation; the H_2S is converted in one step to elemental sulfur making it an economically attractive process both from the lack of raw materials and the lack of any solvent regeneration.

INTRODUCTION AND THEORY

Gas separation using perm-selective membranes is a strong and growing unit operation. We here describe the development of an economical membrane process for the selective removal of hydrogen sulfide from natural gas. The main difference, however, between conventional membrane separation processes and the one discussed here is that the driving force for removal is an electrical potential gradient across the membrane rather than a pressure gradient.

The removal of H_2S is accomplished by passing a heated process stream of raw natural gas across the surface of a porous electrode. Reduction of hydrogen sulfide, producing a sulfide ion and hydrogen gas, takes place at the cathode. The hydrogen gas from this reaction exits in the process gas stream and the sulfide ion moves along the electrical potential gradient through a molten salt electrolyte to the opposite electrode. The electrolyte is suspended in an inert ceramic matrix. At the anode, another electrochemical reaction oxidizes the sulfide ion to elemental sulfur which is carried off in an inert sweep gas stream and condensed as a by-product (see Figure 1) [1]. Since electrons are used to form the sulfide ion and removed to produce elemental sulfur, current must flow between the electrode on the process gas side and the electrode on the sweep gas side. Thus, the process gas electrode, where reduction occurs, is the cathode and the sweep gas electrode, where oxidation occurs, is the anode. The desired reaction is the reduction of hydrogen sulfide at the cathode:

$$H_2S + 2\ e^- \Rightarrow S^{2-} + H_2 \qquad (1)$$

This reaction is thought to proceed by the following mechanism:

$$S_2^{2-} + 2\ e^- \Rightarrow 2\ S^{2-} \qquad (2)$$

$$S^{2-} + H_2S \Leftrightarrow S_2^{2-} + H_2 \qquad (3)$$

where polysulfide, S_2^{2-}, is the catalytic species.[2] Reduction of H_2S at the cathode is accompanied by oxidation of the sulfide ion at the anode as follows:

$$S^{2-} \Rightarrow 1/2\ S_2 + 2\ e^- \qquad (4)$$

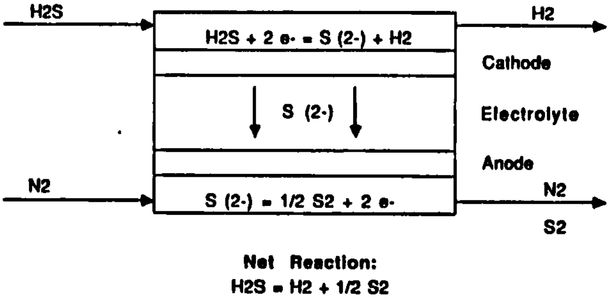


Fig. 1. Electrochemical H_2S removal Cell Reactions and Schematic

CO_2 and H_2O reduction to the carbonate ion, CO_3^{2-}, can also occur at the cathode at the same electrical potential as reaction (1):

$$CO_2 + H_2O + 2e^- \Rightarrow CO_3^{2-} + H_2 \qquad (5)$$

Reaction (5) would be accompanied by oxidation of carbonate at the anode as the following reaction:

$$CO_3^{2-} \Rightarrow CO_2 + 1/2O_2 + 2e^- \qquad (6)$$

The sum of the half-cell reactions (1) and (4) gives the overall cell reaction for sulfide transport and its equilibrium potential.

$$H_2S \Rightarrow 1/2S_2 + H_2 \qquad E^\circ = -0.362 \text{ Volts} \qquad (7)$$

Summing the half-cell reactions (5) and (6) for carbonate transport gives the following overall reaction and potential:

$$H_2O \Rightarrow H_2 + 1/2O_2 \qquad E^\circ = -1.024 \text{ Volts} \qquad (8)$$

Thus, if the operating potential of the cell is maintained between the equilibrium potentials of reactions (7) and (8), there should be selective transport of the sulfide ion between the electrodes.[3] This process has been used with success in the case of H_2S in N_2 (0.65% H_2S) by Lim [1], and simulated coal gas (35% H_2, 25% CO_2, 1.5% H_2S, balance N_2) by Weaver [3].

