Quarterly Progress Report

High Temperature Electrochemical Polishing of H$_2$S

from Coal Gasification Process Streams

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by

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Abstract

An advanced process for the separation of hydrogen sulfide from coal gasification streams through an electrochemical membrane is being perfected. H_2S is removed from a synthetic gas stream, split into hydrogen, which enriches the exiting syn-gas, and sulfur, which is condensed downstream from an inert sweep gas stream. The process allows for continuous removal of H_2S without cooling the gas stream while allowing negligible pressure loss through the separator. Moreover, the process is economically attractive due to the elimination of the 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.

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Executive Summary

This quarter's experiments were designed to test the performance of the Electrochemical Membrane Separator (EMS) at carbonate transport and H_2S removal. Specifically, we wanted to determine if aluminum plasma covered cell housings would improve upon the low current efficiencies which plagued earlier EMS experiments with stainless steel cell housings. A passivation layer over the stainless steel would prevent excess molten carbonate from contacting exposed stainless steel, thus preventing a pathway for parasitic reactions which diminish current desired for H_2S removal. It is important to apply a nonporous passivation layer since any crack in the layer will allow the molten carbonate to creep to the exposed stainless steel cell housing.

The EMS successfully transported carbonate across the cell in both full cell runs attempted this quarter. Once H_2S was added to the synthetic gas stream, however, data collection was nearly impossible due to weak cathode outlet flow. Post run analysis of the cell housing revealed that a solid had plugged the cathode cell housing flow chamber. X-ray diffraction of the solid revealed that NiO and K_2SO_4 were present in the solid plugging the flow chamber. K_2SO_4 formation was more than likely due to a leak in the system which allowed oxygen to come into contact with the cathode. While leaks in the system are not common, they do sometimes arise due to excess cell manipulation during a full cell run.

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 H_2S below 10 ppm) using the Electrochemical Membrane Separator (EMS). H_2S removal efficiencies over 90% were achieved at these stringent conditions of low H_2S 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 H_2S, the transport of S^{2-}, and the competing transport of CO_2 will be investigated. The model should identify the maximum current efficiency for H_2S 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:

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

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.

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

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^oC - 1000^oC, 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

sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies.
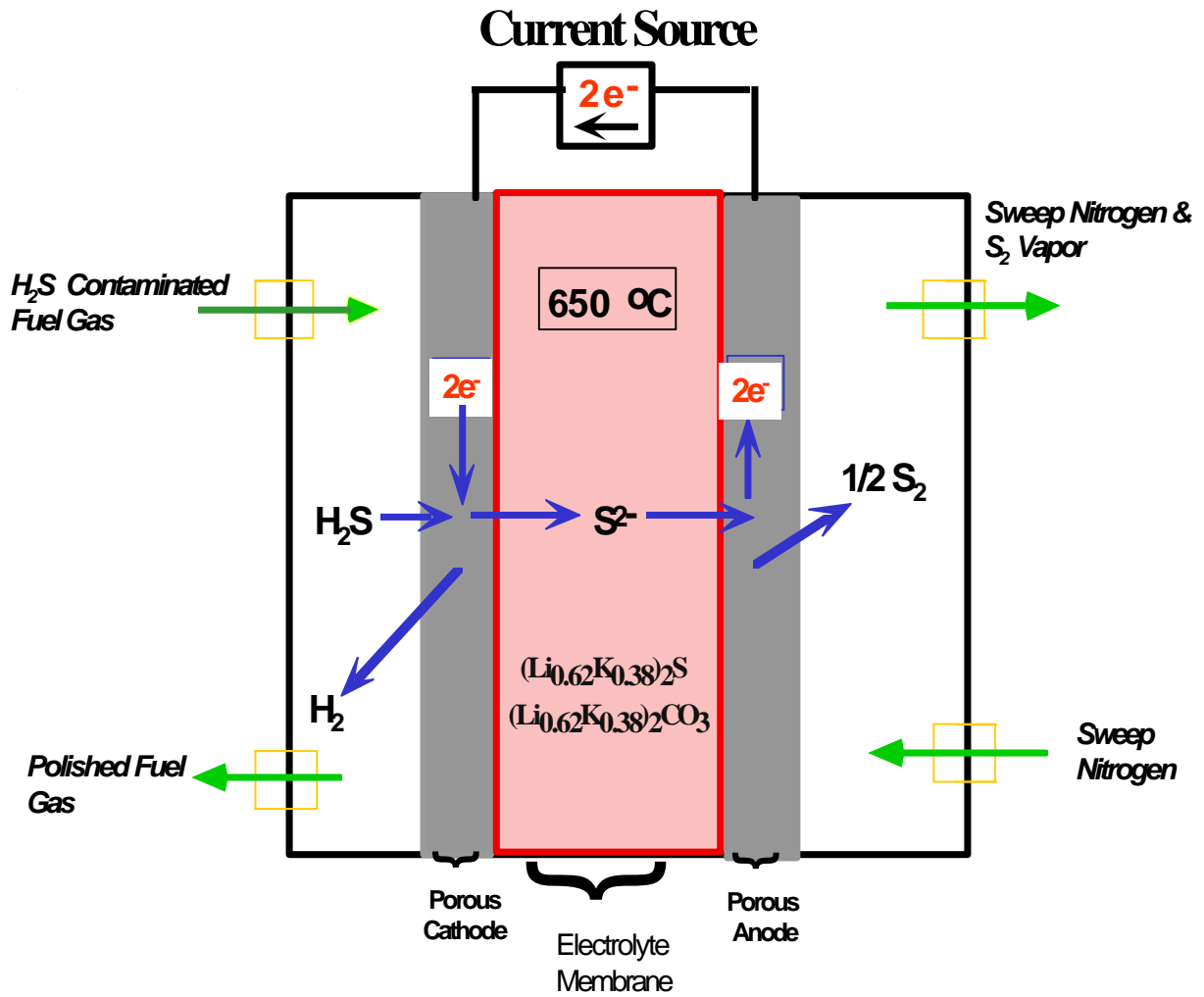

