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Quarterly Progress Report:
High Temperature Electrochemical Separation
Of H₂S from Coal Gasification
Process Streams
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by

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Objective

A method of polishing coal synthesis gas by an electrochemical membrane operation is being perfected. The operation takes advantage of an electrochemical potential gradient rather than conventional techniques, separating the H_2S from the coal gas stream, leaving only H_2 to enrich the exiting fuel gases. Sulfur is the by-product that is carried away by a separate inert sweep gas and condensed downstream. The technology is attractive due to simplicity as well as economics when compared to alternatives.

Experiments this quarter focused on removing 100 ppm inlet H_2S , utilizing laboratory fabricated cobalt cathodes.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid, electron acceptor, will be reduced. In this case H₂S is favored, resulting in the following:

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

The vaporous sulfur is condensed downstream.

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^{1,2}.

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds³ or inefficient molten salt sorbent processes⁴ 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. Conceptual Electrochemical Membrane Separator

Experimental Results

Two experiments (Run #17 & #18) examining the removal capability of the EMS with cobalt cathode were performed this quarter. The focus dealt with H₂S removal as well as impeding hydrogen cross-over from the process gas side (cathode) of the membrane to the sweep gas side (anode).

Gas cross-over Management

The cross-over of bulk process gases to the opposite electrode reduces cell performance. Current bench-scale membranes provide a complete barrier to bulk gas cross-over, although singular diffusion of hydrogen from the process gas remains a concern. An approach used by Molten Carbonate Fuel Cell (MCFC) technologists to reduce gas cross-over and reinforce the electrolyte matrix utilizes a *bubble pressure barrier* (bpb)^{5,6}, which consists of a mid-size pore region (relative to the membrane & electrode) between the membrane and the anode or cathode; a schematic representation is shown in Figure 2. If micro-cracks occur in the membrane from processing or thermal strains, the bpb provides an electrolyte-filled barrier to reinforce the membrane against gas cross-over. The bpb must have a uniform pore structure with intermediate pore size corresponding to existing membranes and electrodes to insure complete electrolyte entrainment; this provides a low resistance path for ion migration and diffusion as well as strong capillary forces to deter cross-over. A bubble barrier was incorporated into the EMS system for experiment #18 with minor success; increased amounts of electrolyte to infiltrate the bpb created a greater importance in retention to maintain an ionic pathway between electrodes.

Figure 2. Bubble Barrier Set-up

Electrolyte Management

Loss of electrolyte is a consistent problem with the use of molten salt electrolytes; the mechanism of such losses is not well understood with electrolyte evaporation and alternate reactions involving system materials. Proposed mechanisms for the loss of electrolyte in the EMS are:

- 1) Material reactions upon process-gas seal formation:

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

- 3) Evaporation into the surroundings:

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

Quantitative evaporation studies were performed duplicating full-cell conditions. Three electrolyte filled crucibles placed in a controlled atmosphere furnace containing only nitrogen (similar to but less stringent than full-cell anode conditions) provided a large gradient for the evolution of CO_2 ; five days of testing released on average 1.6 grams of electrolyte. The crucibles were then placed in a conventional oven to duplicate evaporation by mechanism (3); 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li_2O_2 & Li_2O by:

Absolute verification of Li_2O by X-ray diffraction could not be accomplished due to sample contamination, but future membrane analysis by x-ray should provide

conclusive evidence of Li_2O formation; Li_2O_2 is not in the x-ray diffraction software package so uncertainty exist in verification of this molecule.

Run#17

Cell materials consisted of a cobalt cathode (80% porous), Ni anode (85% porous), a fabricated zirconia membrane (69% porous), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(\text{Li/K})_2\text{CO}_3$ (5 grams) corresponding to the void volume in the zirconia membrane. Electrode materials were verified by x-ray diffraction.

Initial examination of the cobalt-cathode electrochemical membrane separator (EMS), produced stoichiometric transport of CO_3^{2-} ; however, material problems (i.e. cracking of ceramic housings and loss of flow-tube seals), prompted immediate shut-down after 24 hours of operation.

Run#18

Cell materials consisted of a cobalt cathode (80% porous), Ni-mesh anode (95% porous), a fabricated zirconia membrane (69% porous) coupled with a bpb (purchased zirconia membrane (66% porous)), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(\text{Li/K})_2\text{CO}_3$ (14 grams) corresponding to the void volume in the two zirconia matrices. Electrode materials were verified by x-ray diffraction.

Problems arose early in the start-up process after the electrolyte converted to the molten state. Consistent addition of electrolyte provided only temporary solutions to the problem of high cross-cell resistance from loss of electrolyte. A consistent ionic pathway between electrodes was never established negating efforts to transport carbonate; therefore, H_2S was never introduced into the cell. Shut-down occurred after 168 hours.

Summary

The cobalt cathode used in the EMS proved stable and efficient. Removal of H₂S was deterred by extensive electrolyte loss discussed earlier. Mechanism 1 is the least imposing upon complete conversion of Al to LiAlO₂ (time ~ 200 hrs). Mechanism 2 representing full-cell anode conditions exhibited minor evaporation by natural convection of electrolyte in crucible tests, but should increase considerably in real-time experiments due to the convective flow of N₂ over the anode pores. The solution of CO₂ evolution at the anode involves a mixture of CO₂ & N₂ (CO₂ = cathodic concentration) reducing the driving force for electrolyte loss. Mechanism 3 creates the greatest problem due atmospheric evaporation. Reducing the surface area exposed to the atmosphere is the only solution, a method of which is still under development.

Planned Work for Next Quarter

The main focus will be on H₂S current efficiency using a fabricated zirconia membrane and bubble barrier with 100 ppmv H₂S fuel gas; hopefully, preventing alternate reactions due to hydrogen cross-over. Implementation of CO₂ with the anode gas should alleviate anodic electrolyte evaporation.

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