In addition to the electrochemical reactions involving the process gas, there is also a chemical equilibrium established between the process gas and the molten electrolyte. The composition of the molten electrolyte in the membrane is determined by the equilibrium reached with the process gas stream with respect to the following reaction:

$$M_2CO_3 + H_2S \Leftrightarrow M_2S + CO_2 + H_2O \qquad (9)$$

where M is any cation (in these experiments, $Li_{0.62}K_{0.38}$) with a +1 valence. The equilibrium constant can be calculated at the process temperature by finding the standard Gibb's free energy of reaction (9) at the process temperature. The standard Gibb's free energies of several inorganic substances have been tabulated as a function of temperature ([4], [5]), so at a given temperature:

$$\ln K_a = \Delta G^\circ/RT \qquad (10)$$

where:

$$K_a = P_{CO2}\, P_{H2O}\, a_{M2S} \,/\, P_{H2S}\, a_{M2CO3} \qquad (11)$$

If the activity coefficients of the molten phase constituents, namely M_2CO_3 and M_2S, are assumed to be unity, equation (11) reduces to the following:

$$K_a = P_{CO2}\, P_{H2O}\, X_{M2S} \,/\, P_{H2S}\, X_{M2CO3} \tag{12}$$

with X_{M2S} and X_{M2CO3} the mole fractions of sulfide and carbonate species in the electrolyte melt. Since sulfide and carbonate species are assumed to be the only chemical species present in the electrolyte melt, equation (13) follows:

$$X_{M2S} + X_{M2CO3} = 1 \tag{13}$$

Thus, the equilibrium molten phase composition can be estimated from equations (10), (12), and (13) for a specific gas composition and process temperature. Figure 2 shows the *calculated* equilibrium electrolyte composition as a function of H_2O content in the process gas and process temperature at a system pressure of 1 atmosphere.

The inert ceramic matrix which holds the electrolyte in place between the cathode and anode serves two purposes; first, it holds the electrolyte by capillary action and prevents the molten salts from completely flooding the porous electrodes; second, the membrane acts to prevent the bulk diffusion of gases between the cathode side and the anode side of the cell. While the membranes used in previous experiments have served the purpose of holding the electrolyte adequately, they usually formed micro-cracks during the experiment. If the electrolyte is not in chemical equilibrium with the process gas, localized density changes in the electrolyte caused by reaction (9) will cause the membrane to crack and allow bulk mixing of the process and sweep gas streams.

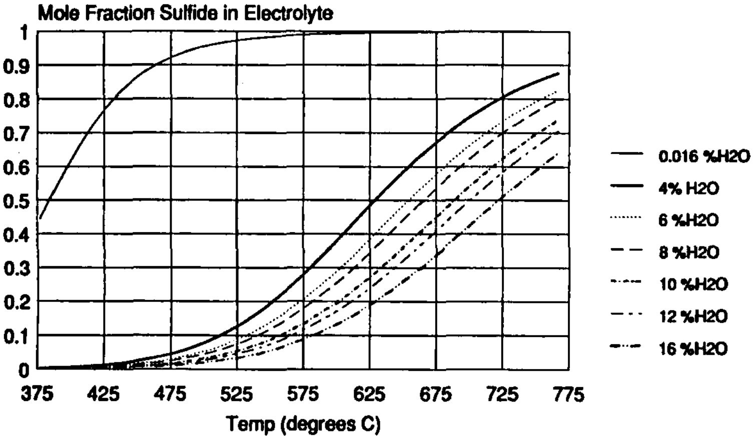


Fig. 2. Calculate Equilibrium Electrolyte Composition.
Cation Ratio Li(.62) K(.38)
Dry Gas Composition: 0.2% H_2S, 1.0% CO_2
System Pressure of 1 atmosphere

In Weaver's studies with coal gas, he identified several promising cathode materials and some potential anode materials.[3] A successful anode material will depend upon identifying an anode material capable of overpotentials below about 500 mV at current densities of 100mA/cm^2. This would seem possible since it has been achieved with graphite and since cathodes have been operated at relatively high current densities well within these limits [3].