Figure 1. Single-Cell View of the Electrochemical Membrane Separator

Quarterly Summary

This quarter, experiments utilizing stainless steel 316 (2"x2"x1") as the cell housing were performed. In addition, the success of utilizing Ni as a cathode material at reduced temperature (decreased from 650 °C to 530 °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. Cell housings were plasma coated with aluminum in order to passivate the exposed stainless steel. This was done to prevent interactions between the molten carbonate electrolyte and the exposed stainless steel. The plasma coating was performed by Plasma Coatings, Inc., based in Memphis, Tennessee. Run #37 had the exterior of the cell housings coated, however the wet seal area was covered with an aluminum foil gasket and not plasma coated. The cell housings in run 38 were not aluminum plasma covered. These were aluminized by 3 successive aluminum applications followed by drying at elevated temperatures.

Both runs this quarter resulted in successful CO_2 transport. 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	Passivation
37	580	Ni	Ni	Fabricated ZrO_2	Stainless steel (316)	Exterior -Al plasma Wet seal - Al foil
38	530-580	Ni	Ni	Fabricated ZrO_2	Stainless steel (316)	Exterior -Al paint Wet seal-Al paint, foil

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**):

$$CO_2 + H_2O + 2e^- \rightarrow H_2 + CO_3^{2-} \tag{3}$$
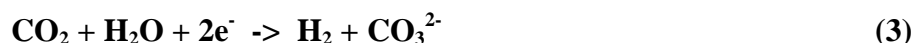
and anode CO_2 evolution due to carbonate oxidation (**4**):

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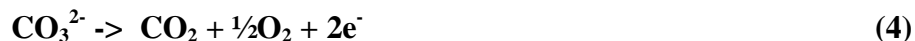
This is the first test performed during a full-cell run which displays the EMS cell's performance. Based on 2 Faraday's of charge transferred per mole of species reduced or oxidized, the actual carbon dioxide removed/produced can be compared to theoretical amounts. A current step method is utilized to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

Run #37

The removal cell was tested for CO_2 removal at the cathode and CO_2 production at the anode. In both cases, the experiment was run twice to demonstrate reproducibility. In addition, potentials were recorded versus applied current. The cathode inlet flow rate was approximately 200 cc/min while the cathode outlet flow rate was near 160 cc/min. Stoichiometric removal values were based on cathode outlet flow rates coming out of the CO_2 analyzer, which ranged between 95 and 120 cc/min. The anode inlet and outlet values were 184 and 150 cc/min, respectively. For CO_2 removal experiments, the cathode inlet gas concentration after the water-

gas shift reaction was 4.00 % CO_2, 2.56 % CO, 7.87 % H_2O, 16.33 % H_2, and balance N_2. A current step experiment was employed to determine the CO_2 removal and cell potentials versus increasing applied currents. CO_2 removal data is displayed in Figure 2, and cell potential data is illustrated in Figure 3. Current step experiments were also performed for CO_2 production at the anode. The cathode and anode inlet gas concentrations remained the same for this experiment. Cell potential data is given in Figure 4.

Run #38

The removal cell was tested for CO_2 removal at the cathode. Again, CO_2 removal experiments were run twice for reproducibility. At a cathode inlet flow rate of 102 cc/min and outlet flow rate of 63 cc/min, the gas concentrations entering the cell were 4.77 % CO_2, 2.74 % CO, 7.35 % H_2O, 18.63% H_2, and balance N_2. Figure 5 illustrates CO_2 removal versus a stepwise increase in applied current. Meanwhile, Figures 6 and 7 depict CO_2 production and cell potentials for CO_2 production experiments. As evidenced by Figures 2 through 7, excellent agreement with expected performance was observed. Moreover, required cell voltages were within anticipated bounds. Therefore, H_2S removal experiments were attempted.

