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Electrochemical Membrane Separation (EMS) of Hydrogen Sulfide from Coal Gasification Streams

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Introduction

Coal gasification processes operate from 550-2000° C at 1-35 bar. At present, low temperature absorption processes and Claus plants are used to remove sulfur and salvage it as a salable by-product. Hydrogen sulfide, in particular, is a very corrosive contaminant and is also highly toxic. Levels must be reduced to 100 ppm for turbine applications and below 1 ppm for fuel cell systems. Sulfur removal procedures can often be as extensive as the rest of the gasification plant. (Nowacki, 1981) High temperature absorption processes offer a more compact, energy efficient route for dry fuel streams, but the regeneration of the metal-oxide sorbent is an expensive and difficult process. In addition, the high flow rates of fuel processing (on the order of 7000 lb/day) dictate that vast amounts of sorbent would have to be used and then treated. (Atimtay and Harrison, 1998)

Objective

Our goal is to prepare an electrolytic cell for scale-up that is capable of removing H₂S continuously. The major hurdles that remain are cathode selection and optimizing cell design and operating conditions. Studies have focused upon determining critical cell parameters for process scale-up as well as finding more stable and catalytically active cathode materials.

Approach

To compete with current processes, a high temperature electrochemical membrane separation (EMS) has been proposed to remove H₂S in one continuous step: polishing the fuel gas stream while extracting elemental sulfur. (Winnick, 1981) This negates the need for both catalyst regeneration and reheating. The theoretical basis of this separation is an extension of membrane separations driven by pressure gradients. The difference here is that an electric potential, $\Delta\Phi$, is

also used to drive species across the membrane, thus adding to the chemical potential to attain the difference in electrochemical potential for species i , $\Delta\bar{\mu}_i$.

$$\Delta\bar{\mu}_i = RT \ln(a_i / a_i') + z_i F \Delta\Phi_{(i-i)} \quad (1)$$

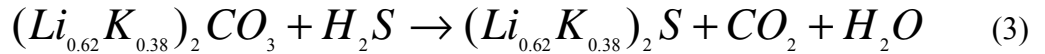
a_i and a_i' are the respective activities of component i on either side of the membrane (with ' indicating the extract phase), z_i is the charge of the transferred species, R is the ideal gas constant, T is the temperature, and F is Faraday's constant.

Preliminary analysis indicated that the removal rate of H_2S could be limited either by gaseous mass transfer from the fuel stream to the cathode-electrolyte interface or by liquid diffusion of sulfur ions through the electrolytic membrane. The rate-limiting step depends on operating conditions (i.e. temperature and inlet H_2S concentration) and cell design (such as membrane thickness, membrane porosity, and flow channel design). By isolating membrane thickness as the only variable and monitoring H_2S removal, one can determine whether or not sulfide diffusion across the membrane is the rate-limiting step for this process. Kinetic studies have shown that this reduction and oxidation of sulfur should not be rate-limiting. (Banks and Winnick, 1985; and White, III and Winnick, 1985)

The maximum H_2S removal flux determined from diffusion limitations through the membrane can be characterized in the balance below. Equation (2) results from assuming that the

$$Flux = \frac{i_{diff}}{nF} = D_{S^{2-}-Elec} \frac{\epsilon \rho_{Elec} C_{S^{2-}}^{cath}}{\tau x} = \frac{\Delta \dot{n}_{H_2S}}{A} \quad (2)$$

migration term in the sulfide flux balance is negligible because of the vast amount of carbonate in the electrolyte. Key assumptions are that the activity coefficients of carbonate and sulfide are equal, the concentration of sulfide species at the cathode is at equilibrium with the fuel stream, and the concentration of sulfide at the anode is zero. The sulfide mole fraction at the cathode, $c_{S^{2-}}^{cath}$, is calculated from the log-mean bulk concentration of H_2S in the gas and the equilibrium of reaction (3).