Since this process for the removal of H_2S from hot gas streams had never been applied to natural gas processing, and since there are still aspects of the process which merit closer study, full cell experiments were carried out to verify the feasibility of this process for cleaning H_2S from natural gas streams and to examine the behavior of membrane and electrode materials in this application.

EXPERIMENTAL PROCEDURE

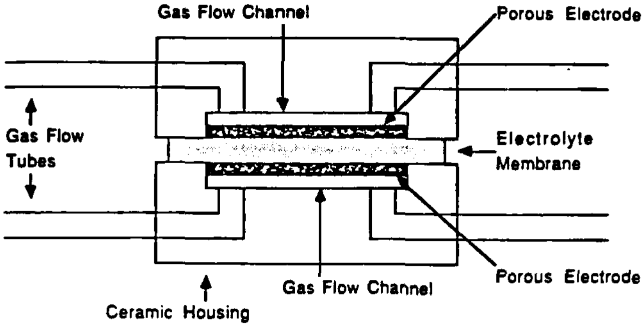
The primary purposes of these experiments were to verify electrochemical separation of hydrogen sulfide from natural gas and to evaluate the effects of the process variables involved. The actual experimental procedures for these tests are outlined below.

Cell Geometry. The cell housings were machined from 2" by 2" by 1" MACOR blocks. Gas flow channels were machined from the square surfaces of the blocks and gas flow tubes were connected to supply process and sweep gases to the cell as shown in Figure 3. Once electrode and membrane materials were ready for testing, the electrodes were set onto gold wire current collectors placed on top of the gas flow channels on one side and contacting the surface of the membrane on the other. The full cell was then assembled by placing the membrane between the MACOR blocks and connecting the gas supply lines to the assembly. Electrode and membrane manufacture and actual test procedure are described below.

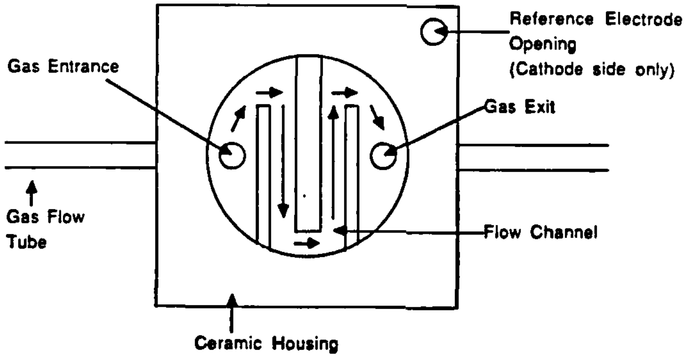
Electrode preparation. Several potential electrode materials have been identified by Weaver [3]; of these, carbon and CoS_2 were used in these experiments. The carbon electrodes were obtained from Ultra Carbon; the cobalt disulfide electrodes were manufactured in the following manner:

High purity (99.9%) cobalt disulfide was obtained from Alfa Chemicals and mixed with hydroxyethyl cellulose (HEC) from Union Carbide Corp. Void percentages of nearly 40% were obtained using a mixture of 7.5 weight % HEC and 92.5 weight % CoS_2. To obtain an electrode thickness of 0.176 cm (diameter of 3.5 cm), 4.7 grams of this mixture were loaded into a stainless steel die and pressed with a total force of 10 tons under a hydraulic ram.
The resulting electrode wafer was then heated to 350 °C for 30 minutes to burn out the HEC. The final electrode was then cooled,

weighed, and stored for use in the electrochemical cell.



(Side View)



(Top View of Cell Half)

Fig. 3. Removal Cell Set-up and Configuration

Membrane preparation. Early experiments were performed using Molten Carbonate Fuel Cell (MCFC) tiles obtained from the Institute of Gas Technology (IGT). These membranes were a 50/50 weight ratio of electrolyte to matrix material. The electrolyte was a mixture of 62 mole % Li_2CO_3 and 38 mole % K_2CO_3, the matrix material was $LiAlO_2$. These membranes were allowed to reach the equilibrium sulfide compositions in situ.