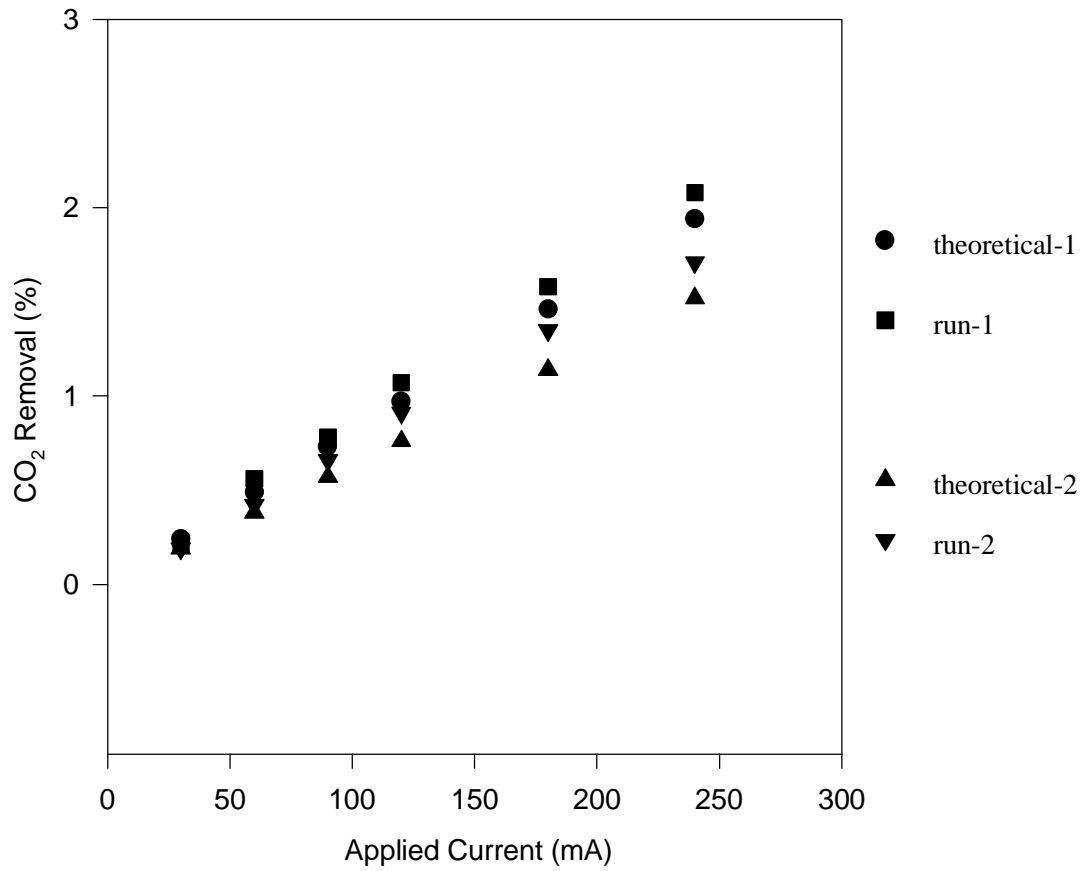# CO$_2$ Removal vs. Applied Current

Figure 2. Run #37. Carbonate transport - CO₂ Removal vs. Applied Current
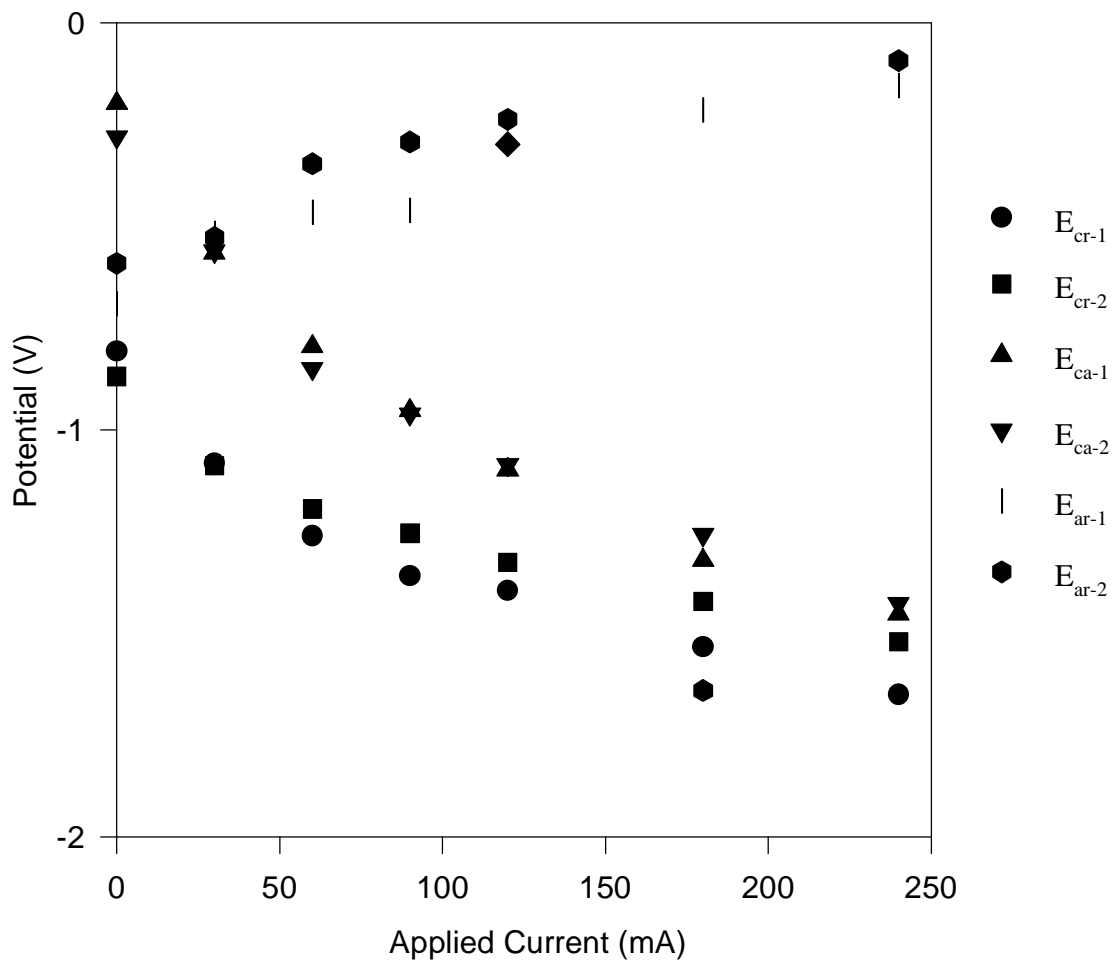
