Quarterly Progress Report

High Temperature Electrochemical Polishing of H_2S

from Coal Gasification Process Streams

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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].

H_2S 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 H_2S during gasification. Problems arise due to the corrosive nature of H_2S on metal components contained in these cycles. Because of this, H_2S 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 efficiency[1] incorporates gas turbines that cannot tolerate H_2S levels above 100 ppm. Coal gasification/Molten Carbonate Fuel-Cell(MCFC) systems, achieving conversion efficiencies around 60%[2], function properly only if H_2S is below 1 ppm.

An advanced process for the separation of hydrogen sulfide (H_2S) from coal gasification product streams through an electrochemical membrane is being developed using funds from this grant. H_2S 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 H_2S 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% H_2S from gases containing only H_2S in N_2[3], simulated natural gas[4,5], and simulated coal gas[6]. 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 S^{2-}, and the competing transport of CO_2 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 H_2S. This is done by reducing the most electro-active species in the gas stream. In this case, H_2S is reduced by the following:

$$H_2S + 2e^- \rightarrow H_2 + S^{2-} \qquad (1)$$
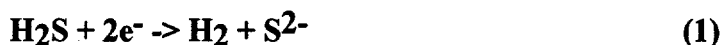
A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H_2 diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.

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

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 $500^{\circ}C$ - $1000^{\circ}C$, 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[10,11].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[12] or inefficient molten salt sorbent processes[13] 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

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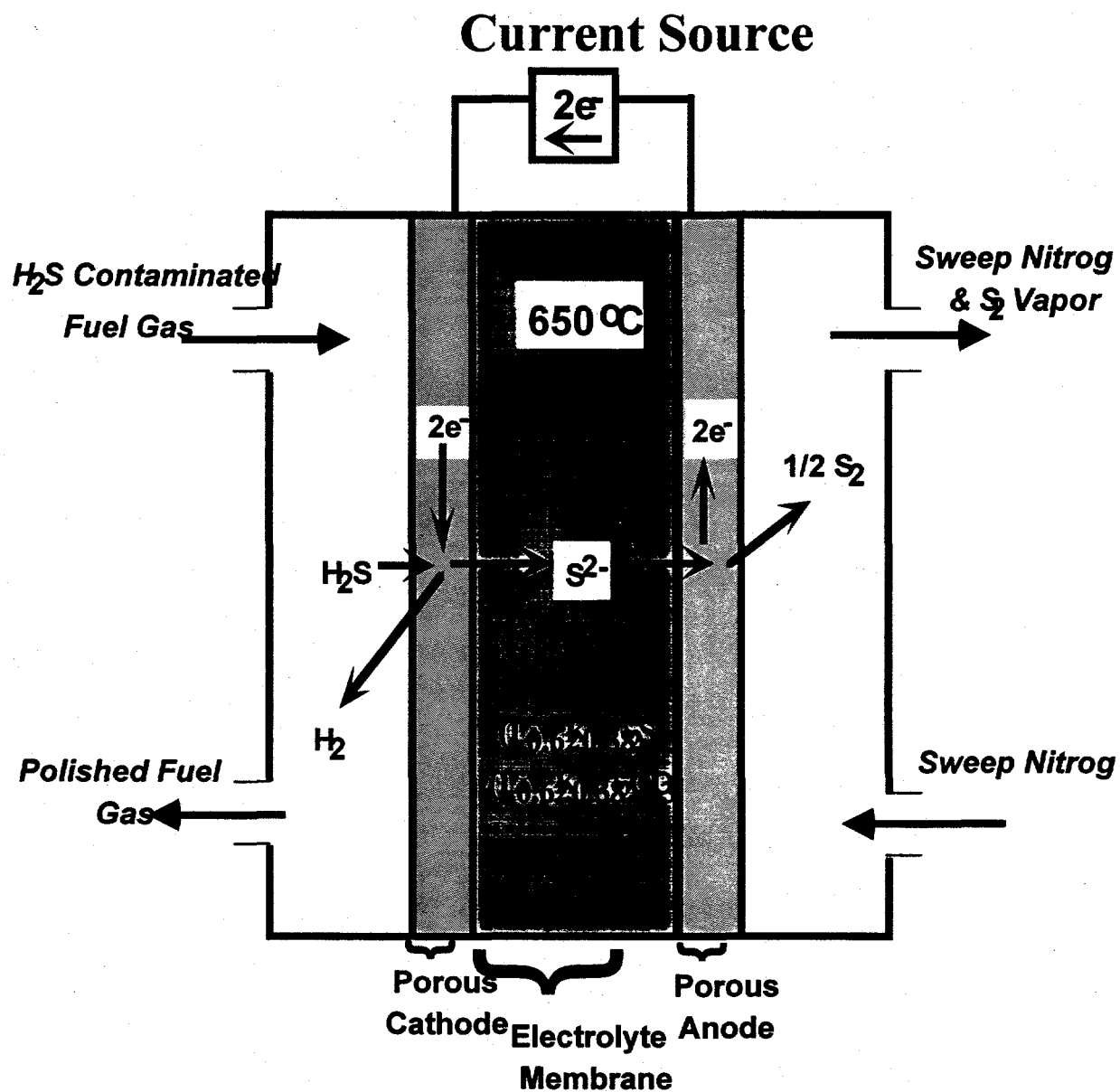
Current Source

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

Quarterly Summary

This quarter focused on replacing the MACOR cell housings with stainless steel, which is more industrially suitable. Moreover, the success of utilizing Ni as a cathode material at reduced temperature (decreased from 650 °C to 580 °C) in full-cell experiments was also continued this quarter. An 85 % porous nickel cathode purchased from ERC was employed in all the full-cell experiments. Fabricated membranes purchased from Zircar Corporation were used in these full-cell experiments. In addition, stainless steel 316 (2" x 2" x 1") was employed as the cell housing, replacing the MACOR housings primarily used in past experiments.

Three runs (Runs 32-34) were attempted this quarter, with successful results achieved in Run 34. The purpose of these experiments was: 1) test the electrochemical membrane separator's ability to concentrate CO_2; 2) test the electrochemical membrane separator's ability to remove H_2S; and 3) test stainless steel as an alternative cell housing to MACOR as well as test nickel cathode performance at the reduced temperature.