Also, the concentration profile of carbonate and sulfide in the membrane is linear. n is the number of electrons transferred per mole reacted (2 mol⁻¹ in this reaction), ϵ the membrane porosity, τ membrane tortuosity, ρ_{Elec} electrolyte molar density in mol/cm³, x membrane thickness in cm, and $D_{S^{2-}/Elec}$ the diffusivity of sulfur ions in the electrolyte (10⁻⁵ cm² s⁻¹ as given by Majewski and Walker, 1998). All parameters in Eq. (2) except τ are independently evaluated.

In the search for sulfur-tolerant cathode materials, various metal oxides conductive at high temperatures have been tested for chemical and electrochemical stability under process conditions. First, powder samples are mixed with electrolyte (12-15% sulfide and the rest carbonate) and exposed to sour gas at 750° C for 40-60 hours. X-ray diffraction analysis of cleaned samples can verify whether or not the powder has changed either composition or structure.

If a material passes the chemical stability test, then a small pellet is compressed to explore the conductivity of the material under sour gas and high temperature. If the material is stable and shows promising conductivity, then a porous disk is prepared for a full cell trial.

Project Description

A lab-scale electrochemical cell has been used for desulfurization of a synthetic coal gasification process stream. The cell has been run at temperatures from 600-700° C and ambient pressure. The cell has five basic components: cell housing, an inert ceramic membrane, a molten electrolyte, an anode, and a cathode. The cell housing provides the channel medium by which the fuel and purge gas streams flow across their respective electrode surfaces. The metallic cell housing also acts as a current collector to which metal leads are attached.

The inert ceramic membrane creates a barrier between the two gas streams and electrodes, and it holds the molten electrolyte within its porous structure. Lithiated alumina and yttria-stabilized zirconia (YSZ) have each been popular choices because of their high bubble pressure as well as inertness and stability in molten carbonate. YSZ is used in this research because it performs well with sulfide present.

The electrolyte in this system must be liquid at operating temperature and allow sulfide species to form. It must also be stable and conductive while exposed to the fuel gas and temperature used. The molten carbonate fuel cell (MCFC) electrolyte, $(\text{Li}_{0.62}\text{K}_{0.38})\text{CO}_3$, was chosen for this work as it satisfies these criteria.

The anode material, lithiated NiO, has been selected because it is the predicted stable phase under operating conditions. (Ingram and Janz, 1965) Lithiated NiO has performed adequately in all runs by maintaining stability in the oxidizing environment.

The cathode material has not yet been finalized; therefore, various materials have been tested throughout this study such as Ni, CoS_2 , $\text{Y}_{(0.9)}\text{Ca}_{(0.1)}\text{FeO}_3$, and $\text{Gd}_2\text{TiMoO}_7$.

The cell was assembled as shown in Figure 1, and heat-up took place at $100^\circ \text{C hr}^{-1}$. A pneumatic piston, applying about 5 psi, was used to compress the materials together once the electrolyte melted (at $\sim 490^\circ \text{C}$).

Constant current was applied via a Perkin-Elmer 273A Potentiostat/Galvanostat, and the flow rates of gases were controlled by rotameters. Cells were run at open circuit until the outlet H_2S level reached a magnitude comparable to the inlet. Outlet flow was measured using a bubbler to verify a good seal and no gas crossover. At this point, the cell was operated galvanostatically to initiate electrochemical transfer. Current was stepped upward until the amount of H_2S removal showed no response. This was determined to be the maximum achievable H_2S removal rate under the given operating conditions (cell design, temperature, $[\text{H}_2\text{S}]_{\text{inlet}}$, and flow rate). Each step was held for at least 3 hours to ensure steady state operation.

Hydrogen sulfide levels were measured using a flame-photometric gas chromatograph (Perkin-Elmer Auto System XL). Infrared spectroscopy was used to monitor the CO_2 levels leaving at the anode side. The data was used to verify continued electrochemical activity because CO_2

transport is a side reaction that can be monitored according to Faraday's law (due to the abundance of carbonate).