Cell Potential vs. Applied Current

Figure 3. Run #37. Carbonate Transport - Cell Potentials vs. Applied Current
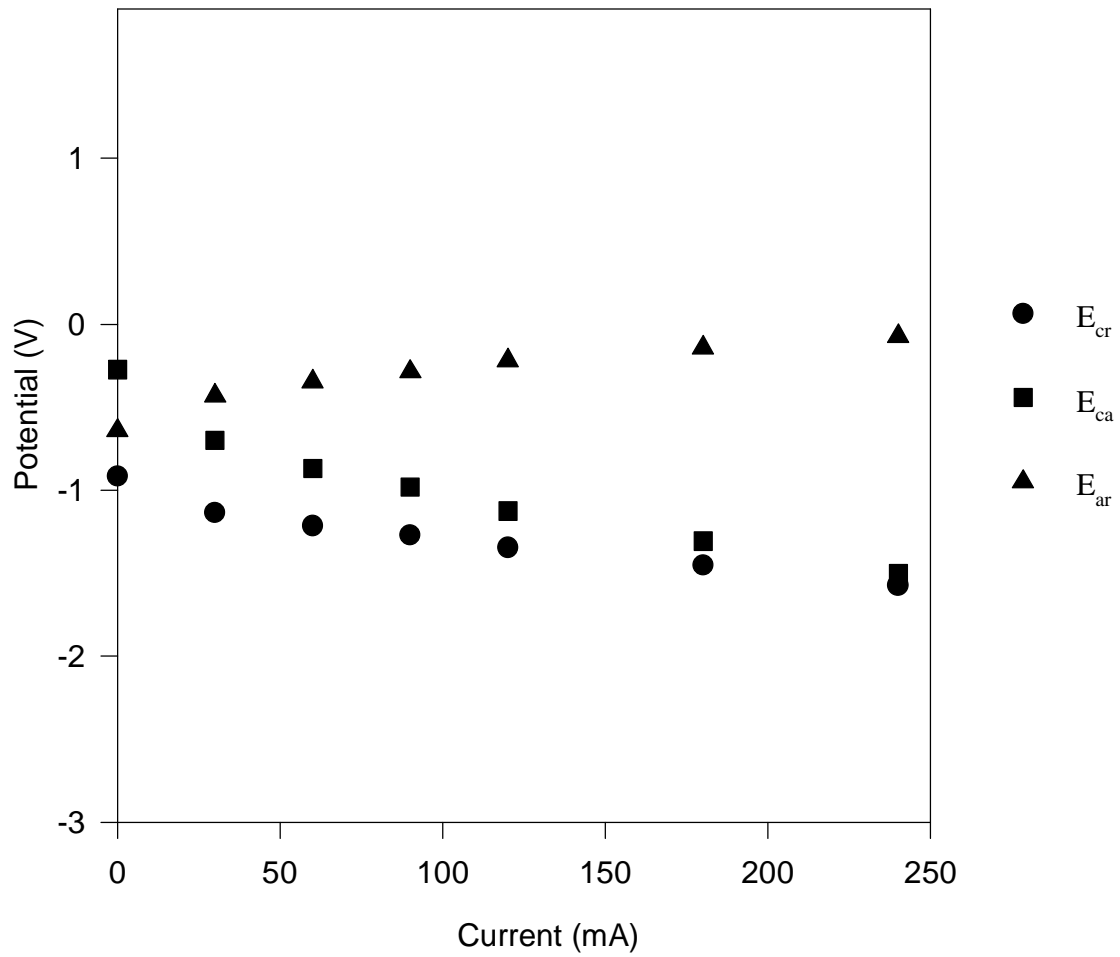
Cell Potentials vs. Applied Current