Table I. Experimental Conditions

Run #	Temp (°C)	Cathode	Anode	Membrane	Housings	Electrolyte
32	580	Ni	Ni	Fabricated ZrO_2	Stainless steel (316)	$(Li_{0.62}K_{0.38})_2CO_3$
33	580	Ni	Ni	Fabricated ZrO_2	Stainless steel (316)	$(Li_{0.62}K_{0.38})_2CO_3$
34	580	Ni	Ni	Fabricated ZrO_2	Stainless steel (316)	$(Li_{0.62}K_{0.38})_2CO_3$

Run 32 was ineffective due to the lack of cathode seal formation which hindered data calculation. The seal never developed and thus cathode outlet concentrations (of CO_2 and H_2S) could not be detected. Excess electrolyte added in an attempt to form the cathode seal eventually clogged the process tubes and the run was halted. Run 33 was hindered by lack of seal development as well

as problems with the reference electrodes. These problems were addressed and corrected which lead to data collection in Run 34.

Carbonate Transport

Before the addition of H_2S to the cell, it is necessary to evaluate the electrochemical membrane separator's ability to transport carbonate across the cell. This is accomplished by CO_2 removal from the process gas (cathode coal syn-gas) (3):

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

and anode CO_2 evolution due to carbonate oxidation (4):

$$CO_3^{2-} \rightarrow CO_2 + \tfrac{1}{2}O_2 + 2e^-$$
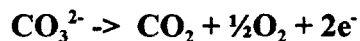
This is the first test performed during a full-cell run which displays the EMS cell's performance. Based on 2 Faraday's of charge transferred per mole of species reduced or oxidized, the actual carbon dioxide removed/produced can be compared to theoretical amounts. A current step method is utilized to determine the carbon dioxide removal, carbon dioxide production, as well as cell potential at varying applied currents. Carbon dioxide removal data is displayed in Figure 2, carbon dioxide production data is shown in Figure 3, and cell potential data is illustrated in Figure 4.

Figure 2 demonstrates that the EMS cathode outlet CO_2 values agree well with theoretical stoichiometric values, especially at the larger applied currents. This is the first time such positive results have been accomplished with stainless steel. In Figure 3, the amount of CO_2 produced at the anode corresponds with theoretical expectations. At higher currents, experimental values deviate from theory. This is probably due to not allowing sufficient response times. The required cell voltages, illustrated in Figure 4, were within anticipated bounds for CO_2 removal. As applied current was increased, the expected trends were noticed: the anode-reference potential increased and the cathode-reference and cathode-anode potentials both decreased.

CO$_2$ Removal vs. Applied Current
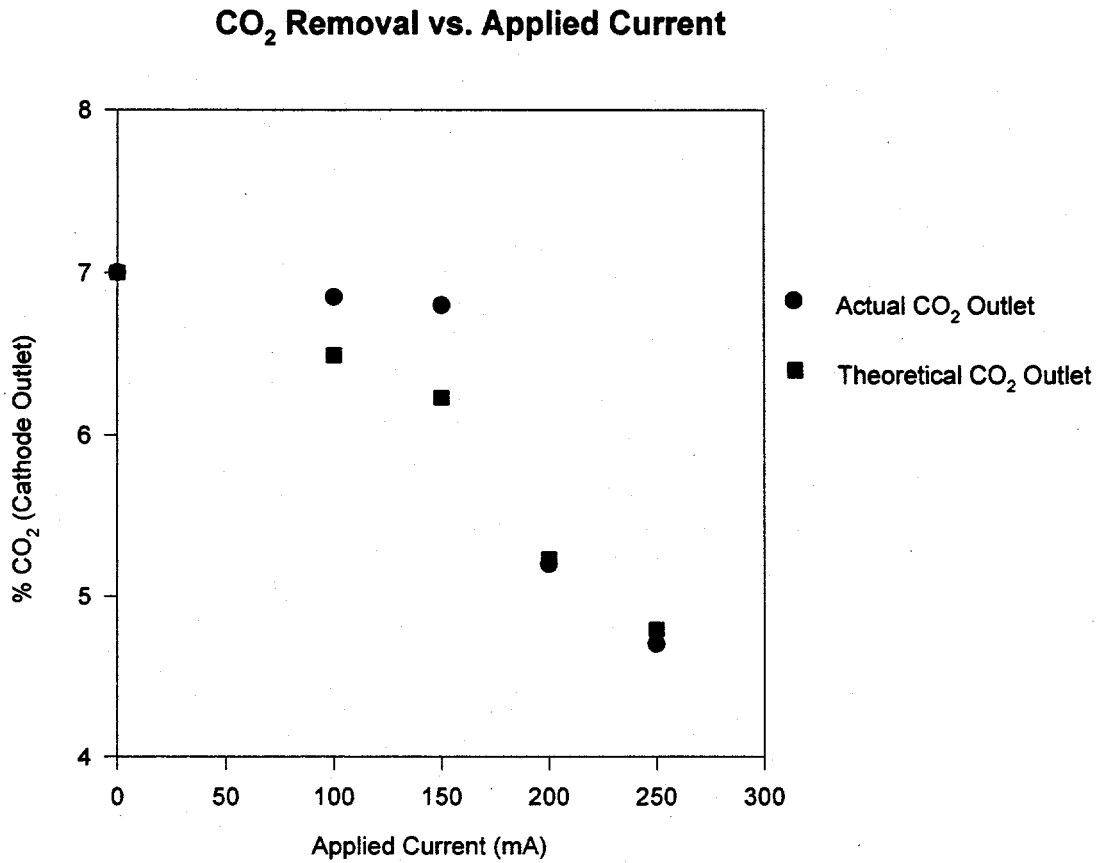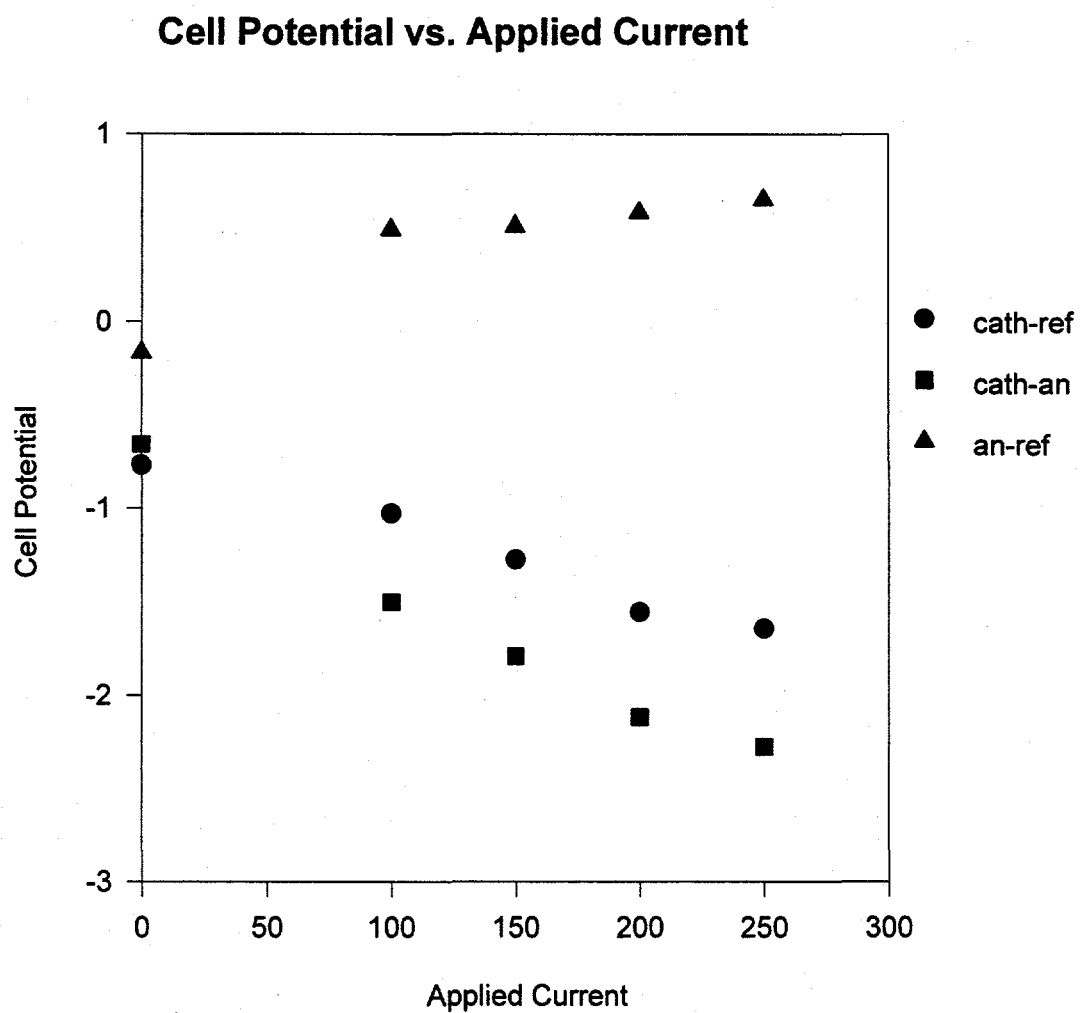
Cell Housings: Stainless Steel

