Quarterly Progress Report

High Temperature Electrochemical Polishing of H2S

from Coal Gasification Process Streams

Grant DE-FG22-94-PC94207

October 1, 1994 - December 31, 1994

by

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Objective

A high temperature electrochemical cell capable of polishing hydrogen sulfide from fuel gas streams is being perfected. The operation, to be used in compliance with high efficiency energy conversion systems, takes advantage of an electrochemical potential gradient instead of typical separation techniques to separate hydrogen sulfide from the fuel gas stream leaving hydrogen to enrich the exiting gases. Vaporous sulfur is the by-product carried downstream by a separate inert sweep gas and condensed.

Work continued this quarter to improve experimental conditions (laboratory & equipment enhancement). The oven containing the Electrochemical Membrane Separator(E.M.S.) is the main focus of improvement readjusting spatial requirements conforming to the controlled environmental emissions equipment while creating a controlled atmosphere gauntlet to unfavorable reactions with electrolytic species.

Manufacturing of yttria-stabilized zirconia matrices was the primary focus of laboratory experimentation while full-cell testing is not possible.

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°C - 1000°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[1,2].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[3] or inefficient molten salt sorbent processes[4] 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.
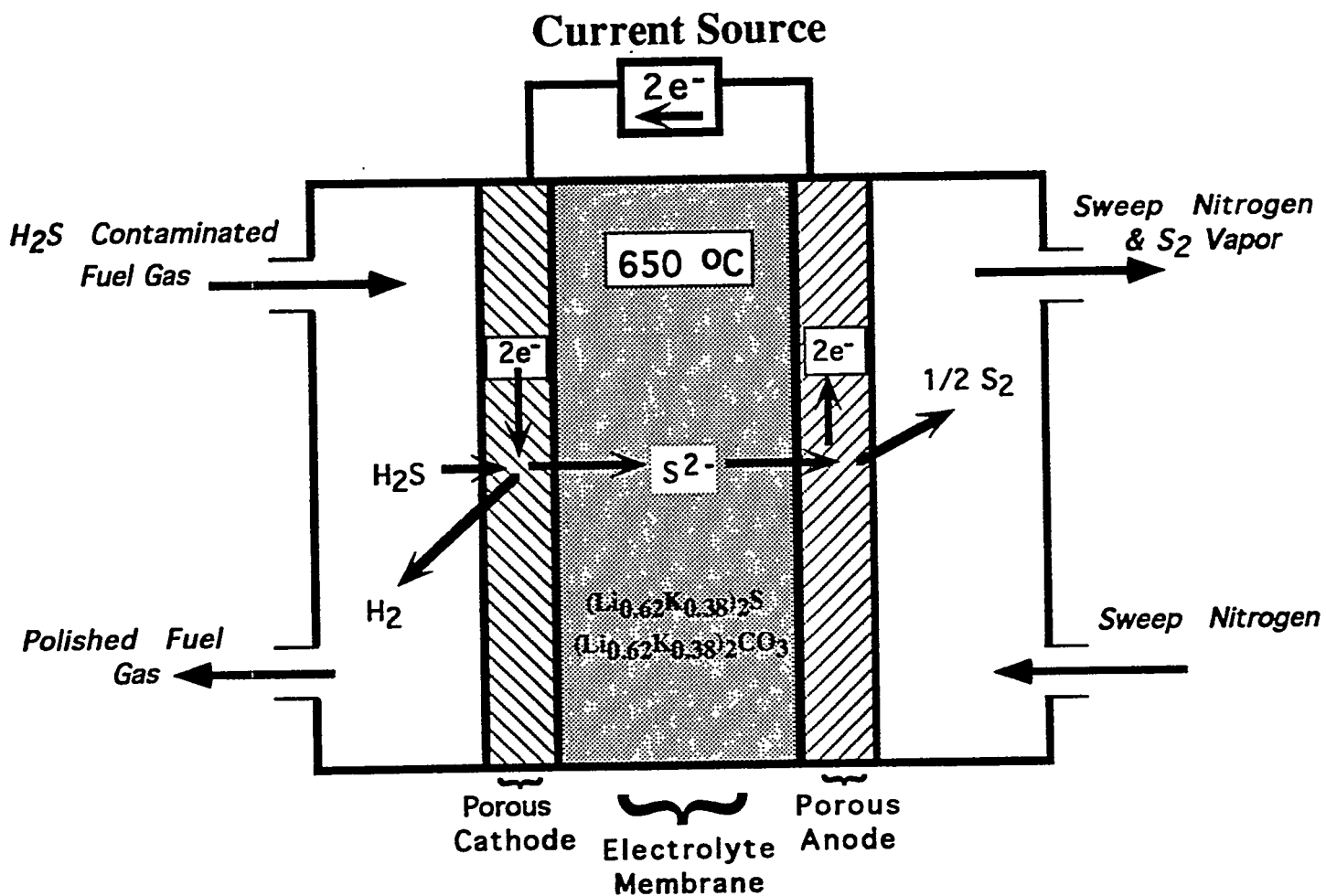
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Figure 1. Conceptual Electrochemical Membrane Separator