Figure 4. Run #37. Carbonate Transport - Cell Potentials vs. Applied Current
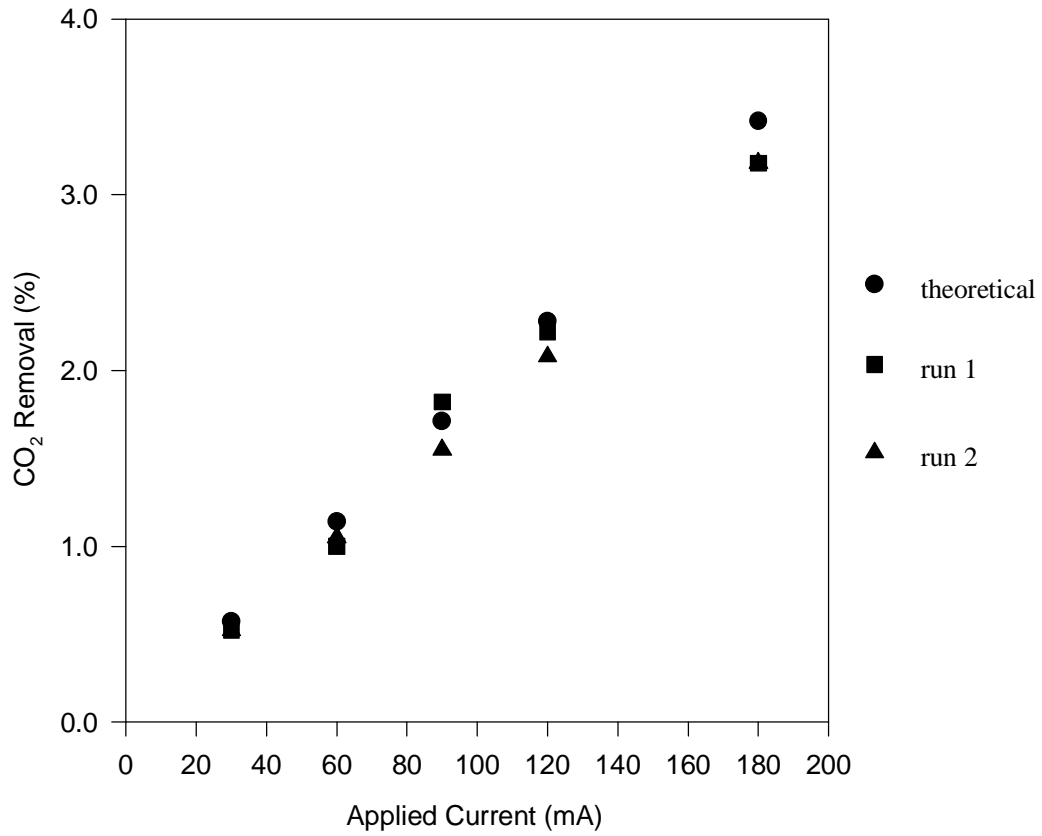
CO$_2$ Removal vs. Applied Current