Figure 2. Run #34. Carbonate Transport - CO$_2$ Removal versus Applied Potential

Carbon Dioxide Production at Anode
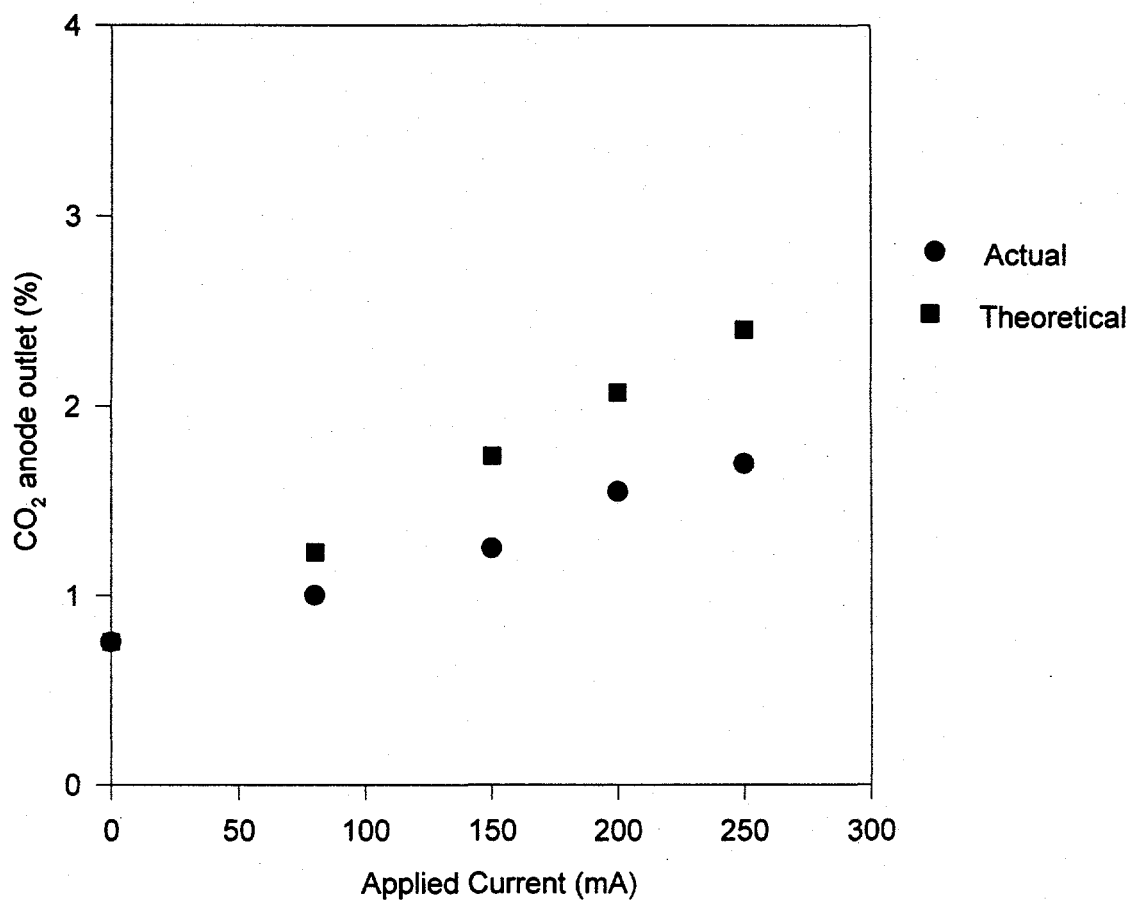
Cell Housings: Stainless Steel