Results

For a 200 mL min^{-1} gas flow with a molar composition of 34.14% CO, 22.16% CO₂, 35.13% H₂, 8.51% H₂O and 1200 ppm H₂S at 600° C, the maximum removal rate of H₂S was obtained by ramping the current until the H₂S removal rate no longer responded to current increase (thus reaching a maximum). Using a membrane 1.8 mm thick, about half the maximum removal rate of H₂S was obtained in relation to a system using a membrane 0.9 mm thick (see Figure 2). This is strong evidence that the membrane thickness and structure are critical properties to consider in process scale-up. The cell achieved removal fluxes on the order of $1.1 \times 10^{-6} \text{ g mole H}_2\text{S min}^{-1} \text{ cm}^{-2}$ at 650° C with a 0.9 mm thick membrane that was 60% porous.

Y_(0.9)Ca_(0.1)FeO₃, CoS₂, Ni, and Gd₂TiMoO₇ were tested as cathode materials in full-cell runs, but conversion to sulfide compounds generated certain limitations in the materials. For example, Ni, turning to Ni₃S₂ upon exposure to the sour gas, has temperature limitations because Ni₃S₂ melts at 635° C. In Figure 3, SEM analysis indicates that structural changes occurred in the cathode as it underwent compositional change from a pure metal to a sulfide compound(s). The breakdown of the porous electrode structure results in a loss of the 3-phase boundary layer which is vital for sulfur absorption into the electrolyte.

The process was limited by sulfide diffusion through the membrane at temperatures up to 650° C and H₂S inlet concentrations up to 3000 ppm. At higher H₂S inlet concentrations and/or at higher operating temperatures, gaseous mass transfer may become the limiting process because a higher sulfide concentration in the electrolyte is favored, allowing for higher diffusion rates.

While reducing membrane thickness or increasing its porosity is another avenue for enhancing the sulfide diffusion rate, there are restrictions as to how thin the membrane can be. It must remain thick enough to resist cracking under pressure (from the half-cell above it) and to prevent excessive H₂ crossover, which can drastically decrease cell efficiency (not to mention the fuel gas calorific value). Under the given operating conditions, a minimum membrane thickness appears to be less than 1 mm to satisfy these two criteria. The exact thickness will ultimately depend upon the specific design of the cell and is still under investigation.

The Y_(0.9)Ca_(0.1)FeO₃ and Gd₂TiMoO₇ cathodes offer enough stability to study the system at higher temperatures, but long-term cathode stability is still a concern. Breakdown of the porous microstructure of the cathode decreases the active 3-phase boundary layer required to reduce H₂S from its gaseous state to a liquid sulfur ion, which can be transported across the electrolytic membrane. Preliminary analysis of Gd₂TiMoO₇ has shown the most resilience to pore deformation thus far, but XRD analysis shows that there is still conversion to a sulfide.

Application

This electrochemical cell can be used in place of current technology that is required to remove sulfur from coal. Being a high temperature process, the fuel stream will not have to be cooled as is generally done when absorbing H₂S with organic solvents such as methanol. This absorption takes place at near ambient temperatures whereas the fuel stream leaving the gasifier is often

near 1000°C and at elevated pressure. The polished stream is then reheated to about 400°C before entering the turbine to generate electricity.

Figure 4 shows how electrochemical cells may be incorporated into an integrated gasification combined cycle (IGCC) facility. Using EMS to remove H₂S offers valuable savings in operating costs since the gasified stream can remain at high temperature, which is also beneficial for solid-oxide fuel cells in place of turbines. The power required to apply potential to the cell is the only operating cost. Preliminary estimates place our operating costs in the range of \$10-13 per kg of sulfur removed. (Nagl, 2001) This price is competitive with liquid and solid scavenging systems but is still much higher than either liquid-redox or Claus plant operating costs. Yet, it should be noted that this estimate does not include the savings from omitted heat exchangers between the gasifier and turbine/fuel cell.