Figure 5. Run #38. Carbonate Transport - CO$_2$ Removal vs. Applied Current

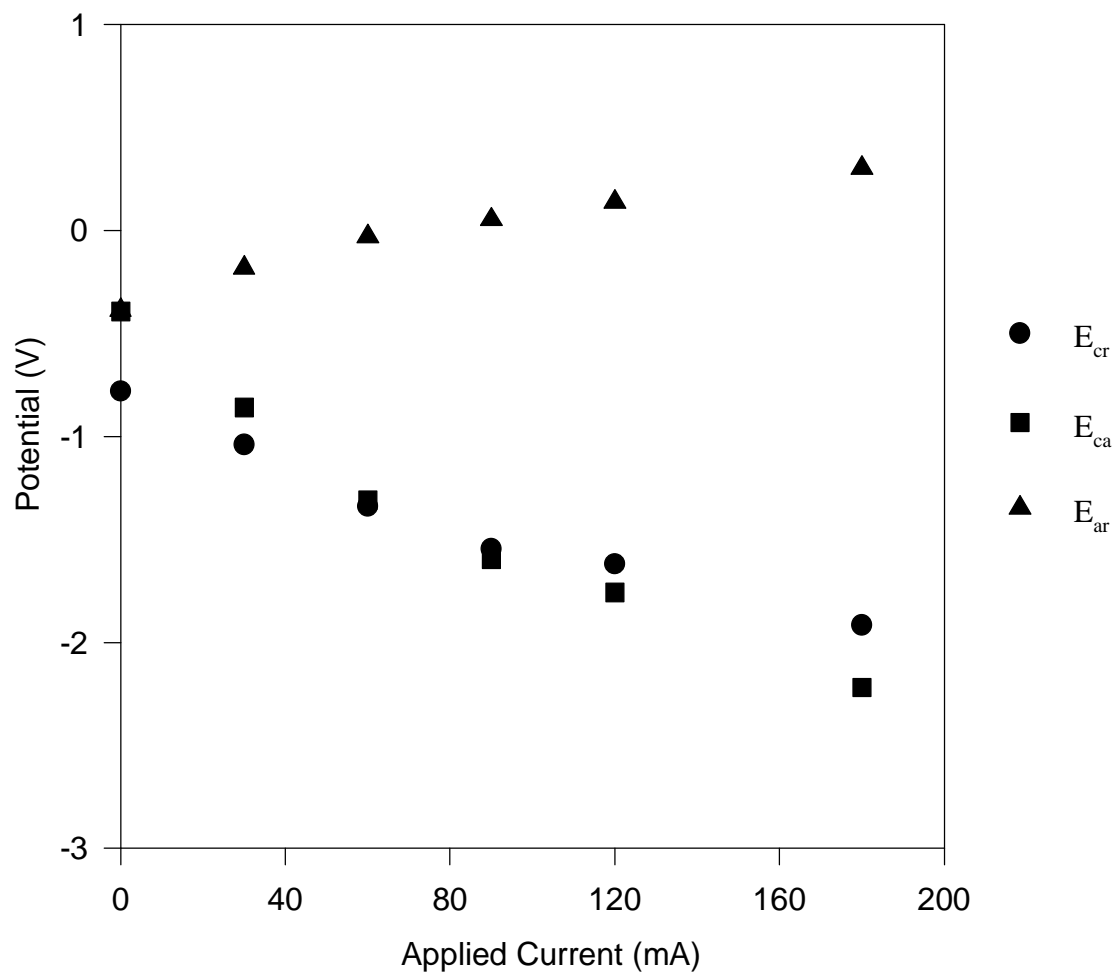# Cell Potentials vs. Applied Current

Figure 6. Run #38. Carbonate Transport - Cell Potential vs. Applied Current
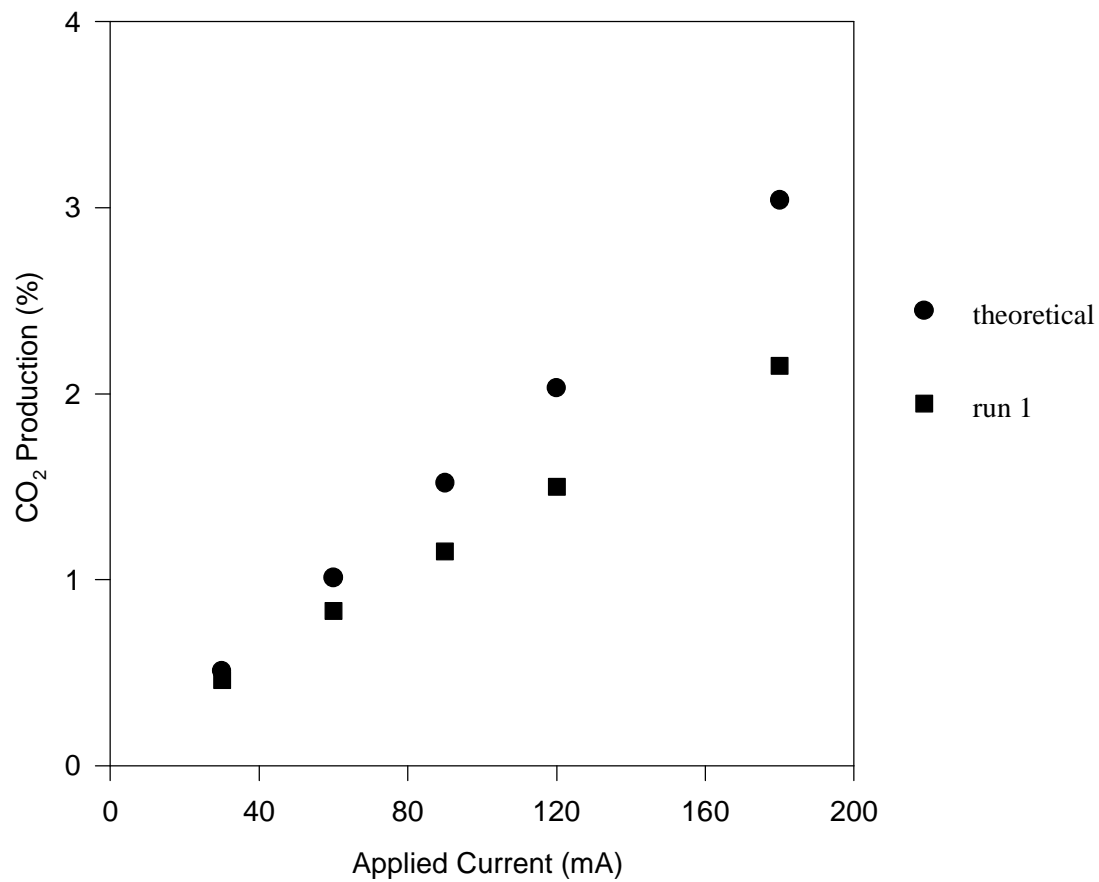
CO$_2$ Production vs. Applied Current