Later experiments included attempts at manufacturing membranes already at the equilibrium composition for a specific gas stream. Membranes were manufactured by mixing Li_2S, K_2S,K_2CO_3, and Li_2CO_3 to give a composition which would be in equilibrium with a specified process gas composition at a specified run temperature. This powder mixture was then added to $LiAlO_2$ to yield a 50/50 weight ratio mixture with $LiAlO_3$ and ball milled for 24 hours.

Once the mixture was prepared, a carbon-steel die was prepared for pressing the membrane by coating all interior surfaces with graphite powder and Union Carbide Grafoil tape. The main pressing surfaces of the piston sections of the die were separated from the membrane materials by four layers of Grafoil. The die was loaded with enough membrane material to produce an estimated final membrane thickness of 0.2 cm. Care was taken when loading the die to ensure that the powder mixture was loaded evenly and then cold-pressed under a bench-top hydraulic ram to a load of 15000 pounds. In order to ensure the purity of the highly hygroscopic materials, all mixing and loading took place in a glove box under dry nitrogen.

The closed die was then moved to an oven and heated to a temperature 100 °C below the melting temperature of the mixture, identified by Babcock [6]. After the die was at temperature for 3 hours (long enough to ensure uniform heating), the die was quickly removed from the oven and pressed under a load of 15000 pounds. The die was then returned to the oven and allowed to cool overnight to room temperature. Once cool, the die was removed and disassembled in the glove box. Excess graphite was removed from the surface of the membrane by sanding.

Cell assembly and heating. The electrodes were arranged on either side of the membrane as shown in Figure 3. Current was carried to the electrode surfaces by 0.009" diameter 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.

Once assembled, the cell was loaded into a custom-made oven and connected to process gas and sweep gas supply lines. The exit gas from the cathode was routed through a UV scanner for reading H_2S levels and an IR scanner for reading CO_2 and CO levels. The sweep side was allowed to vent directly to the hood. At this point, 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 CO_2 / O_2 mixture to maintain a stable thermodynamic reference voltage.

Initially, dry nitrogen was blown through both sides of the cell as the assembly was heated at a rate of 100 °C / hr. Melting of the electrolyte was verified by a sudden improvement in the seals formed by the ccntact of the membrane with the MACOR surfaces and conductivity through the cell. Process gas, consisting of specified levels of H_2S, CO_2, H_2O, and the balance of 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 measured 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 in steps of 25 mA and the cell was allowed to equilibrate for 15 minutes after each current step. Once equilibrated, potentials with respect to the reference electrode and cathode exit concentrations were again measured.

RESULTS AND DISCUSSION

Run 8/3/89
Carbonate Tile
Carbon Cathode, Cobalt Disulfide Anode

While several experiments have been performed, in the interest of brevity, only the results of two representative runs are presented here. The first experiment presented (8/03/89) used a standard MCFC tile obtained from IGT (62% Li_2CO_3, 38% K_2CO_3). The cathode in this experiment was carbon and the anode was CoS_2 (50.1 void percent). The process gas had a dry composition of 1% CO_2 and 2000 ppm H_2S by volume and the balance of CH_4. Water vapor was added to a level of 12.1 volume percent by passing the process gas through a heated water bubbler. This water concentrating was chosen to equilibrate with the carbonate electrolyte to a composition of approximately 20 mole percent sulfide at the run temperature of 607 °C (see Figure 2). The process gas was supplied at a rate of 109 cc/min; the sweep gas of pure N_2 was supplied at a rate of 104 cc/min.