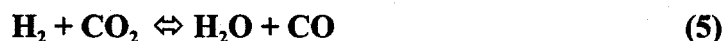**Figure 3. Run #34. Carbonate Transport - CO₂ Production vs. Applied Current**

Figure 4. Run #34. Carbonate Transport - Cell Potential vs. Applied Current

Removal of H$_2$S from Sour Coal Gas

Once carbonate transport across the cell was demonstrated, H$_2$S was added to the process syn-gas. The process gas was equilibrated by the following two reactions:

$$H_2 + CO_2 \Leftrightarrow H_2O + CO \qquad (5)$$
$$H_2S + CO \Leftrightarrow H_2 + COS \qquad (6)$$

via a stainless steel shift reactor before entering the cell housing. Once process gases entered the cell housings, they equilibrated with the molten electrolyte by:

$$(Li_{0.68}K_{0.32})_2CO_3 + H_2S \Leftrightarrow (Li_{0.68}K_{0.32})_2S + CO_2 + H_2O \qquad (7)$$

which creates a conversion of carbonate ions to sulfide ions depending on the concentration of H$_2$S in contact with the electrolyte. Typically, at least twenty-four hours is necessary for this reaction to reach equilibrium.

Run #34

Run #34 allowed for successful collection of data for 3 flow rates for cathode inlet H$_2$S levels ranging between 2100 - 2800 ppm. The flow rates were 254 cc/min, 254 cc/min (to check data replication), and 366 cc/min. At a cathode flow of 254 cc/min, the process gases equilibrated to: 6.05% CO$_2$, 2.61% CO, 6.46% H$_2$0, 9.06% H$_2$, 2359 ppm H$_2$S, and 41 ppm COS. Gas phase limiting current density was estimated at 82.1 mA/cm^2 while the membrane limiting current density was estimated at 49.6 mA/cm^2. The membrane limiting current density is typically greater than the gas phase limiting current density. However, the latest batch of membrane purchased from Zircar Corporation were highly porous (~85%, compared to the desired 66% in other batches). Nevertheless, the applied current in these experiments never approached the membrane limiting current density. The resulting molten salt equilibrium was estimated at 94.7 mol% (Li$_{0.68}$K$_{0.32}$)$_2$CO$_3$ and 5.3 mol% (Li$_{0.68}$K$_{0.32}$)$_2$S. Like the carbonate transport experiments, a current step was applied to determine the H$_2$S outlet levels, % H$_2$S

removal, and the potential profile versus applied current. Figures 5-7 demonstrate these values, respectively. Over 75% H_2S removal is demonstrated, the first positive result ever with stainless steel housings. Internal resistance ranged from 1.8 to 3.5 Ω in this set of experiments.

Cathode flow was increased to 366 cc/min while maintaining inlet H_2S levels around 2500 ppm. Process gases equilibrated to reach estimated values of: 4.40% CO_2, 1.19% CO, 7.22% H_2O, 6.34% H_2, 2472 ppm H_2S, and 28 ppm COS. Limiting current densities in the gas and membrane were 85.8 mA/cm^2 and 63 mA/cm^2, respectively. Molten salt equilibrium was estimated at 93.3 mol% $(Li_{0.68}K_{0.32})_2CO_3$ and 6.7 mol% $(Li_{0.68}K_{0.32})_2S$. Internal resistance was ~ 3 Ω during these current step experiments. Once again, over 75% H_2S removals were realized, as shown in Figures 5 and 6. Figure 7 illustrates the cell potentials at this flow rate.

Figure 5 demonstrates the trend of decreasing cathode outlet H_2S levels as applied current increases. This agrees well with the theoretical model. Figure 6, a different interpretation of Figure 5, also corroborates with the theoretical model which states that more H_2S will be removed as applied current is increased. Figure 7 displays the relationship between cell potential and applied current. The required cell voltages were within the anticipated bounds for our experimental conditions.

Run #34 was eventually shut down after 432 hours (18 days) due to loss of the cathode side process-gas seals. The broken cathode seal can be attributed to membrane fracture due to stresses in cell handling and dramatic cathode inlet H_2S fluctuations.