Figure 7. Run #38. Carbonate Transport - CO$_2$ Production 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:

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

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

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 #37

Attempts at H$_2$S removal were unsuccessful for this run. Data collection was prohibited due to a variety of problems including poor seals, low zero current H$_2$S concentrations, and eventual membrane cracking leading to H$_2$ crossover. The reference electrode also malfunctioned during the course of data collection. Once it was established that the membrane was cracked, the run was halted after 11 days.

Run #38

H$_2$S removal was observed during the course of this run, but data collection was difficult due to plugged gas flow chambers which restricted cathode gas flow through the cell. H$_2$S outlet

levels dropped as current was applied to the cell. However, H_2S removal was probably not due to direct reduction of H_2S at the cathode, but rather via a catalytic mechanism. First, the nickel sulfide electrode is reduced to form Ni metal, which then reacts with H_2S to reform the nickel sulfide, thus lowering the H_2S levels in the outlet stream. The experiment was plagued by the blocked gas flow, thus inhibiting the bulk diffusion of H_2S from the gas stream to the cathode. Ohmic losses for Run #38 ranged from 3 to 5 ohms. This run was ended after 19 days..

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:

$$\eta_{H_2S} = \frac{\% \, H_2S \, Removal_{actual}}{\% \, H_2S \, Removal_{theoretical}} \tag{8}$$

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:

$$\% \, H_2S \, Removal = \frac{Inlet \, H_2S - Outlet \, H_2S_{(I_{app})}}{Inlet \, H_2S} \quad x100 \tag{9}$$
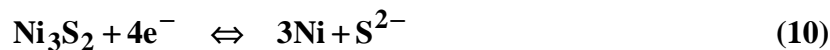
Aluminum Plasma Covered Cell Housings

As stated earlier, Run #37 had cell housings which were plasma coated with aluminum on the exterior of the cell. The cell housing's wet seal had an aluminum foil gasket to prevent wet seal corrosion. The purpose of the aluminum plasma coating is to prohibit parasitic reactions between the excess external carbonate and exposed stainless steel. Carbonate transport results are favorable, as evidenced by Figures 2-4. However, H_2S removal data collection was

impossible due to other circumstances. Therefore, further attempts with the plasma coated cell housings are being planned.
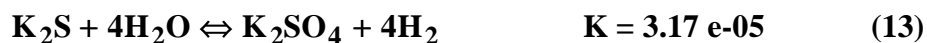
Nickel / Nickel Sulfide Electrodes

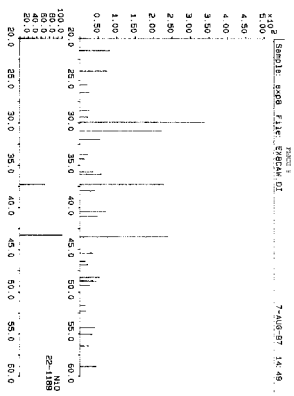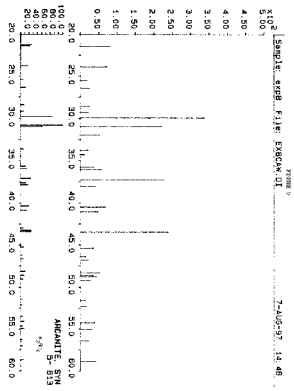A catalytic mechanism exists for the reduction of H_2S at a nickel sulfide cathode, as shown by:

