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 that 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 that 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.

Experiments this quarter focused on removing 100 ppmv 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 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.

Figure 1. Conceptual Electrochemical Removal Cell

Alternate Cathode Material

Materials used in our electrochemical membrane separator(EMS) replicate molten carbonate fuel cells(MCFC). Process compatibility, once integrated into gasification plants, will exist due to identical set-up as the power application(MCFC). Lithiated nickel electrodes, used in MCFCs, have been tested in the EMS with favorable results. H₂S removal efficiencies over 90%, using inlet H₂S levels of 100ppmv and 20ppmv, were recorded at varying flow rates(170-814cc/min). However, H₂S current efficiencies remained low, notably with 100ppmv inlet H₂S. Recent experiments(#11 - #14) using nickel cathodes and 100ppm inlet H₂S revealed significant reduction in cathode diameter along with enclosure of platinum current collectors. Nickel cathodes in 20ppmv H₂S streams exhibited stable behavior.

Variant nickel cathode behavior with different inlet concentrations can be explained by a phase transition at 650°C(experimental temperature). Equilibrium process gas compositions, with >100ppmv inlet H₂S may react with the nickel cathode to form Ni_{3+x}S₂, a conductive molten state. Ten ppmv inlet H₂S equilibrates to NiO, a conductive metal oxide.

Phase transition, Ni to Ni_{3+x}S₂, is detrimental primarily from loss of reaction sites for H₂S electronation. The high porosity, semi-conducting metal transforms to a conductive, molten disk losing interstitial pore area. Predominantly superficial area exists, resulting in smaller

electronation area, creating the necessity of higher current densities for H₂S removal. The problem of Ni phase transition, in the presence of high concentrations of H₂S, had its genesis in the early MCFC experiments using NiO electrodes. The solution was a conversion to cobalt electrodes; however, present MCFC's operate efficiently only with H₂S levels below 1ppmv, alleviating the problem.

A suitable cathode material stable in the removal environ, fabricated to continue 100ppmv experiments, Co forming Co₉S₈ (a conductive ceramic), performed efficiently. Experimental H₂S removal results utilizing the fabricated cobalt cathode follow.

Experimental Results

Due to the instability of nickel as a cathode material under conditions of high H₂S concentrations(>100ppmv) alternate materials were investigated. The best material, from experience and phase stability when using 100ppmv H₂S, is cobalt. Using various methods to replicate previous electrode morphology, eventually produced a >80% porous cobalt electrode, similar in porosity and pore structure to previous nickel cathodes. Scanning electron microscopy(SEM), Figure 2, to investigate pore diameter and in lab test to confirm interconnecting pore channels finalized electrode testing. The necessity of pore size and interconnecting channels derives from the electrode-electrolyte interface where H₂S electronation occurs. Without adequate electrode

wetting, by the electrolyte, and the availability of contaminated fuel gas reaching this interface, H₂S removal is not possible.

a)

b)

Figure 2. a) Lithiated Ni anode and b) Co cathode

An experiment(Run#15) examining the removal capability of the EMS with cobalt cathode was performed this quarter. The focus dealt with H₂S removal along with H₂S current efficiency using inlet H₂S greater than 100ppmv.

Run#15

Cell materials consisted of a cobalt cathode, the anode material remained Li_xNi_{1-x}O, a stabilized zirconia membrane, housings of MACOR(machineable ceramic), aluminum foil gasket seals, and a prepressed disk of (Li/K)₂CO₃(6grams) corresponding to the void volume in the zirconia membrane. Examination of the cobalt-cathode EMS, produced stoichiometric CO₂ removal and addition at both cathode and anode, respectively, before addition of H₂S. After introducing H₂S to the EMS system, equilibration to 120ppmv H₂S occurred before applying current. H₂S removal at varying currents was attempted, starting with stoichiometric current(3mA for a flow of 150 cc/min), and increasing to 200mA. H₂S removal did not appear significant(< 10ppmv), with continued stoichiometric CO₂ removal at the cathode and production at the anode. Other concerns were high internal resistance(4 to 6 Ohms) as well as addition of electrolyte(> 10grams, 40% more than initially calculated).

Minimal H₂S removal at varying currents, resulted from three possible reasons:

- 1) The cathode pore diameter was too small, causing pores to be flooded by electrolyte drawn from

the membrane. In other words, the capillary forces from the cathode were stronger than those of the membrane due to smaller pore diameter in the cathode. Mass transfer would be inhibited, due to slower diffusion through the molten electrolyte filled pores to the electrode surface, instead of typical gaseous diffusion to the electrode surface. This possibility seemed unlikely due to stoichiometric CO₂ removal along with post-mortem examination of the electrode, Figure 2, revealing unflooded and intact pores.

2) Mechanical breakdown in the current carriers. High internal resistance throughout the experiment created concern of faulty circuitry, but post-run analysis proved negative.

3) Micro-cracks in the membrane that would enable hydrogen to cross from the process gas side(cathode side) to the sweep side(anode side). If hydrogen cross-over occurs, two reactions are possible at the anode. One reaction is the oxidation of hydrogen and the sulfide ion to hydrogen sulfide.

Anode exit gases checked by gas chromatography showed no evidence of H₂S. The other possible reaction is the oxidation of hydrogen and carbonate to water and carbon dioxide.

However, condensation of water was not evident, although low current levels(5mA) produces only 0.05% water in a flow rate of 70 cc/min on the anode side.

The second oxidation reaction, causing loss of carbonate from the electrolyte, induces the favorability of carbonate reduction at the cathode over H₂S due in part to the higher pressure of CO₂ and H₂O available at the cathode(order of 10⁵ higher than H₂S) promoting the parasitic reaction.

Electrolyte loss

The high internal resistance experienced in run#15 corresponds to electrolyte reduction due to formation of process-gas seals. The aluminum foil gaskets, placed on both sides of the membrane between the membrane and outer edge of the housings(outside the electrode well), initially oxidizes in the cell environ at elevated temperatures forming the non-conductive oxide alumina(Al₂O₃). Upon formation of alumina the conversion to LiAlO₂ by reaction with lithium carbonate present in the electrolyte occurs. Loss of lithium carbonate, the more conductive of the electrolytic species(more conductive than potassium carbonate), occasions

an increase in resistance throughout the membrane. Therefore continued addition of electrolyte is necessary until complete system equilibrium is attained.

Proof of the formation of other aluminate species was evidenced when post-mortem analysis revealed a blue tint around the cathode side of the EMS. Research revealed that CoAl_2O_4 (cobalt aluminate) is a bluish color (Thenard's blue), the only of the possible Co reactions found to coordinate.

Summary

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by the possibility of hydrogen cross-over from process gases creating alternate reactions unfavorable to the removal system. Application of back pressure from the anode side of the cell would be the simplest solution to H_2 cross-over. Examination of water vapor in the anode exit gases would provide proof of the aforementioned reaction hypothesis. Cobalt aluminate formation should not prove problematic, since degradation of the Co cathode did not occur as a result. Once equilibrium is reached electrolyte addition is not necessary, therefore not a major concern.

Planned Work for Next Quarter

Work will continue with the Zirconia membranes and aluminum foil gaskets from previous quarter experiments. The main focus will be on H₂S current efficiency using the fabricated cobalt cathodes with 100ppmv H₂S fuel gas and preventing alternate reactions due to hydrogen cross-over. Initial test of anode gas water vapor content should indicate the actual reaction mechanism.

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