Cathode Outlet H$_2$S versus Applied Current
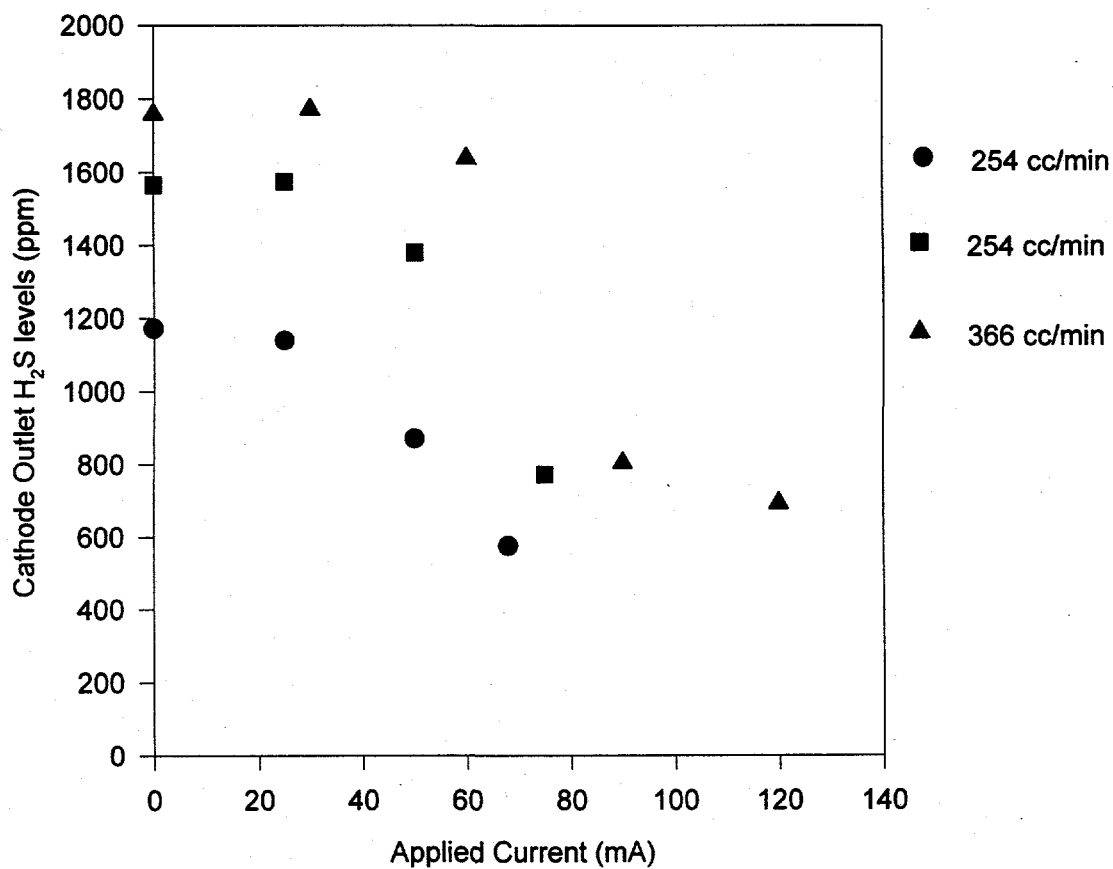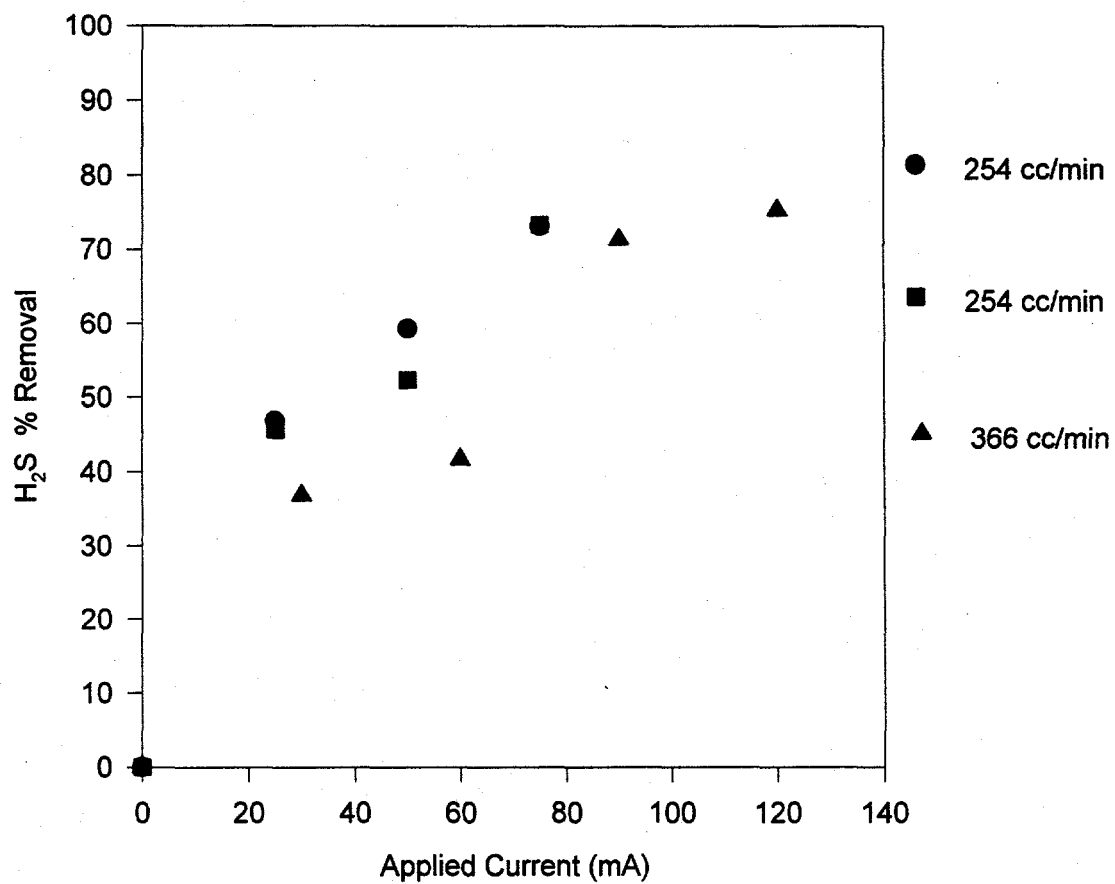