$$Ni_3S_2 + 4e^- \quad \Leftrightarrow \quad 3Ni + S^{2-} \tag{10}$$

followed by

$$3Ni + 2H_2S \quad \Leftrightarrow \quad Ni_3S_2 + 2H_2 \tag{11}$$

The only downside of this catalytic mechanism is the expansion of the cathode as it is sulfurized from nickel to nickel sulfide. Post-run analysis of the cathode cell housing indicated that the gas flow channels were plugged by a solid. While the cathode seal was very strong during carbonate transport experiments, it deteriorated when H_2S is added to the synthetic gas stream. This trend has also been noticed in previous runs utilizing stainless steel cell housings. Both the cathode material and the substance which plugged the gas flow channels were recovered and analyzed using X-ray diffraction. The cathode could be distinguished as NiO and Ni_3S_2. However, it was more difficult to ascertain the components of the plugged material. Two compounds which could be distinguished from the diffraction pattern were NiO and K_2SO_4 (see Figures 8 & 9). K_2SO_4 is a rather surprising result, but is possible due to the availability of K_2S as a result of electrolyte equilibrium (7). There are numerous possibilities for the formation of K_2SO_4. Some possible pathways are listed below (with equilibrium constant at 800 K):

$$K_2S + 2CO_2 \Leftrightarrow K_2SO_4 + 2C \qquad K = 1.01 \text{ e-03} \qquad (12)$$

$$K_2S + 4H_2O \Leftrightarrow K_2SO_4 + 4H_2 \qquad K = 3.17 \text{ e-05} \qquad (13)$$

$$K_2S + 4CO \Leftrightarrow K_2SO_4 + 4C \qquad K = 1.01 \text{ e+01} \qquad (14)$$

$$K_2S + 2O_2 \Leftrightarrow K_2SO_4 \qquad K = 4.67 \text{ e+48} \qquad (15)$$

Sample: exp6 File: E78DAM DI

7-AUG-97 14:49

x10³
5.00.
4.50.
4.00.
3.50.
3.00.
2.50.
2.00.
1.50.
1.00.
0.50.

100.0
80.0
60.0
40.0
20.0

20.0   25.0   30.0   35.0   40.0   45.0   50.0   55.0   60.0

OID
22-1989

FIGURE 9

Sample: exp8 File: EX8CAN.DI

7-AUG-97 14:46

x10³
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50

ARCANITE, SYN 5-613

Reaction **(15)** has a very large equilibrium constant, signifying the reaction as written is thermodynamically favorable. Our synthetic gas does not have O_2 in the mixture, but any leak in the system will allow O_2 to diffuse from the atmosphere. Care must be taken to ensure that no leaks are present in the system. Future work will hopefully avoid the blockage of the gas flow channels so that the effectiveness of the aluminum plasma covered cell housings can be determined. Although reaction **(14)** appears thermodynamically possible, no elemental carbon has ever been formed, indicating this reaction is kinetically inhibited, and unlikely to be problematic.

Conclusion

This quarter's research demonstrated the effectiveness of the EMS at carbonate transport. The only difference from the previous quarter was the passivation technique. This quarter, cell housings were aluminum plasma covered. This was done in order to prevent a nonconductive path for excess molten carbonate to the stainless steel cell housings. H_2S removal experiments were unsuccessful, but these results are not due to the plasma covered cell housings.

Both experiments this quarter were halted because the cathode gas flow channel became clogged with a solid. In both cases, the cathode seal was strong during carbonate experiments but weakened with time once H_2S was added to the synthetic gas stream. Preliminary X-ray diffraction results of the material in the flow channels indicate that NiO and K_2SO_4 are present. The cathode fits flush into the electrode well, thus it expands when it converts from pure nickel to a nickel/nickel sulfide mixture. Since the electrode fits flush, the expansion will occur in the path of least resistance which is into the gas flow channels.

Projected Work

Work this quarter will focus on the cathode material. The expansion of the sulfurized nickel cathode into the gas flow channels must be inhibited such that desired H_2S reduction at the cathode can occur. The typical initial Ni cathode thickness is 0.12 mm. This quarter, the Ni

cathode will be sanded down to a thickness of 0.65-0.75 mm. Hopefully, the reduced initial thickness will prevent the cathode from creeping into the flow channels.

Once the problem of cathode creepage has been solved, the effectiveness of the plasma covered aluminum cell housings can be determined. Although these were utilized once this quarter, their capability was unresolved due to the electrode creepage. These cell housings will be utilized in all experimental runs this quarter.

Another alternative is to replace the cathode material from Ni to $LiCoO_2$, which has received attention in the Molten Carbonate Fuel Cell literature as a possible replacement for Ni as the cathode material. Many researchers[14-16] have been able to fabricate $LiCoO_2$ electrodes and successfully utilize these in the MCFC. This material has been just as effective as the NiO cathodes that are commonly used in MCFC's. However, the cathode in the EMS must be able to withstand sulfurizing conditions. Attempts at $LiCoO_2$ manufacture will be undertaken this quarter. In addition, other cobalt containing electrodes including Co and CoS_2 will also be fabricated. Analyzing these electrodes in a sulfurizing environment will then allow us to determine whether they can be employed in the EMS.

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