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

Process Streams
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by

Professor Jack Winnick
Georgia Institute of Technology
School of Chemical Engineering
Atlanta, GA 30332-0100

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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.

Experiments this quarter focused on production of cobalt electrodes capable of sustaining pore symmetry in the cell environs.

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.
Electrochemical Fuel Gas Desulfurization 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 our 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) shown in Figure 2. 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 the Ni-O-S phase diagram at 650°C(experimental temperature). Figure 3, using equilibrium process gas compositions, shows 100ppmv H₂S may react with the nickel cathode to form Ni_{3+x}S₂, a conductive molten state. 10 ppmv inlet H₂S equilibrates to NiO, a conductive metal oxide, also in Figure 3.

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 all interstitial pore area.

Figure 2 (a) 20ppmv Inlet H₂S, (b) 100ppmv Inlet H₂S

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

Figure 4 Phase diagram for the Co-O-S system at 650°C.

Only superficial area exists, resulting in zero H₂S surface concentration.

A suitable cathode material stable in the cell environ, must be fabricated to continue 100ppmv experiments. From Figure 4, Co forming Co₉S₈ a conductive metal should perform efficiently. The next step is to develop a Co electrode identical in morphology to the aforementioned nickel cathodes.

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 past 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) 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.

Initial Electrodes

Initial attempts to replicate electrodes used 2 micron cobalt powder singularly and with a mix of 25 wt% methocel, followed by 149 micron powder singularly and with mixtures of methocel and naphthalene.

I.) Pressing the 2 micron powder without any binding additive provided a cohesive disk, sintered at 800°C. The resulting electrode was completely conductive, but dense(40% porosity) and unusable for efficient H₂S removal.

II.) Pressing a mixture of 2 micron cobalt powder with 25 wt% methocel, in order to increase porosity, then sintering at 800°C in a nitrogen atmosphere provided more favorable results. The electrode was higher in porosity(55%) and conductive, due to the nitrogen atmosphere preventing oxidation to non-conductive cobalt oxide. However, incomplete binder(methocel) burn-out caused a fragmented disk not conducive for efficient electrode material.

III.) Sintering a 3 wt% methocel, 97 wt% 149 micron cobalt powder disk to 1000°C proved unfavorable, attributed to incomplete binder burnout along with incohesive particle structure. The electrode characteristics remain similar to the previous mixture(II) of methocel and 2 micron powder.

IV.) Using pure 149 micron cobalt powder was attempted but difficult due to the larger particle size lacking coherence, once pressed. The disk, sintered to 1100°C in N₂ atmosphere, densified to an unacceptable porosity(50%), similar to the 2 micron powder electrode(I).

V.) Sintering to 1000°C in an oxygen atmosphere using a pressed disk of 2 wt% methocel balance 149 micron cobalt powder, in an attempt to completely burn-out the binder, did not conform. The electrode flaked, prompting another binder alternative, preferably a sublimating substance requiring low temperature phase transition; therefore, releasing without combustion process interference.

VI.) Naphthalene was chosen as a sublimating binder and pressed with 149 micron powder, 1gram to 30grams respectively. The disk, after sintering to 700°C, failed to solidify forming a mound of conductive powder. The predominant problem arose from agglomeration of the naphthalene particles preventing uniform heterogeneity.

First Batch Electrodes

A consortium of mixtures were next attempted given the previous information. The various mixtures used were batch sintered in a nitrogen atmosphere to 1195°C. The temperature increase generated more particle interaction due to the

proximity of cobalt's melting temperature(1492°C). Nine different disk were pressed each varying in components as follows:

- 1) Pure 2 micron cobalt powder
- 2) 3wt% methocel balance 2 micron powder
- 3) 12wt% methocel balance 2 micron powder
- 4) 56wt% methocel balance 2 micron powder
- 5) 16wt% naphthalene balance 2 micron powder
- 6) 30wt% 2 micron powder 70wt% 149 micron powder
- 7) 8wt% methocel balance 149 micron cobalt powder
- 8) 6wt% naphthalene balance 149 micron powder
- 9) Pure 149 micron cobalt powder

with 4 providing favorable results. The mixture(4) densified to 2.36 g/cm³ with a porosity of 75%. Next investigation shifted to other major concerns, aforementioned pore diameter and interconnecting channels. Without the previous two criteria lack of reaction sites for H₂S electronation results in unfavorable current efficiencies. After SEM pictures, Figure 5, showed pore size acceptability(compared to previous electrodes) and electrode bubble testing proved interconnecting channels existed, other test incorporating high wt% binding materials followed.

Second Batch

Success with high wt% methocel, resulted in test mixtures, sintered conditionally identical as follows:

- 1) 63wt% methocel balance 2 micron powder
- 2) 40wt% methocel 15wt% 2 micron 65wt% 149 micron
- 3) 55wt% hydroxyethylcellulose balance 2 micron
- 4) 64wt% methocel balance 149 micron powder
- 5) 43wt% methocel balance 149 micron powder
- 6) 23wt% methocel balance 149 micron powder
- 7) 20wt% hydroxyethylcellulose balance 149 micron

1, with similar component make up as 4, densified to 1.998 g/cm³ with high conductivity. Favorable porosity(78%) and disk morphology from Figure 5 provided proof of an electrode solution.

Summary

Fabrication of electrodes similar to previous nickel electrodes were produced using a mixture of ~60wt% methocel with the balance 2 micron cobalt powder. Two large diameter disk sintered component and condition similar have been developed with promising results.

Planned Work for Next Quarter

Work will continue with the self-produced 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.

Figure 5 (a) Previous Ni cathode, (b) #4 first batch,
(c) #1 second batch

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