Inlet H$_2$S = 2100 - 2800 ppm   Temperature = 580 C

Cell Housings = Stainless Steel

Figure 5. Run #34. Outlet H$_2$S vs. Applied Current
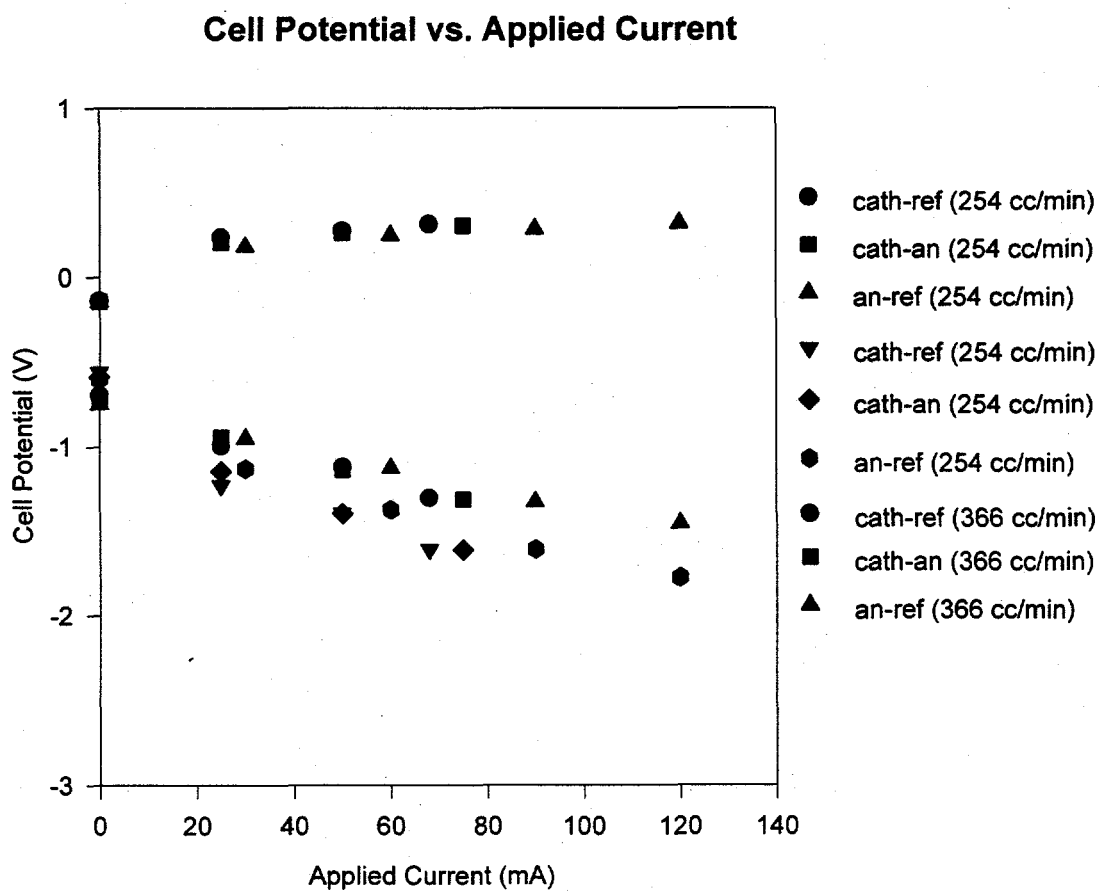
H$_2$S Removal vs. Applied Current

Inlet H$_2$S = 2100-2800 ppm   Temperature = 580 C

Cell Housings: Stainless Steel

Figure 6. Run #34. H$_2$S % Removal vs. Applied Current

Cell Potential vs. Applied Current

Inlet H$_2$S = 2100-2800 ppm   Temperature = 580 C

Cell Housings: Stainless Steel

Figure 7. Run #34. Cell Potential vs. Applied Current

Cell Housings

The cell housings utilized in the EMS system must be able to withstand high system temperatures as well as the acidic nature of the process gas. To date, only MACOR (a machineable ceramic) has been utilized to successfully remove H_2S at high current efficiencies. MACOR, which is composed primarily of SiO_2 with lesser amounts of Al_2O_3, has a decomposition temperature of 800 °C. Moreover, SiO_2 and Al_2O_3 are highly reactive with Li_2CO_3, a component of the electrolyte used in the EMS. Possible equilibrium reactions between MACOR and the electrolyte are shown below (corresponding equilibrium values are at 900 K):

$$Li_2CO_3 + SiO_2 \Leftrightarrow Li_2O \bullet SiO_2 + CO_2 \qquad K = 2059 \qquad (8)$$

$$Li_2CO_3 + Al_2O_3 \Leftrightarrow 2\ LiAlO_2 + CO_2 \qquad K = 165 \qquad (9)$$

Therefore, while MACOR is suitable for bench scale testing, it is not practical at the industrial level.

In order to achieve commercialization of this process, a suitable inert cell housing will need to be identified. Stainless steel is the hardware utilized in MCFC's. However, earlier EMS experiments with stainless steel housings have yielded unacceptable results due to low current efficiencies. This can be attributed to the reaction of process gases and carbonate with the highly conductive stainless steel. If oxygen and carbon dioxide contact exposed stainless steel at the cathodic housing in the presence of excess external electrolyte, oxygen and carbon dioxide will be reduced. At the anodic housing, excess external carbonate in contact with exposed stainless steel will oxidize to produce carbon dioxide and oxygen. Since there is no net cell reaction, current in the cell housings will run around the exterior of the cell, leaving only modest amounts of current to drive H_2S removal. Consequently, current efficiency for the process will be vastly reduced. Stainless steel housings are also subject to corrosion mainly in the wet seal area due to the potential gradient between the fuel gas on the inside of the cell and the ambient environment on the outside.

Passivating the stainless steel housing seems to be the best method of deterring parasitic reactions and corrosion. In Run #34, passivation was attempted by aluminizing the wet seal area of the cell housing. This was accomplished by: 1) applying Al paint to the exposed stainless

steel, 2) applying an Al foil gasket over this thin layer of paint, 3) applying another layer of Al paint over the aluminum foil gasket just prior to cell assembly.

Discussion

The goal of full-cell experiments is to validate the removal capabilities of the EMS system while maintaining economically feasible current efficiencies (high current efficiencies at high inlet H_2S concentrations). H_2S current efficiency is calculated by:

$$\eta_{H_2S} = \frac{\% \, H_2S \, Removal_{actual}}{\% \, H_2S \, Removal_{theoretical}} \tag{10}$$

which represents the ratio of H_2S actually removed to the amount that should be removed at a specified applied current. The following equation calculates the amount of H_2S removed from the process syn-gas:

$$\% \, H_2S \, Removal = \frac{Inlet \, H_2S - Outlet \, H_2S_{(I_{app})}}{Inlet \, H_2S} \, x100 \tag{11}$$

Inlet H_2S values were utilized in this calculation rather than outlet values at zero applied current. Outlet H_2S values for this set of experiments were within 60% of the inlet values, but time considerations required beginning removal experiments before inlet/outlet H_2S equilibrium. Therefore, electrolyte scrubbing had a slight effect on H_2S removals at lower applied currents.