Figure 4 shows the overall removal of both CO_2 and H_2S. The overall removal is defined as the removal based on the inlet process gas composition minus the exit process gas composition.

$$\text{\% Removal}_{(\text{overall})} = [(\text{Inlet Comp.} - \text{Exit Comp.})/\text{Inlet Comp.}]100 \qquad (14)$$

The zero current basis removal is based on the exit concentration of the process gas with no current applied to the cell minus the concentration with current applied.

$$\%\ \text{Removal}_{(0\ \text{current basis})} = [(\text{Exit Comp.}_{(0\ \text{current})} - \text{Exit Comp.}_{(\text{with current})}) / \text{Exit Comp.}_{(0\ \text{current})}]\ 100 \qquad (15)$$

The stoichiometric removal is based on the assumption that two electrons remove one molecule of gas phase constituent. Thus, the current carried by the cell would be a linear relationship with the moles of species removed. This current is described as follows:

$$I_{\text{Stoich.}} = (P\ V\ X_{\text{species removed}}\ n\ F) / R\ T \qquad (16)$$

where: $I_{\text{Stoich.}}$ = current in Amp
P = 1 atmosphere
V = volumetric flowrate (STP cc/sec)
$X_{\text{species removed}}$ = mole fraction of species removed by current
n = electrons involved in transfer (in this case, 2 equivalents/mole)
F = Faraday's Constant, 96500 Coulombs / equivalent
R = Gas Constant 82.05 cc atm / K mole
T = temperature of gas when flowrate is measured (298K)

When the constants are pulled together in equation (16), it simplifies to:

$$I_{\text{Stoich.}}\ (\text{mA}) = 130\ X_{\text{species removed}}\ V\ (\text{cc/min}) \qquad (17)$$

From equation (17), the stoichiometric concentration of species removed under a given applied current can be calculated by algebraic manipulation:

$$X_{\text{species removed (stoich.)}} = I_{\text{applied}}\ (\text{mA}) / (130\ V\ (\text{cc/min})) \qquad (18)$$

Therefore, by equation (18), the removal of total species on a stoichiometric basis can be found by the following equation:

$$\%\ \text{Removal}_{\text{Stoich.}} = [(I_{\text{applied}}\ (\text{mA}) / (130 * V\ (\text{cc/min}))) / \text{Inlet Comp.}]\ 100 \qquad (19)$$

Since the electrolyte used in this experiment was initially pure carbonate, there is a chemical removal of H_2S and corresponding production of CO_2. There is also production of CO_2 by chemical degradation of the carbon electrode used for the cathode by reaction with water vapor. These effects could account for the initial total removal below zero % which would mean a production of removable species (see Figures 4 and 5).
This degradation of the cathode could be avoided by the use of the cathode materials identified by Weaver [3]. The number reported

as the zero current basis assumes that over short periods of time these chemical effects are constant and thus reports the removal which is attributed to applied current alone. The chemical effects were checked periodically during the run by shutting off the current supplied to the cell and recording the concentrations in the exit gas from the cathode. Figure 5 shows the removal as broken down into individual species.

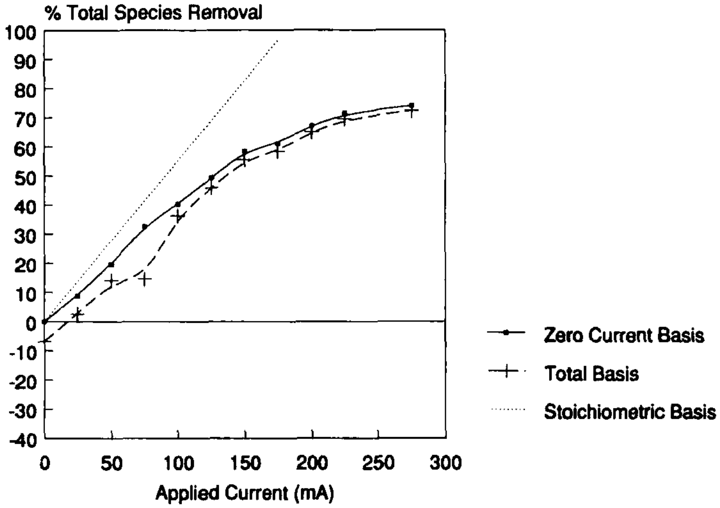


Fig. 4. Run 08/03/89
Total Species Removal vs. Current

The deviation from the stoichiometric removal increases with current, Figure 4, and is explained by the gas phase mass transfer effects. At high current densities in the cell, it becomes more difficult to supply sufficient reactant through the gas phase to the surface of the electrodes and the negative deviation from the stoichiometric removal results. These effects are discussed later.