Electrolyte Management

Electrolyte losses associated with molten carbonate salts is a consistent problem; the mechanism of such losses is not fully understood with CO_2 evolution and reactions with system materials comprising possible mechanisms. Proposed mechanisms for the loss of electrolyte in the E.M.S. are:
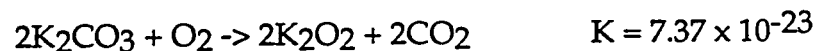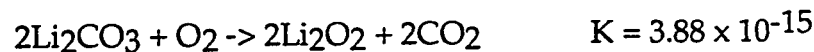
1) Material reactions upon process-gas seal formation:

$$2Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad K = 2.81 \times 10^{78}$$

$$Al_2O_3 + Li_2CO_3 \rightarrow 2LiAlO_2 + CO_2 \qquad K = 154$$

2) Evaporation at the anode due to a deficiency of CO_2:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \qquad K = 2.51 \times 10^{-5}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad K = 5.31 \times 10^{-15}$$

3) Evaporation into the surroundings:

$$2Li_2CO_3 + O_2 \rightarrow 2Li_2O_2 + 2CO_2 \qquad K = 3.88 \times 10^{-15}$$

$$2K_2CO_3 + O_2 \rightarrow 2K_2O_2 + 2CO_2 \qquad K = 7.37 \times 10^{-23}$$

with lithium carbonate, comprising 62 mole% electrolyte, being the least stable (larger K).

Quantitative evaporation studies were performed duplicating full-cell conditions[7]. Mechanism (2) & (3) were investigated with evaporation by mechanism (3) entailing the predominant amount of electrolytic losses; 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li_2O_2 & Li_2O by:

$$Li_2O_2 \rightarrow Li_2O + 1/2\ O_2 \qquad \Delta G = -41.54\ KJ/mol \qquad K = 225$$

Matrices & Cathode Materials

From results obtained in previous studies, the path to a commercial process is now clear. The primary unresolved components are the cathode and membrane. The cathode must be chemically and mechanically stable in the sulfide/carbonate/hydrogen sulfide environment, and be electronically conductive at 650°C. Lithium-doped NiO has already proven effective in polishing applications; however, the Ni phase transition to liquid $Ni_{3+x}S_2$ when contacting gas with >100 ppm H_2S, requires alternate cathode materials. Co, which converts to Co_8S_9 in-situ, has recently been shown[8], using Scanning Electron Microscopy (SEM), to be morphologically stable in full cell testing with 100 ppm H_2S. The microscopic view revealed adequate porosity and pore size were maintained in the harsh cell environment. Production of cobalt electrodes in the laboratory is ongoing; consistently manufacturing these electrodes with a pore size and arrangement comparable to the Ni electrodes has been accomplished although current attempts have been less successful. Dry pressing the cobalt powder (d_p = 2 microns) with ~ 40wt% binder (methylethlycellulose) stabilized the metal in disk form to accomplish the burnout and sintering steps. Stress fractures often occur due to the non-uniform release of binder and apparent temperature inequality within the furnace. Adjustments dealing with binder content and temperature cycling will be the impetus of future membrane production.

Several membranes have been utilized in the EMS since its genesis. MCFC tiles used by Weaver[9], sulfided in-situ, resulted in micro-crack development; however MCFC tile technology will be used in scale-up applications of electrochemical separations, due to success in real-time MCFC. The technology has been refined, but replication in our laboratory is expensive and inefficient for bench-scale testing. Tape-cast membranes of MgO were somewhat more efficient

but inconsistent laboratory replication proved detrimental[10]. The most promising membranes for bench-scale experiments have been manufactured zirconia membranes purchased from Zircar Corporation. Polishing of the gasification streams with these membranes confirms their usefulness; however micro-cracks are still evident from SEM analysis[8] and must be controlled. Alternative laboratory-densified membranes with fiber mats replicating the preprocessed membranes from Zircar Corporation are also being investigated. Positive removal results (over 90% H_2S removal) have been obtained from full-cell testing with these membranes[11]; however, more work is needed to improve the manufacturing techniques.

