

Quarterly Progress Report
High Temperature Electrochemical Polishing of H₂S
from Coal Gasification Process Streams

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by

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Project Objectives

Coal may be used to generate electrical energy by any of several processes, most of which involve combustion or gasification. Combustion in a coal-fired boiler and power generation using a steam-cycle is the conventional conversion method; however total energy conversion efficiencies for this type of process are only slightly over 30%¹. Integration of a gas-cycle in the process (combined cycle) may increase the total conversion efficiency to 40%¹. Conversion processes based on gasification offer efficiencies above 50%¹.

H₂S is the predominant gaseous contaminant in raw coal gas. Coal depending on the type and area of extraction can contain up to 5 wt% sulfur, which is converted to gaseous H₂S during gasification. Problems arise due to the corrosive nature of H₂S on metal components contained in these cycles. Because of this, H₂S concentrations must be reduced to low levels corresponding to certain power applications. For example, an integrated coal gasification-combined cycle (IGCC) process producing electricity from coal at nearly 50% overall efficiency¹ incorporates gas turbines that cannot tolerate H₂S levels above 100 ppm. Coal gasification/Molten Carbonate Fuel-Cell(MCFC) systems, achieving conversion efficiencies around 60%², function properly only if H₂S is below 1 ppm.

An advanced process for the separation of hydrogen sulfide (H₂S) from coal gasification product streams through an electrochemical membrane is being developed using funds from this grant. H₂S is removed from the syn-gas stream, split into hydrogen, which enriches the exiting syn-gas, and sulfur, which is condensed from an inert sweep gas stream, Figure 1. The process allows removal of H₂S without cooling the gas stream and with negligible pressure loss through the separator. The process is made economically attractive by the lack of need for a Claus process for sulfur recovery. To this extent the project presents a novel concept for improving utilization of coal for more efficient power generation.

Past experiments using this concept dealt with identifying removal of 1-2% H₂S from gases containing only H₂S in N₂³, simulated natural gas^{4,5}, and simulated coal gas⁶. Data obtained from these experiments resulted in extended studies into electrode kinetics and

electrode stability in molten melts^{7,8,9}. The most recent experiments evaluated the polishing application (removal of H₂S below 10 ppm) using the Electrochemical Membrane Separator (EMS). H₂S removal efficiencies over 90% were achieved at these stringent conditions of low H₂S concentrations proving the technologies polishing capabilities.

Other goals include optimization of cell materials capable of improving cell performance. Once cell materials are defined, cell experiments determining maximum removal capabilities and current efficiencies will be conducted.

Also, a model theoretically describing the preferred reduction of H₂S, the transport of S²⁻, and the competing transport of CO₂ will be investigated. The model should identify the maximum current efficiency for H₂S removal, depending on variables such as flow rate, temperature, current application, and the total cell potential.

Introduction

The Electrochemical Membrane Separator (E.M.S.), the focus of experimental work, purges a fuel gas contaminated with H₂S. This is done by reducing the most electro-active species in the gas stream. In this case, H₂S is reduced by the following:



A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H₂ diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.



Processes to remove H₂S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H₂S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H₂S levels required by MCFC, there are several disadvantages inherent to these processes^{10,11}.

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds¹² or inefficient molten salt sorbent processes¹³ negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H₂S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H₂S removal and direct production of elemental