Figures 8 - 10 represent current efficiencies at various % removal for inlet H_2S concentrations ranging between 2100 - 2800 ppm. These current efficiencies at lower applied currents are high due to the aforementioned electrolyte scrubbing. The current efficiencies drop to ~ 80% at higher % H_2S removal levels. These lower efficiencies may be due to the molten electrolyte creeping underneath the Al foil gasket passivating layer. Molten alkali carbonates are known to be able to creep over any surface and into small crevices.[14] Since the Al foil gaskets in this experiment only covered the wet seal area, excess carbonate which was added during the cell
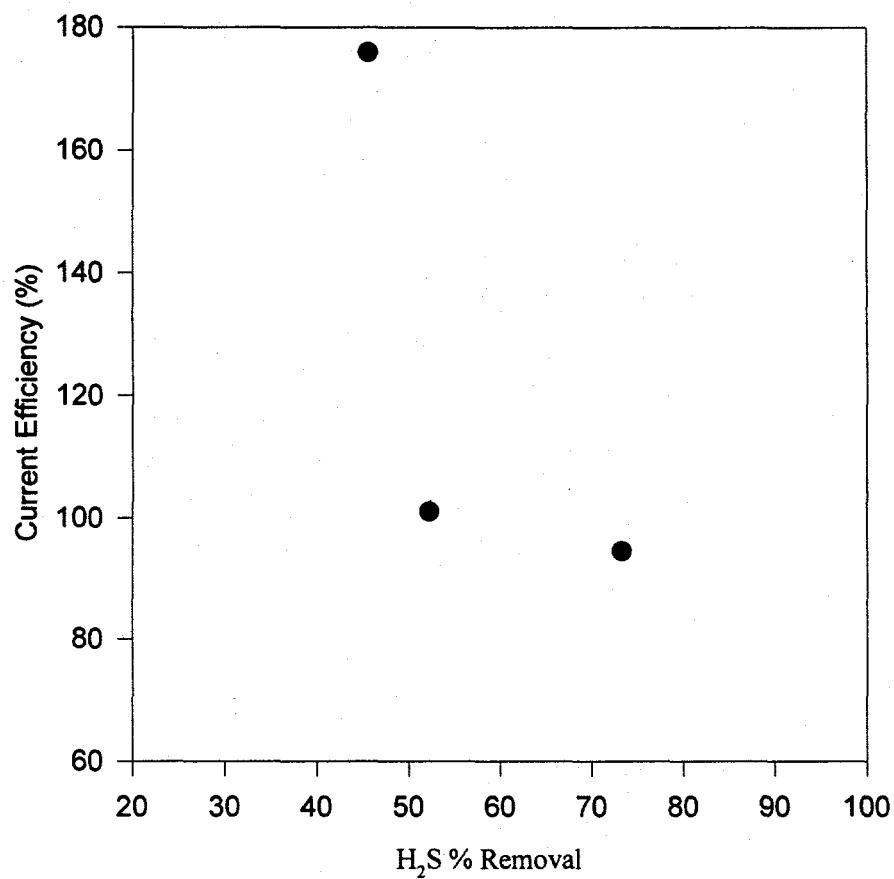
Current Efficiency vs. H$_2$S % Removal
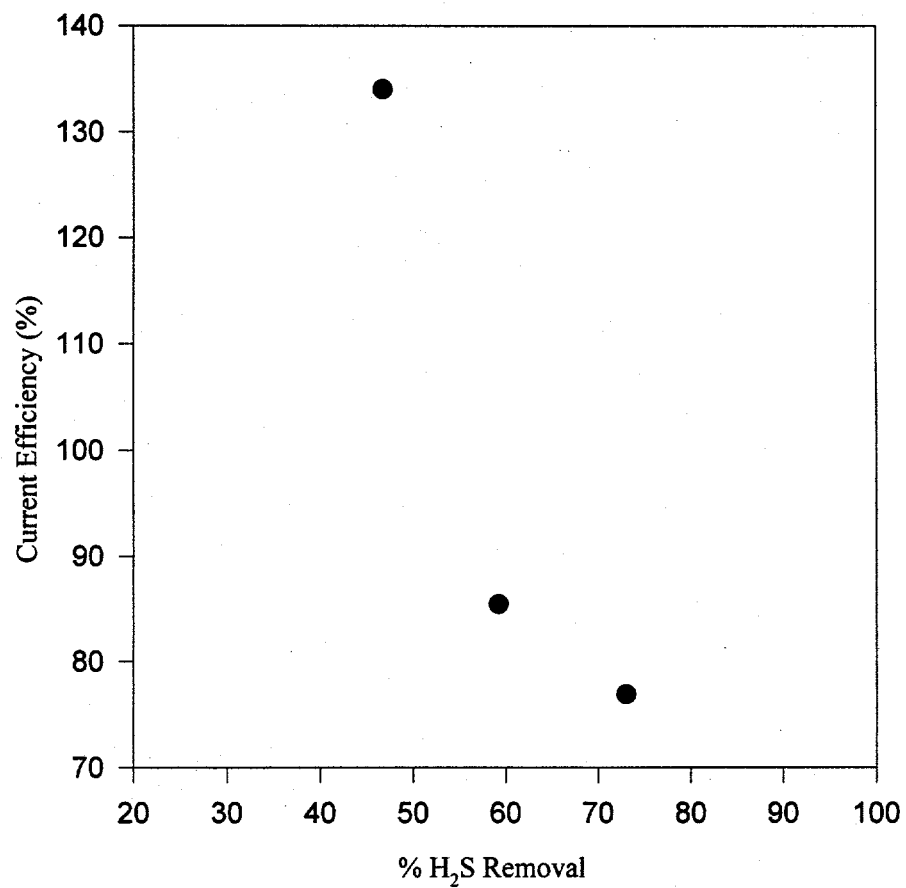
Inlet H$_2$S: 2100 ppm   Temperature: 580 C
Cathode Flow: 254 cc/min   Cell Housings: Stainless steel