Continued cell testing will be done utilizing the purchased zirconia membranes along with laboratory-densified zirconia membranes containing zirconia fibers. Laboratory-densified membranes which have proven successful in the past[11] will be tested further. One reason for this is financial. Conventional purchased zirconia membranes cost approximately $ 150.00 per membrane (7.62 cm (3 in) x 7.62 cm (3 in) x 0.063 cm (0.025 in)), compared to $ 10.00 per membrane (7.62 cm (3 in) x 7.62 cm (3 in) x 0.092 cm (0.036 in)) for self-produced membranes.

Laboratory-densified membranes consist of two knit zirconia mats (7.62 cm (3 in) x 7.62 cm (3 in) x 0.0762 cm (0.030 in) purchased from Zircar Corporation. The initial porosity of the mats is approximately 85%. The objective is to fill (rigidize) the knit to a porosity of approximately 65%, which is essential, according to past experiments, in order to operate efficiently[12]. The material used to rigidize the membrane is an aqueous suspension of sub-micron zirconia particles. The combination of mats are submerged in a container of rigidizer, then placed under a vacuum to evacuate the pores. Once pores are relieved of gaseous fillers, the rigidizer infiltrates the pores.

In previous manufacturing, after the infiltration step, the membrane(cloth plus aqueous suspension of sub-micron zirconia particles) was placed on a flat Teflon surface, covered with weighing paper, and constrained from curling by a metal mesh. More recent techniques relied on the wet matrices being placed atop a thin wire bent into a square configuration and attached to a speed controlled rotor; the rotating of the free body should allow a faster more uniformly dry body(matrices) compared to previous techniques.

Once dry, the membrane is analyzed for void fraction and reprocessed if found unacceptable. In the cell, the 65% porous membrane with infiltrated electrolyte prevents cross-over of harmful amounts of hydrogen and allows a low-resistance path for sulfide diffusion and migration. In order to reach such porosity, the method of rigidization must be performed several times, each reducing the porosity by approximately 10%. Every cycle requires drying, placing mechanical stress on the membrane. The fabricated membrane meeting the 65 % porosity performed adequately in full- cell testing[11].

Thus far improvements in laboratory-densified manufacturing techniques consist of: i) Adding zirconia rigidizer into a knit-zirconia matrix under an extended vacuum (>5 min.). This drastically decreases porosity , reducing the number of steps required to fabricate the membrane. ii) Suspending the mat during drying to increase diffusion since both faces of the mat are exposed, decreasing solvent diffusion distance and iii) vertically rotating the suspended body to uniformily distribute the suspension of zirconia particles throughout the membrane.

Dry pressing of sub-micron zirconia particles with a percentage of binding material coresponding to desiredporosity has also been under taken. S.E.M analysis as well as crystal structure given by X-ray Diffraction will identify the morphology of these membranes, illuminating this technique for future use.

7

Alternate matrix materials also have been investigated including microporous glass membranes with porosities of .2 and .02 microns and a thickness of 60 microns exceeding the probable limit of the bench-scale E.M.S. set-up provisions; thus far, these membranes have shown chemical instabilities with the electrolytic melt.

Membrane Thickness

Once effective membranes have been developed, other variables such as thickness of the membrane will be investigated in high-flow rate experiments in order to lower the resistance to sulfide migration. The rate of mass transport corresponding to sulfide migration through the membrane is given by:

$$i = \frac{nFD\ (C_c - C_a)}{\delta} \tag{3}$$

where n is the charge number, F is Faraday's constant, D is diffusion coefficient, δ is the membrane thickness, and C is the concentration of sulfide species at the cathode and anode. At high process-gas flow rates, mass transfer from the gas is equivalent to the limit of diffusion through the membrane, given by:

$$i_l = \frac{nFD\ C_c}{\delta} \tag{4}$$

The limiting current is a measure of the maximum rate at which sulfide can be transported through the membrane, and occurs when $C_a = 0$. Equation (4) reveals that a thinner membrane creates a higher limiting current for the transport of sulfide. This is extremely important at high flow rates to insure diffusion from the bulk process-gas is the only limiting factor.

Optimization of membrane thickness and porosity will be investigated at high flow rates during full-cell testing using a singular laboratory-densified membrane, thickness ~0.38 mm (0.015 in).

Summary

Controlled atmospheric conditions inside the oven, around the E.M.S. should alleviate the majority of electrolytic losses. A high partial pressure of CO_2 will cause the equilibrium of mechanism 2 & mechanism 3 to shift to the left, reducing the possibility of unfavorable electrolytic conversion. Reactions involving electrochemical cell materials with electrolytic species should only account for a fraction of losses and stabilize upon conversion to an inert component as in mechanism 1.

Upon completion of equipment set-up, cell experimentation will focus on removal of 1000 ppm & 100 ppm H_2S from synthetic coal gas streams. Material issues such as membrane & cathode morphology along with cell housings of stainless steel will be of importance.

Improvements in membrane manufacturing techniques will be the main focus for next quarter.

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