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

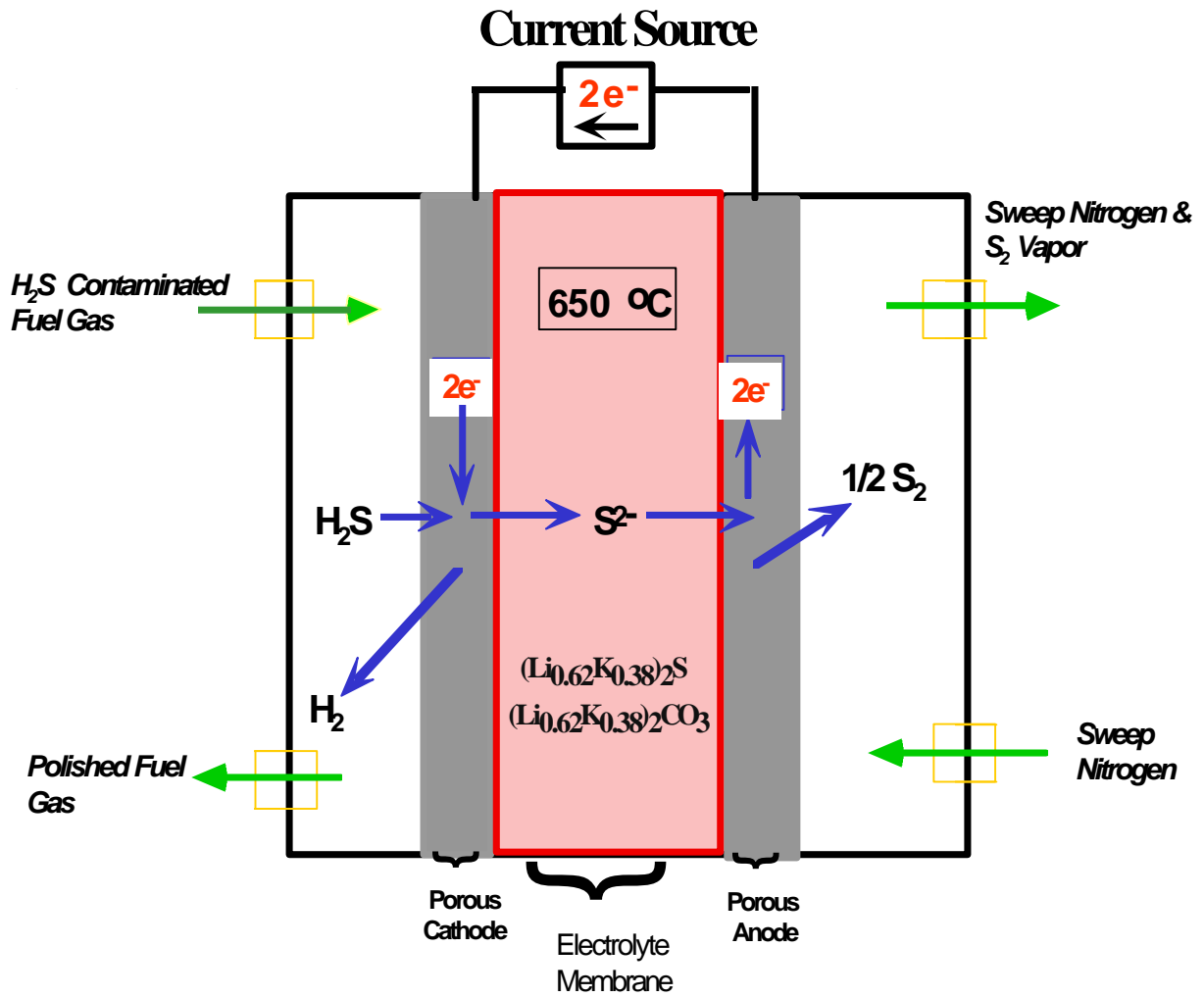


Figure 1. Single-Cell View of the Electrochemical Membrane Separator

Quarterly 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 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.

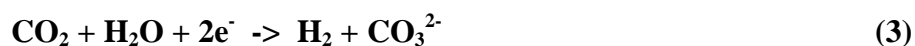
Two runs (Runs 35-36) were attempted this quarter, with successful CO₂ transport in both runs. The purpose of these experiments was: 1) test the electrochemical membrane separator's ability to concentrate CO₂; 2) test the electrochemical membrane separator's ability to remove H₂S; and 3) test stainless 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
35	580	Ni	Ni	Fabricated ZrO₂	Stainless steel (316)	(Li_{0.62}K_{0.38})₂CO₃
36	580	Ni	Ni	Fabricated ZrO₂	Stainless steel (316)	(Li_{0.62}K_{0.38})₂CO₃

Carbonate Transport

Before the addition of H₂S to the cell, it is necessary to evaluate the electrochemical membrane separator's ability to transport carbonate across the cell. This is accomplished by CO₂ removal from the process gas (cathode coal syn-gas) (3):



and anode CO₂ evolution due to carbonate oxidation (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 #35

The removal cell was tested for CO₂ removal at the cathode and CO₂ 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 around 150 cc/min while the cathode outlet flow rate was around 120 cc/min. The anode inlet and outlet values were 154 and 50 cc/min, respectively. For CO₂ removal experiments, the cathode inlet gas concentration after the water-gas shift reaction was 4.32% CO₂, 3.08% CO, 7.68 H₂O, 17.72% H₂, and balance N₂. A current step experiment was employed to determine the CO₂ removal and cell potentials versus increasing applied currents. CO₂ removal data is displayed in Figure 2, and cell potential data is illustrated in Figure 3. Current step experiments were also performed for CO₂ production at the anode. The cathode inlet gas concentration after the water-gas shift reaction for this experiment was 5.98% CO₂, 2.52% CO, 6.52% H₂O, 8.88% H₂, and balance N₂. CO₂ production data is shown in Figure 4 while cell potential data is given in Figure 5.

Run #36

The removal cell was tested for CO₂ removal at the cathode, however, poor anode seals inhibited collection of CO₂ production data at the anode. Poor response times made it too difficult to measure anode outlet CO₂. CO₂ removal experiments were run twice for reproducibility at two different flow rates. At a cathode inlet flow rate of 106 cc/min and cathode outlet flow rate of 90 cc/min, the gas concentrations entering the removal cell were 4.29% CO₂, 3.06% CO, 7.80% H₂O, 18.08% H₂, and balance N₂. CO₂ removal and cell potentials were recorded versus applied current, as shown in Figures 6 and 7, respectively. Next, the cathode inlet flow rate was increased to 184 cc/min with a corresponding cathode outlet of 168 cc/min. The gas concentrations entering the cell for this case were 3.27% CO₂, 1.53% CO, 8.09% H₂O, 12.31% H₂, and balance N₂. Figures 8 and 9 illustrate CO₂ removal and cell potentials versus applied current.