Figure 5 shows that the relative removal of each species follows similar trends, regardless of the cell potentials. Recall that at cell potentials above approximately -1 Volt, H_2S should be selectively removed. Diffusion of H_2 through the membrane to the anode side could cause the cell to act as an electrochemical concentrator, rather than an electrochemical remover, with no net cell reactions taking place across the cell. This would mean that H_2S and CO_2 were simply moved from the cathode side to the anode side as a function of current alone. Some CO_2 and H_2S were observed in the anode sweep gas, but no means were available at the time of these experiments for measuring H_2 content.

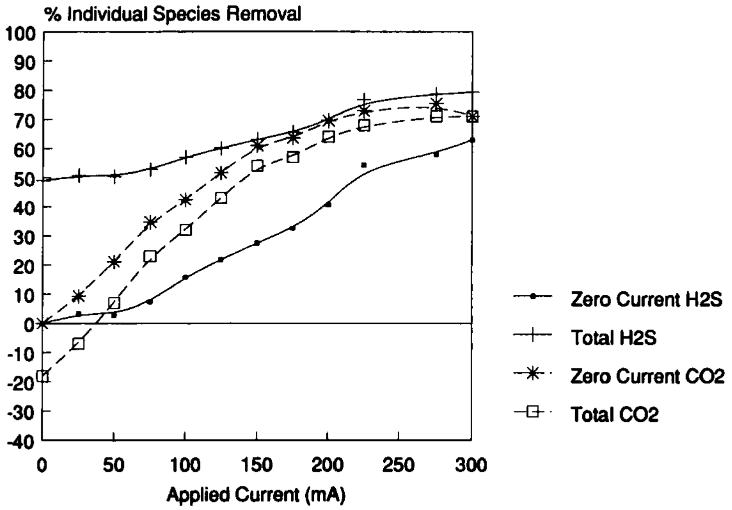


Fig. 5. Run 08/03/89 Individual Species Removal vs Current.

Figure 6 shows the overpotential of the cell as a function of applied current. Overpotential is defined as the deviation of the electrode potential with respect to the reference electrode from the equilibrium (or zero current) value. From Figure 4, the current corresponding to 100 % stoichiometric removal is approximately 190 mA. In Figure 6, one can see that at 200 mA a sudden jump in the rate of change of overpotential with applied current occurs. This sudden increase is explained by the fact that there are no longer enough gas phase reactants in the process gas to support the current being pushed through the cell. Beyond this limiting current, another mechanism must arise; this mechanism is thought to be the oxidation of carbonate. Thus, if currents above the 100% stoichiometric removal value are applied long enough, the electrolyte will be destroyed.

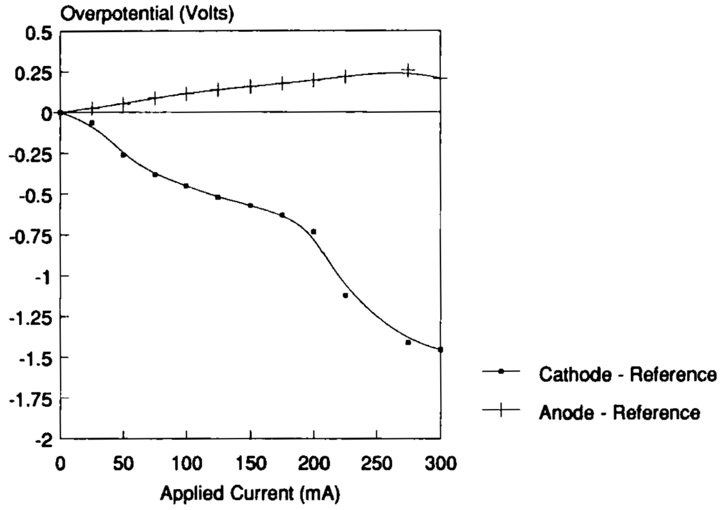


Fig. 6. Run 08/03/89 Overpotential vs. Current.

