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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 operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes poisonous H_2S from the coal gas stream leaving only H_2 to enrich the exiting flue gases. Sulfur is the by-product which is carried away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Current experiments are focusing on production of selective membranes made of zirconia and improving cell housing seals using Aluminum foil gaskets.

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 H_2S is favored, resulting in the following:

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

The vaporous sulfur is condensed downstream.

Experimental Results

Four experiments were performed this quarter. The main focus of these experiments dealt with incorporating the rigidized zirconia membranes produced in our laboratory. A detailed description is given in subsequent paragraphs. Other priorities involved material issues relevant to the longevity of the cell housings, cathode stability, and process friendly sealants.

Figure 1 Electrochemical Fuel Gas Desulfurization Cell

Self-produced Membranes

The driving force behind self-preparing membranes is predominantly financial. Conventional rigidized membranes similar to self-developed membranes cost approximately \$150.00 per tile (3" x 3" x 0.025"), compared to \$10.00 per tile (3" x 3" x .036") for self-produced membranes. The major problem with using the laboratory fabricated membranes arises in the consistency of production. An essential porosity of around 65% must be obtained, according to past experiments, in order to operate the cell efficiently. In the cell environ, the 65% porous membrane, with electrolyte infiltrated, prevents cross-over of harmful amounts of hydrogen and allows a low resistance path for ion diffusion and migration. In order to reach such porosities by laboratory fabrication, the method of rigidization must be performed several times, each reducing the porosity by 10%. Every cycle of rigidization requires drying; thus, putting several mechanical strains on the membrane. All the self-produced membranes that met the 65% porosity perform adequately, but contained micro-cracks from the mechanical strain of rigidization. These micro-cracks allow small amounts of hydrogen to cross the membrane, reducing current efficiency by creating alternate reactions at the anode. The proposed solution to hydrogen cross-over involves application of back pressure from the cathode side of the membrane,

strategically similar to the operation of Molten Carbonate Fuel Cells.

Membrane Preparation

The membrane consist of two thin-weaved zirconia mats (3" x 3" x 0.030"). The initial porosity of the mats falls within the 85% range. The objective is to fill (rigidize) the weave to a porosity of approximately 65%. The material used to rigidize the membrane is an aqueous suspension of sub-micron zirconia particles. The aforementioned mats are submerged in a container full of rigidizer, then placed under a vacuum to evacuate the pores. Once the pores are relieved of gaseous fillers, the rigidizer infiltrates the pores. After infiltration, the membrane is placed on a flat Teflon surface, covered with weighing paper, and constrained from curling by a metal mesh. Once dry the membrane is analyzed for void fraction and re-rigidized if found unacceptable.

Run #11

Stainless steel housed the experiment that focused mainly on removal efficiency. The stainless steel were initially preheated to 600 °C with a coating of 29 wt% aluminum paint. The Al paint was converted to alumina ex-situ which on contact with lithium carbonate in the electrolyte in-situ forms lithium aluminate at high temperatures. Ni electrodes converted in-situ to NiO

provided sites for the electronation of H_2S . The membrane used was a conventional rigid zirconia membrane, 65% porous, purchased from Zircar.

Carbonate transport, which is the initial test of cell efficiency never reached stoichiometry due to reaction of aluminum paint with the electrolyte. The previous reaction formed strong seals but severely deteriorated ability for efficient removal. Other problems such as clogged flow tubes and loss of electrical contact ultimately terminated the experiment. The cell was operable for 60 hours.

Run #12

Housing materials for this experiment consisted of machineable ceramic(MACOR). Aluminum paint coated the surface and upon heating to 600°C , did not convert to alumina as expected. This was evident due to the conductive nature of the coating. Nickel electrodes converted in-situ to nickel oxide provided reaction sites. A Zircar manufactured membrane accommodated the electrolyte made of 62 mole% lithium carbonate and 38 mole% potassium carbonate.

Stoichiometric removal of CO_2 at the cathode provided evidence of adequate cell performance, which incited the addition of H_2S . Equilibrium species concentrations comprised (8.51% CO_2 , 23.49% CO , 9.49% H_2O , 58.51% H_2 , and 115 ppm H_2S). Stoichiometric current, for a flow of 220 cc/min, required 4 mA. Application of stoichiometric current failed to remove any H_2S . Administering several different

current steps (Table 1) showed that removal was possible but at higher currents.

Table 1. Run #12

I_{app} (mA)	H_2S (ppmv)
700	4
350	8
200	32
100	45
50	140
500	5

The logical explanation arises from certain amounts of current being utilized for side reactions within the electrochemical system. The chemistry involving the aluminum sealant seems to be the most obvious deterrent. Due to past troubles emanating from the same problem a solution was devised to reduce the reaction area of the aluminum by decreasing the surface area of the cell housings. The cell was operable for 128 hours.

Run #13

MACOR sealed with aluminum foil gaskets housed this experiment. Ni electrodes were allowed to go to NiO in-situ. A prepressed disk of $(Li_{0.62}K_{0.38})_2CO_3$ infiltrated the 68% porous self-produced zirconia membrane in-situ. Strong seals developed immediately and held the duration of the experiment.

100% stoichiometric CO₂ removal was observed on the cathode side of the cell prompting H₂S addition. Equilibrium gas compositions consisted of (8.51% CO₂, 23.49% CO, 9.49% H₂O, 58.51% H₂, and 219 ppmv H₂S). A laboratory power failure caused the cell temperature to drop below the electrolyte melting temperature(500°C). Membrane thermal shock ensued creating cracks which allowed extensive hydrogen cross-over. Attempts to restart the cell failed, resulting in shut down after 99 hours.

Run #14

Set-up for run #14 was identical to run #13. Once again strong seals lasted throughout the experiment. A self-produced zirconia membrane, 65% porosity, provided electrolyte support. 100% stoichiometric CO₂ reduction occurred on the cathode side of the cell. H₂S addition ensued. The cell reached equilibrium gas compositions of (8.51% CO₂, 23.49% CO, 9.49% H₂O, 58.51% H₂, and 156 ppm H₂S). Current applied to the cell had no effect in removing H₂S. The assumption of electrode degradation on the cathode side was proven by attempts to transport carbonate, resulting in only 50% stoichiometric removal of CO₂. Figure 2 shows the phase transition region that exists using Ni electrodes with the equilibrium gas contents. Once this transition occurs reactions sites for the reduction of H₂S drastically decline resulting in loss of current efficiency. Another alternative such as cobalt (Figure 3) must be used to provide

adequate pore area for the desired reaction to occur. The cell was shut-down after 98 hours.

Summary

Excellent stability has been shown using the self-produced zirconia membranes. The solution to micro-cracks requires the simple application of back pressure from the anode side of the cell. Aluminum foil gaskets provided excellent seals throughout run #13 & run #14. Current effects of the aluminum foil have yet to be determined, however past use resulted in favorable H₂S removal.

Planned Work for Next Quarter

Work will continue with the self-produced membranes and aluminum foil gaskets. The main focus will be on adequate cathode materials providing the proper reduction area for efficient H₂S removal.

Figure 3 Phase diagram for the Co-O-S system at 650°C

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