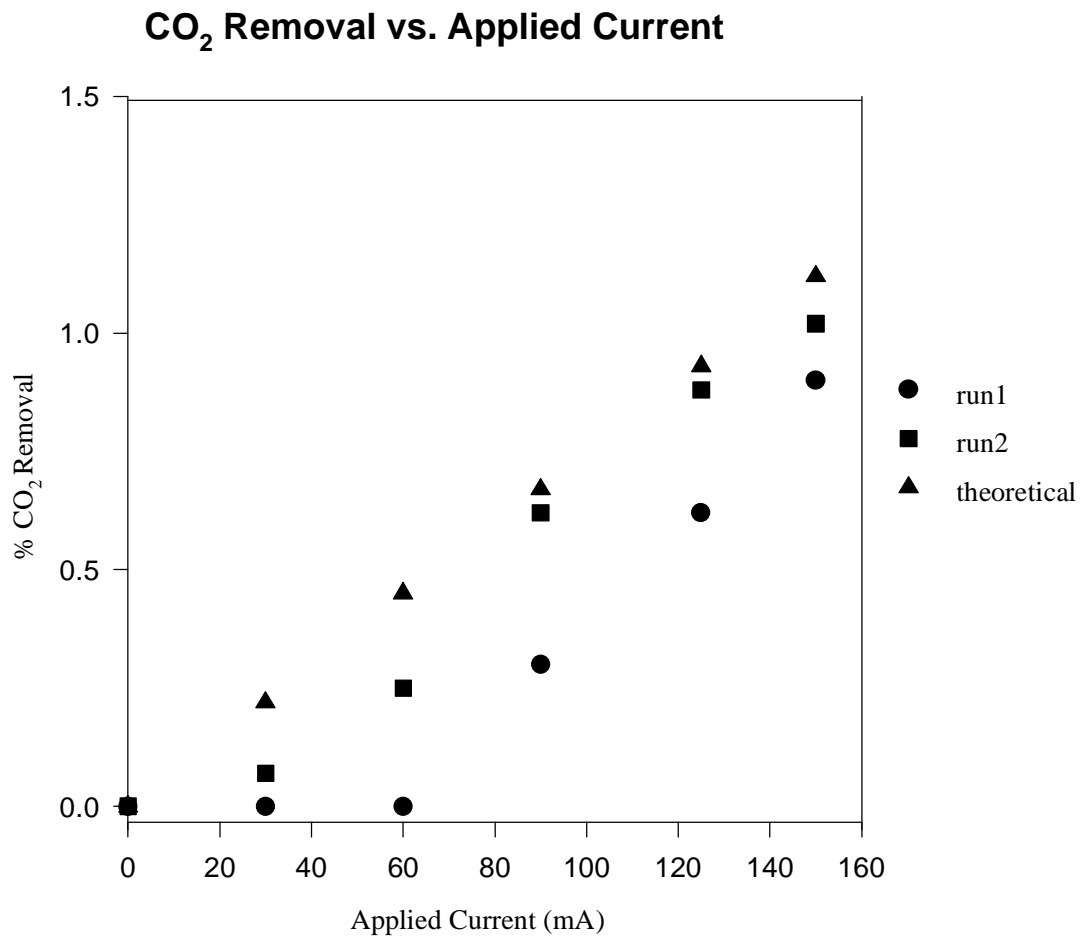


Figure 2. Run #35. Carbonate Transport - CO₂ Removal vs. Applied Potential

Cell Potentials vs. Applied Current

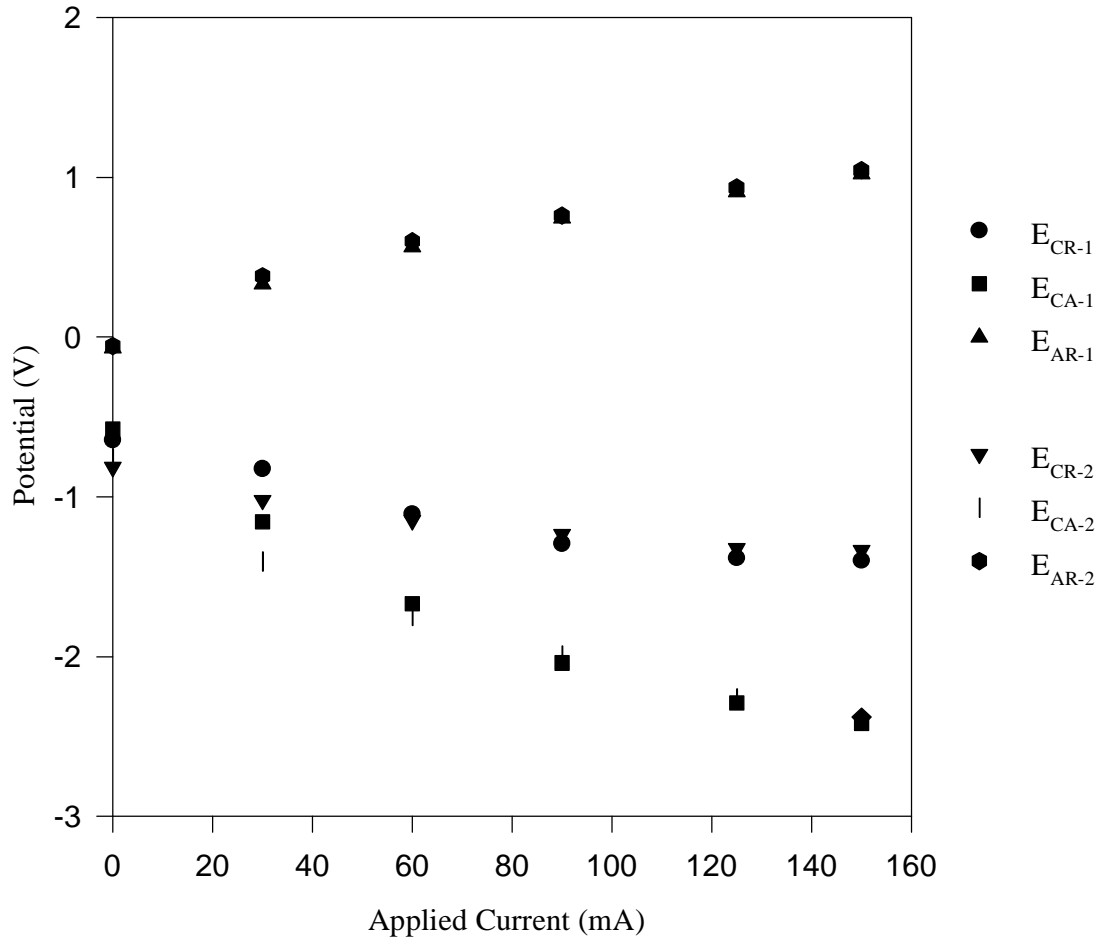


Figure 3. Run #35. Carbonate Transport - Cell Potential vs. Applied Current

Anode CO₂ Production vs. Applied Current

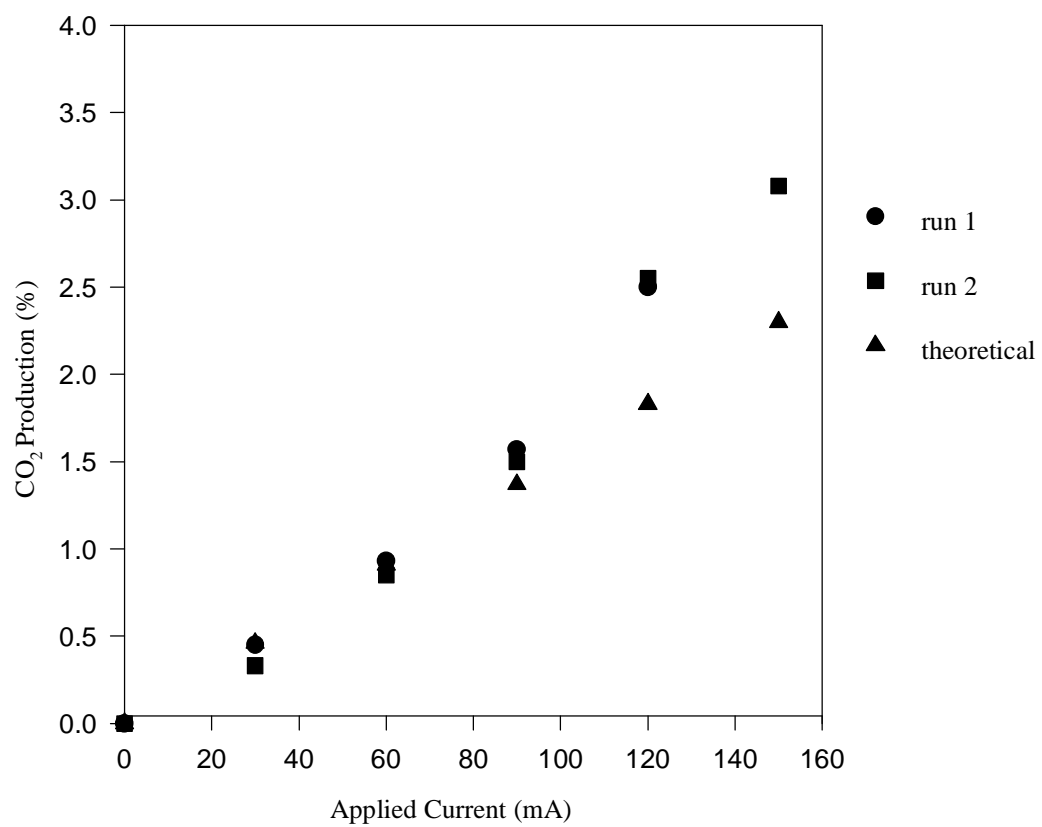


Figure 4. Run #35. Carbonate Transport - CO₂ Production vs. Applied Current

Cell Potentials vs. Applied Current

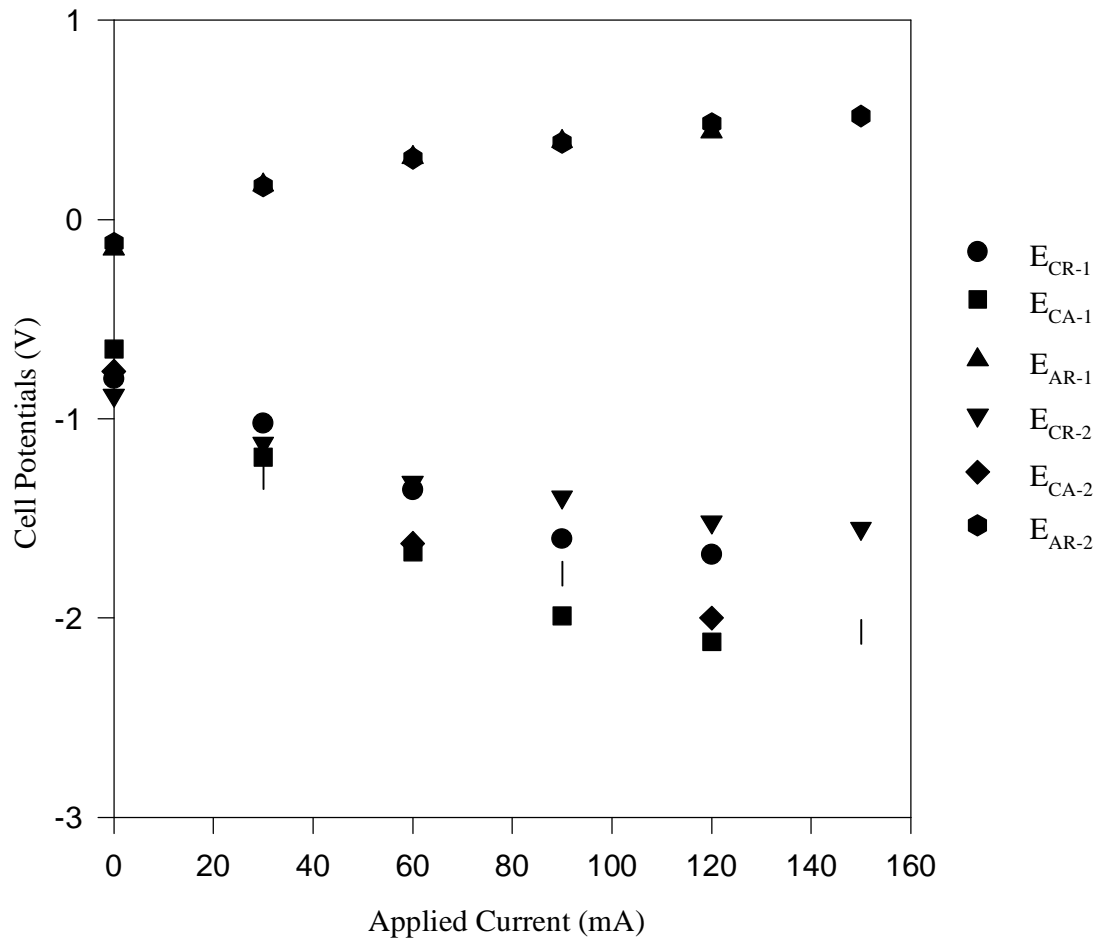


Figure 5. Run #35. Carbonate Transport - Cell Potential vs. Applied Current

CO₂ Removal vs. Applied Current

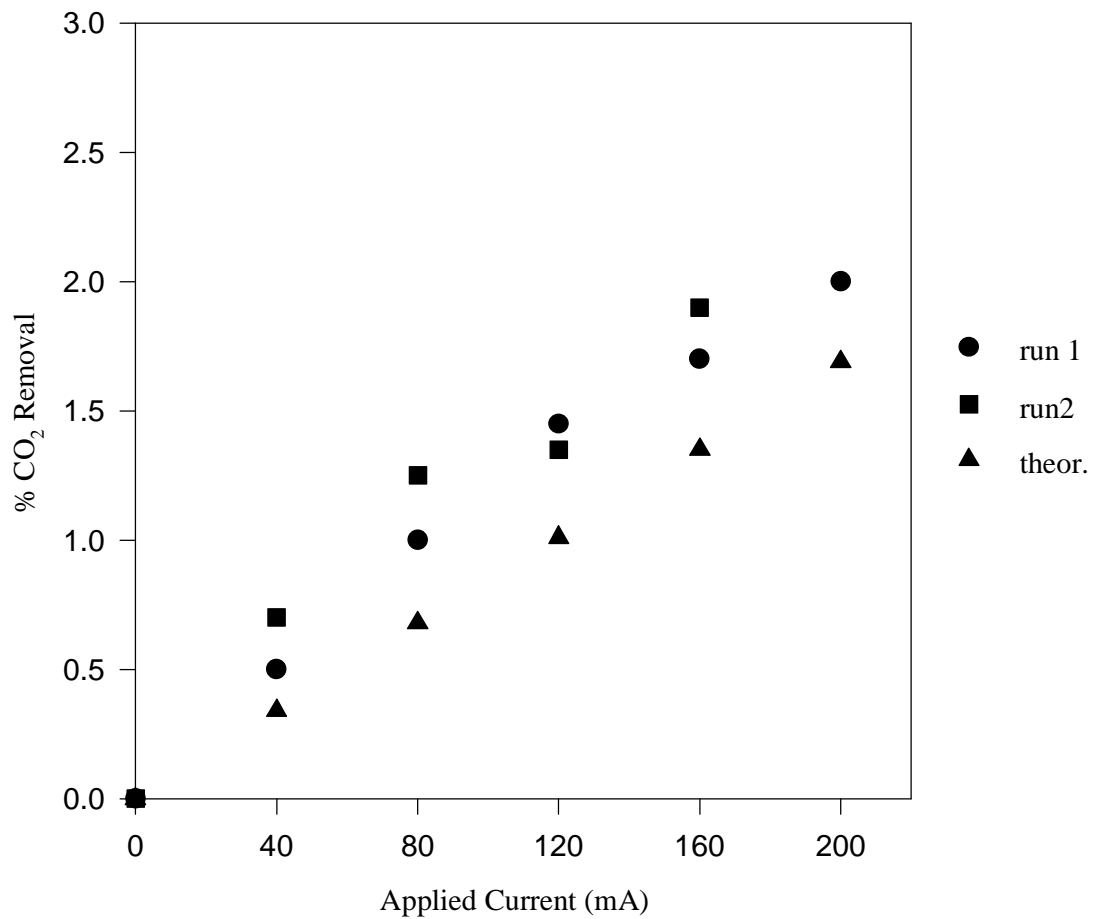


Figure 6. Run #36. Carbonate Transport - CO₂ Removal vs. Applied Potential

Cell Potentials vs. Applied Current

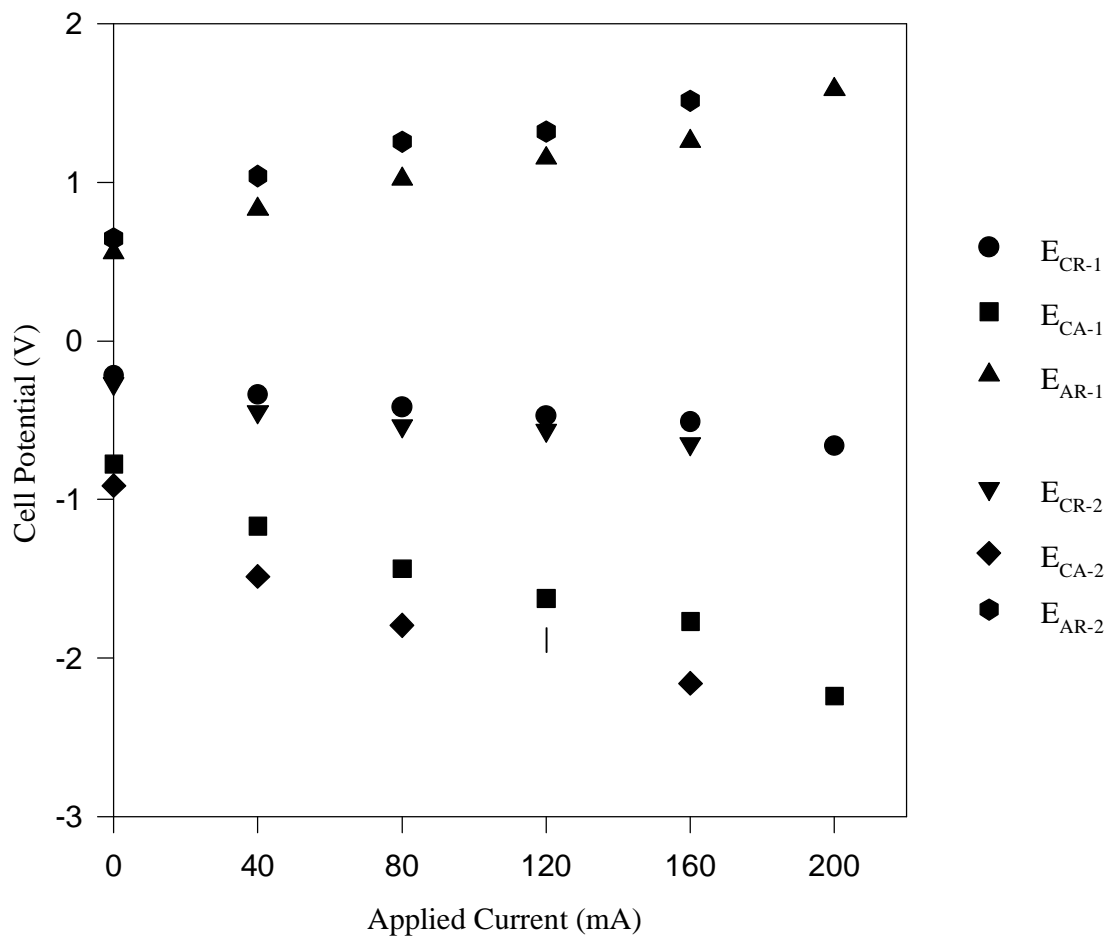


Figure 7. Run #36. Carbonate Transport - Cell Potential vs. Applied Current

CO₂ Removal vs. Applied Current

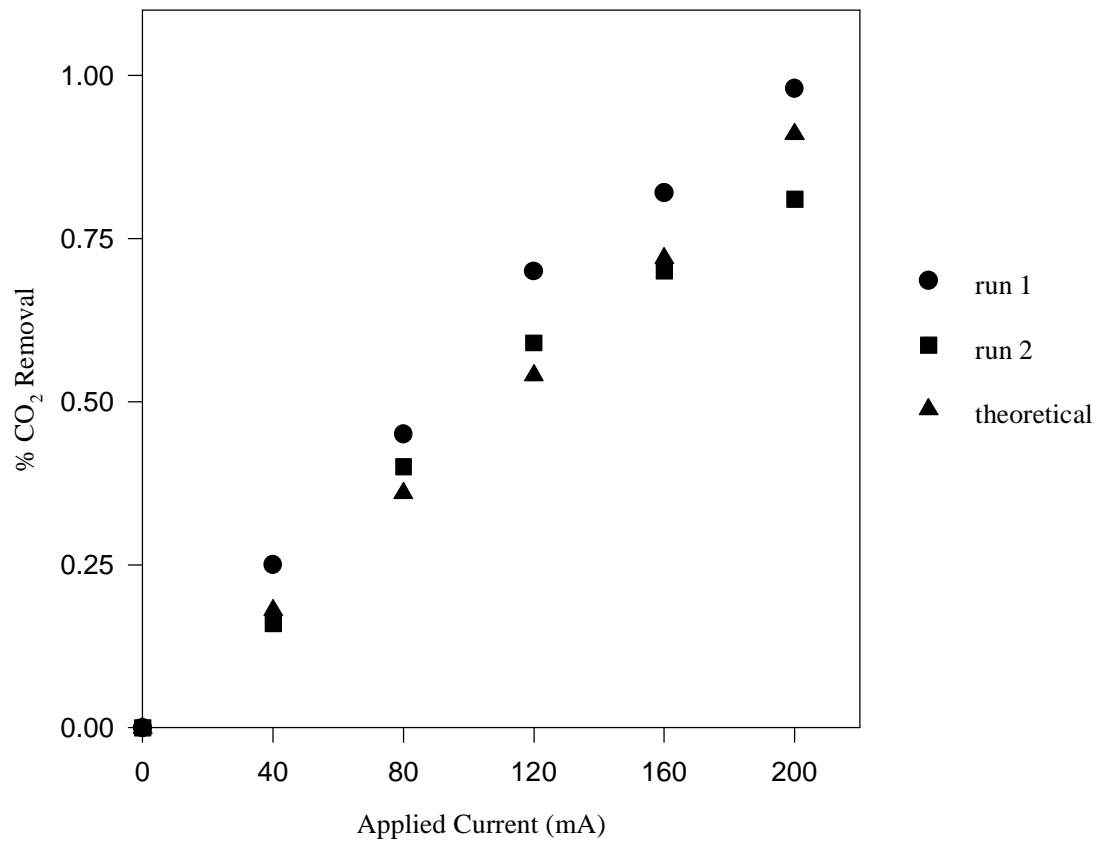


Figure 8. Run #36. Carbonate Transport - CO₂ Removal vs. Applied Current

Cell Potential vs. Applied Current

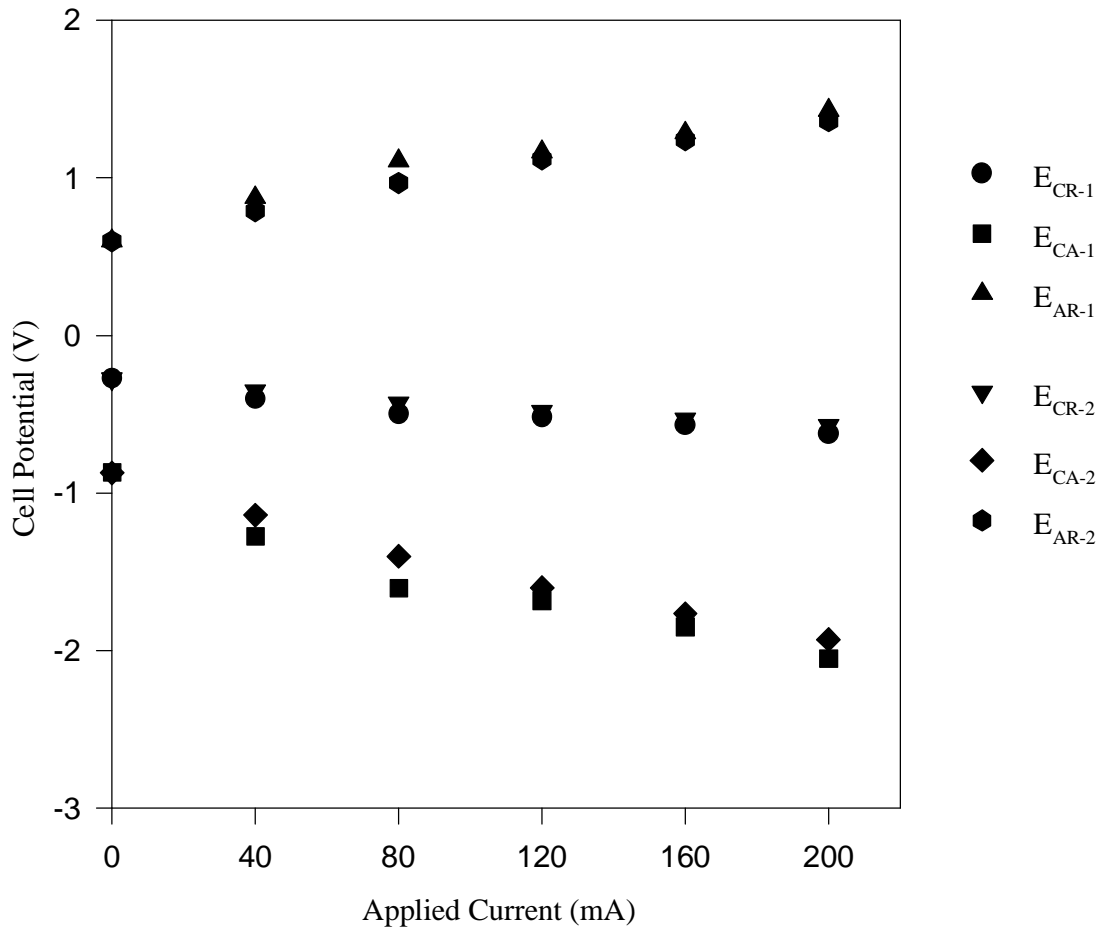