Since the membrane electrolyte and the process gas were allowed to come to equilibrium in situ, localized density changes occurred in the membrane. As the changes progressed, the resulting mechanical stresses cracked the membrane thus allowing bulk mixing of the process and sweep gases. The experiment was terminated at this point. This situation can be avoided by manufacturing a membrane already at the equilibrium composition dictated by the process conditions.

Overall, total removals of up to 70% were recorded. When broken out by species, the results show 80% removal of H_2S and nearly 70% removal of CO_2.

Run 8/28/89
20% Sulfide Membrane
Carbon Cathode, Carbon Anode

Experiment 8/28/89 used a tile manufactured in the laboratory with a sulfide composition of 20%. There was a thin layer of Grafoil left on the surfaces of the tile for fear that too much sanding would generate cracks in the matrix material. Both the anode and the cathode in this experiment were carbon. The process temperature was 607 °C and the process gas was supplied at a rate of 109 cc/min. The sweep gas was pure N_2 and was supplied at a rate of 36 cc/min. The water level in the process gas was maintained at 12%. These experimental conditions corresponded to an equilibrium electrolyte composition of 20% sulfide.

Figure 7 shows the total removal vs current for this run. The differences between the zero current basis removal and the total removal are much less pronounced than in run 8/3/89. This is to be expected since the membrane was manufactured with an electrolyte composition very close to that which would be in equilibrium with the process gas. The mass transfer effects appear to be more pronounced in this run than in 8/3/89 which can be explained by the added resistance to mass transfer provided by the thin layer of Grafoil left on the surface of the tile. The removals of the individual constituents are broken out in Figure 8. As expected, the chemical effects observed with zero current applied to the cell are less than those in run 8/3/89.

The overpotentials versus current are shown in Figure 9. The low overpotentials at the cathode and anode indicate good contact between the electrodes and the electrolyte. Overpotential data were not recorded past the estimated 100% stoichiometric removal. However, the constant slopes of the graphs show the well established electronics of the run.

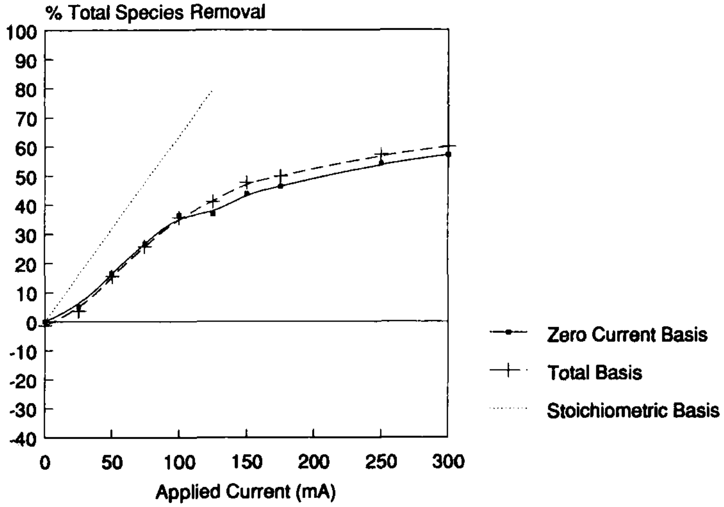


Fig. 7. Run 08/28/89 Total Species Removal vs. Current.

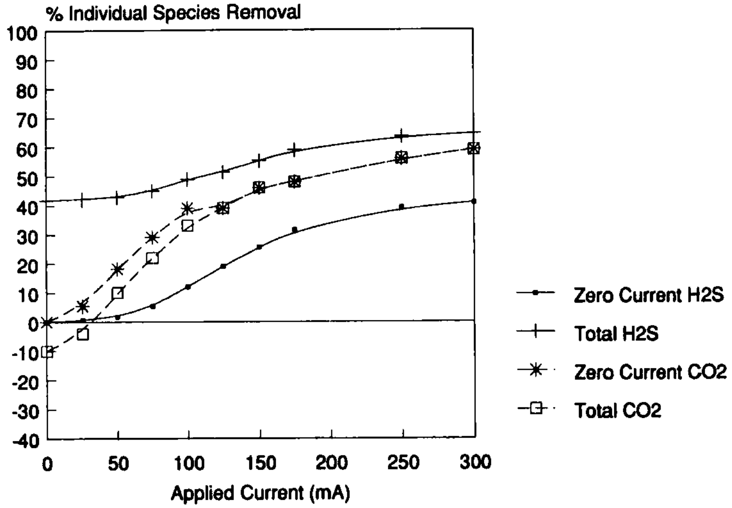


Fig. 8. Run 08/28/90 Individual Species Removal vs. Current.