Figure 8. Run #34. Current Efficiency vs. H$_2$S % Removal

Current Efficiency vs. H_2S % Removal
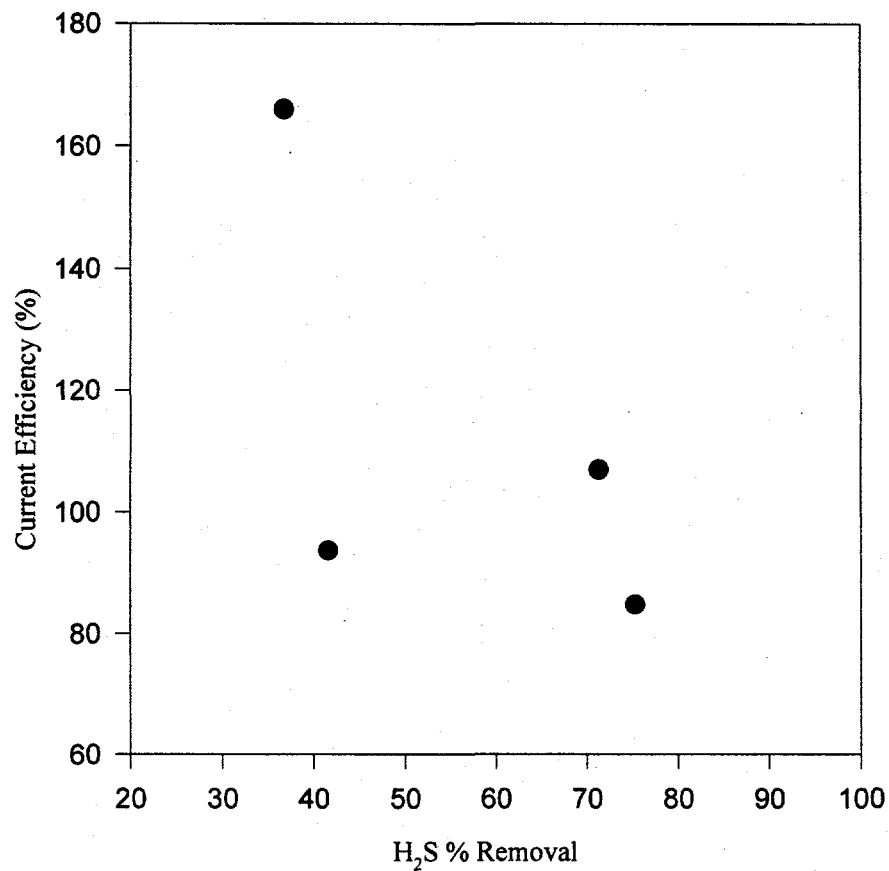

Inlet H_2S: 2800 ppm   Temperature: 580 C

Cathode Flow: 254 cc/min   Cell Housings: Stainless steel

Figure 9. Run #34. Current Efficiency vs. H_2S % Removal

Current Efficiency vs. H$_2$S % Removal

Inlet H$_2$S: 2800 ppm   Temperature: 580 C

Cathode Flow: 366 cc/min   Cell Housings: Stainless steel

Figure   10.   Run   #34.   Current   Efficiency   vs.   H$_2$S   %   Removal

run crept underneath the Al foil and into the wet seal area. Current efficiencies also may be reduced at the higher applied currents as the carbonate transport mechanism becomes more pronounced as cell potential increases. Thus, the current applied to carbonate transport is not available for H_2S removal.

Overall, these results show excellent corroboration with predicted maximum performances. This is the first time this has been achieved utilizing stainless steel cell housings. For sour gas concentrations at these flow rates, current efficiencies are expected to be near 100% for H_2S removal levels up to 90%. Our current efficiencies were always greater than 75%, thus close to agreement with theory. These positive results demonstrate that stainless steel can be effectively utilized as the cell housings in the electrochemical membrane separator. Future work can hopefully perfect stainless steel wet seal passivation to allow near 100% current efficiencies.

Past vs. Present

Like last quarter, experiments this quarter were performed at a temperature of 580 °C. This avoids the $Ni_{3-x}S_2$ eutectic which decreases the cathode's active surface area. This quarter, however, the MACOR cell housings were replaced with stainless steel, which is more suitable for industry. Previous experiments with stainless steel did not demonstrate effective H_2S removals and current efficiencies. The aluminization technique employed this quarter allowed for sufficient wet seal passivation to achieve successful H_2S removals. Moreover, an inert atmosphere (N_2) was provided to decrease the driving force for parasitic reactions between the stainless steel, excess carbonate, and fuel gas constituents. Constant electrolyte addition, which is necessary with MACOR due to MACOR-electrolyte corrosion, is not necessary for stainless steel housings. Once the wet seal was developed, only modest amounts of electrolyte were added to the system. This is due to the aforementioned inert atmosphere as well as the lesser driving force for corrosion between the molten electrolyte and stainless steel. Therefore, less cell maintenance is required for stainless steel cell housings since electrolyte did not have to be constantly added to the EMS as was the case for MACOR.

Conclusion

The Fossil Energy Advanced Research Program requires high temperature separations to remove environmental contaminants form 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 gasification temperatures. This development would enable a simplification of the entire gasification scheme by permitting a continuous one-step removal of hydrogen sulfide and production of elemental sulfur. Energy savings are a direct result of this high temperature processing.

The primary goals of DOE programs relating to gasification for power production more efficient, clean pathways 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 efforts are focusing on determining the most effective wet-seal passivation method for stainless steel cell housings. Due to the creeping ability of molten alkali carbonates, an alternative method of wet seal passivation will need to be developed. Plasma Coatings, Inc. has developed a successful passivation technique for the MCFC. The wet seal area was first cleaned and thoroughly roughened. Then, an aluminum metal coating approximately 4×10^{-3} inches was applied to the wet seal area by flame metallization. This was followed by diffusion bonding at 900 °C in a hydrogen furnace for two hours.[14] This technique will be attempted this quarter. Before full-cell runs, potentiostatic corrosion measurements of an aluminized wet seal will be compared against a non-aluminized wet seal. This will demonstrate the effectiveness of our protective layer. After successful wet seal passivation, full-cell runs with varying cathode process gas flow rates and inlet H_2S concentrations will be attempted.

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