Figure 9. Run #36. Carbonate Transport - Cell Potential vs. Applied Current

Both runs this quarter were proficient at carbonate transport as evidenced by Figures 2 - 9. Excellent agreement with expected performance was observed, and the required cell voltages were within anticipated bounds. There is a discrepancy between Runs #35 and #36 as far as cell potentials are concerned. While cross cell (cathode-anode) potentials between the two experiments agreed, Run #36 yielded cathode-reference and anode-reference potentials that did not seem consistent with past results. This difference can be attributed to a problem with the reference electrode. The gold reference electrode more than likely was not in contact with the molten carbonate impregnated zirconia tile but rather was touching the stainless steel cell housing. Further manipulation of the cell set-up solved this problem for later experiments. However, cross cell potentials, which do not depend on the reference electrode, were within expected bounds necessary for carbonate transport at these conditions.

Removal of H₂S from Sour Coal Gas

Once carbonate transport across the cell was demonstrated, H₂S was added to the process syn-gas. The process gas was equilibrated by the following two reactions:



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:



which creates a conversion of carbonate ions to sulfide ions depending on the concentration of H₂S in contact with the electrolyte. Typically, at least twenty-four hours is necessary for this reaction to reach equilibrium.

Run #35

Attempts at H₂S removal were unsuccessful for Run #35. Ohmic losses were typically around 5 ohms throughout the experiment which suggested resistance problems somewhere in the system. (Li/K)₂CO₃ was added frequently to the membrane to try to reduce this ohmic loss. The excess carbonate in contact with exposed stainless steel may be one reason for poor removals. If oxygen and carbon dioxide contact exposed stainless steel at the cathodic cell 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 H₂S removal.

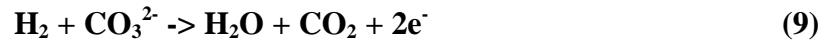
Consequently, current efficiency for the process will be vastly reduced. The run was eventually stopped after 17 days (408 hrs) due to excessive internal resistance.