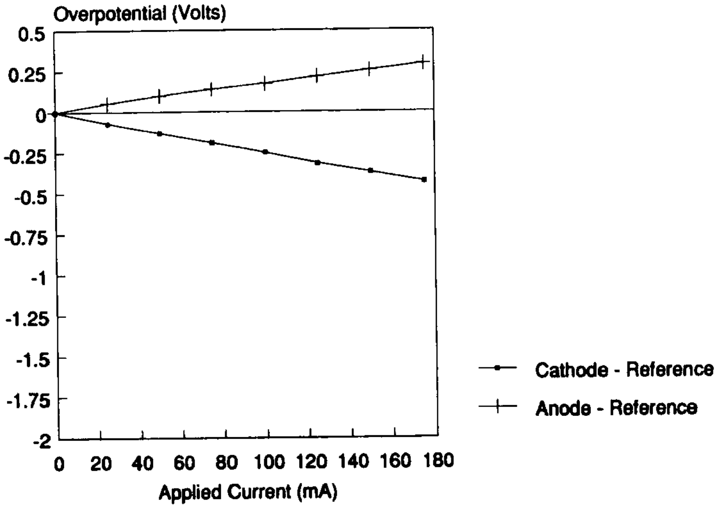


Fig. 9. Run 08/28/89 Overpotential vs. current.

The run was terminated due to cracks forming in the membrane. However, unlike the membrane failure of run 8/3/89, it is felt that the cracks were due to the crude method of tile manufacture. Overall, the cell removed up to 60% of combined CO_2 and H_2S. This total removal is broken down to 60% total CO_2 removal and 65% total H_2S removal.

Mass transfer effects. Transport of the sulfide (or carbonate) ion must take place in three steps:

1) Gas phase transport from the bulk gas stream to the cathode surface.
2) Diffusion from the electrode pore mouth to the catholyte surface where reduction takes place.
3) Liquid phase diffusion through the electrolyte to the anode surface where oxidation takes place. [3]

Calculation of gas phase transport to the surface of the cathode shows that this is the limiting step to the process and examination of the run data seems to confirm this. Assuming that the model corresponds to flow across a flat plate, transport resistance should decrease with increasing flow velocity [7]. This was confirmed during run 8/28/89 when a 135% increase in the gas velocity gas resulted in an 8.4% increase in the removal rate. The actual gas phase resistance of the cell cannot be accurately predicted with the flat plate model since the flow is not infinite, but restricted between the electrode surface and the housing surface.

CONCLUSIONS

This work has shown that the removal of H_2S from natural gas is possible, if not completely selective. Fortuitously, the other component removed for the process gas is CO_2, which is also considered to be a contaminant to natural gas. Therefore, as long as the CO_2 content of the process gas is not so high as to completely mask the H_2S removal, the removal of both species map similar trends. Bulk diffusion of H_2 through the membrane is thought to be the cause of the lack of selectivity in the species removal of the cell. Gas phase mass transfer resistance is presently seen as the limiting factor for overall cell performance. Improved membrane manufacturing techniques resulting in higher membrane densities could solve the problem of H_2 transport and increased gas velocities should help lower the mass transport resistance and increase removal rates.

FUTURE WORK

Work will continue in refining the membrane manufacturing technique. Besides hot pressing, attempts will be made in the areas of tape casting and wicking molten electrolyte into a sintered ceramic matrix in situ. The goal of this work will be a membrane whose electrolyte is in equilibrium with the process gas and dense enough to prevent the cross diffusion of H_2.

The mass transfer coefficient of the cell will be improved by fitting future cells with a process gas recycle pump. This modification will increase the gas velocity per pass through the cell but not affect the average gas residence time.

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