Run #36

Attempts at H₂S removal were also unsuccessful for Run #36. A crack in the zirconia membrane which was found during the experiment was the cause for these poor results. As a result, hydrogen can cross over from the cathode side to the anode side, where two reactions are possible at the anode. The first is the oxidation of hydrogen and the sulfide ion to hydrogen sulfide by:



The second is the oxidation of hydrogen and carbonate to water and carbon dioxide by:



Reaction (8) excludes the possibility of sulfur condensation (2). Reaction (9) is also detrimental to cell performance since carbonate is consumed at the anode, thereby inducing carbonate production rather than sulfide production at the cathode. Low cross-cell potentials while the cell was under medium current loads were a good indicator of hydrogen crossover.

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 H₂S concentrations). H₂S current efficiency is calculated by:

$$\eta_{\text{H}_2\text{S}} = \frac{\% \text{H}_2\text{S Removal}_{\text{actual}}}{\% \text{H}_2\text{S Removal}_{\text{theoretical}}} \quad \mathbf{(10)}$$

which represents the ratio of H₂S actually removed to the amount that should be removed at a specified applied current. The following equation calculates the amount of H₂S removed from the process syn-gas:

$$\% \text{ H}_2\text{S Removal} = \frac{\text{Inlet H}_2\text{S} - \text{Outlet H}_2\text{S}_{(I_{\text{app}})}}{\text{Inlet H}_2\text{S}} \times 100 \quad (11)$$

Both runs this quarter were not proficient at H₂S removal. As stated earlier, the primary problem with stainless steel cell housings is parasitic reactions between excess external carbonate and exposed stainless steel. Passivating the stainless steel with aluminum foil and paint doesn't seem to protect the stainless steel from carbonate attack. Any crack in the aluminum layer is sufficient for carbonate creeping and ultimate cell failure.

Another important result obtained this quarter involved electrolyte maintenance and consumption. In past experiments with MACOR ceramic cell housings, excessive amounts of carbonate were necessary to ensure wet seal formation. SiO₂ and Al₂O₃, the main components of MACOR, are highly reactive with Li₂CO₃, 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):



However, stainless steel cell housings require less maintenance because the electrolyte is not dramatically consumed by the stainless steel cell housings. However, as previously stated, any excess external carbonate decreases cell performance.

Conclusion

The Fossil Energy Advanced Research Program requires high temperature separations to remove environmental contaminants from post-combustion flue gases as well as pre-combustion process gases. This project is aimed at the latter: the removal of hydrogen sulfide from coal gas at 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.

Projected Work

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, a successful method of wet seal passivation will need to be developed. Plasma Coatings, Inc. has applied an aluminum coating to our cell housings. These aluminized cell housings will be tested this quarter for their effectiveness.

References

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