The actual size and capital cost of cells needed to fulfill this role is still under investigation, but we are confident that this is where EMS can have the most economic appeal since Claus plants are rather expensive and physically large. The savings in capital costs and overall plant size can only be calculated once the operating conditions and cell design are specified. The active area of the electrode has also not been optimized; therefore, it is difficult to determine the necessary cell area needed to remove a given amount of H₂S.

High temperature adsorption (scavenging) is another alternative, but handling and regeneration of the solid waste are always issues. While this option is moderately expensive, flags are often raised because disposing of the sorbent is neither environmentally sound nor pleasant work for the plant operators. Regeneration of the sorbent can also be quite costly.

Future Activities

We will continue to examine Gd₂TiMoO₇ and other promising cathode materials such as strontium vanadium oxides in our future research. We are also trying to gather data at 700°C to determine whether membrane diffusion remains the rate-limiting step even at higher temperatures.

The fundamental kinetics of promising materials will also be tested in a molten bath using electrodes sheathed within alumina tubes. Chronoamperometry and cyclic voltammetry will be employed to analyze catalytic properties of promising cathode materials.

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Figures and Tables

Figure 1: Bench-scale design of electrolytic cell

Figure 2: Effect of membrane thickness: data of two-membrane system vs. one-membrane system with specified cathode materials. T = 600° C and inlet [H₂S] = 1200 ppm +/- 50. Fuel gas flow rate was maintained at 200 mL/min. Diffusion-limited plots were calculated using a tortuosity value of 6.

Figure 3: Scanning electron micrograph of nickel cathode before (left) and after (right) run, 1000x. Notice the clogging of pores after the run.

Figure 4: Integrated gasification combined cycle plant with electrochemical cells.

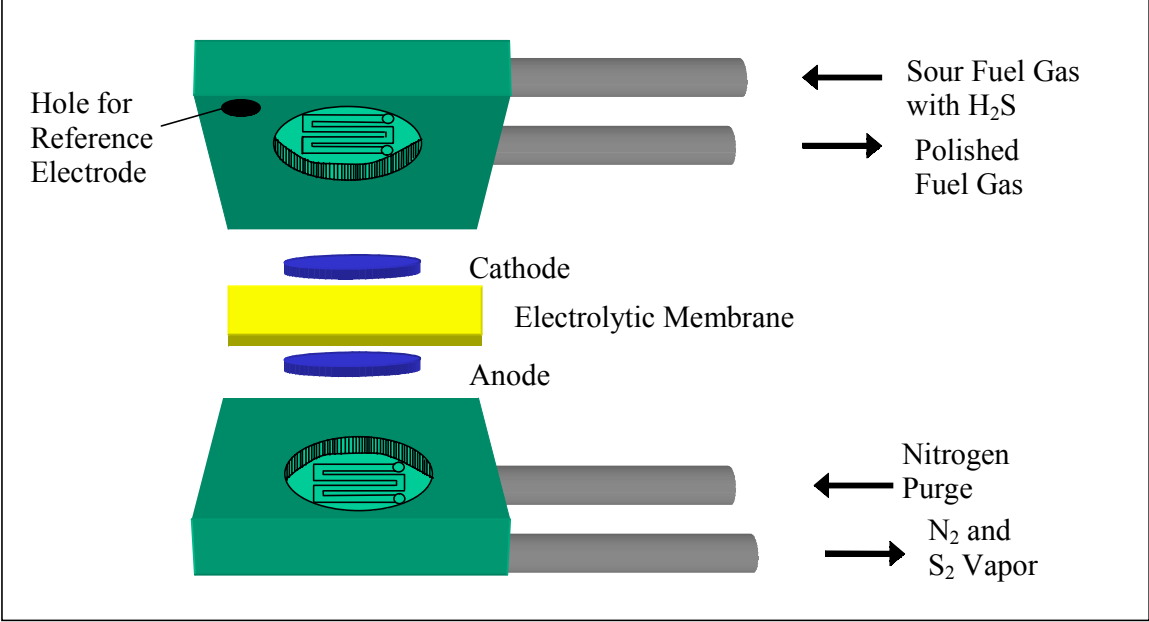


Figure 1.

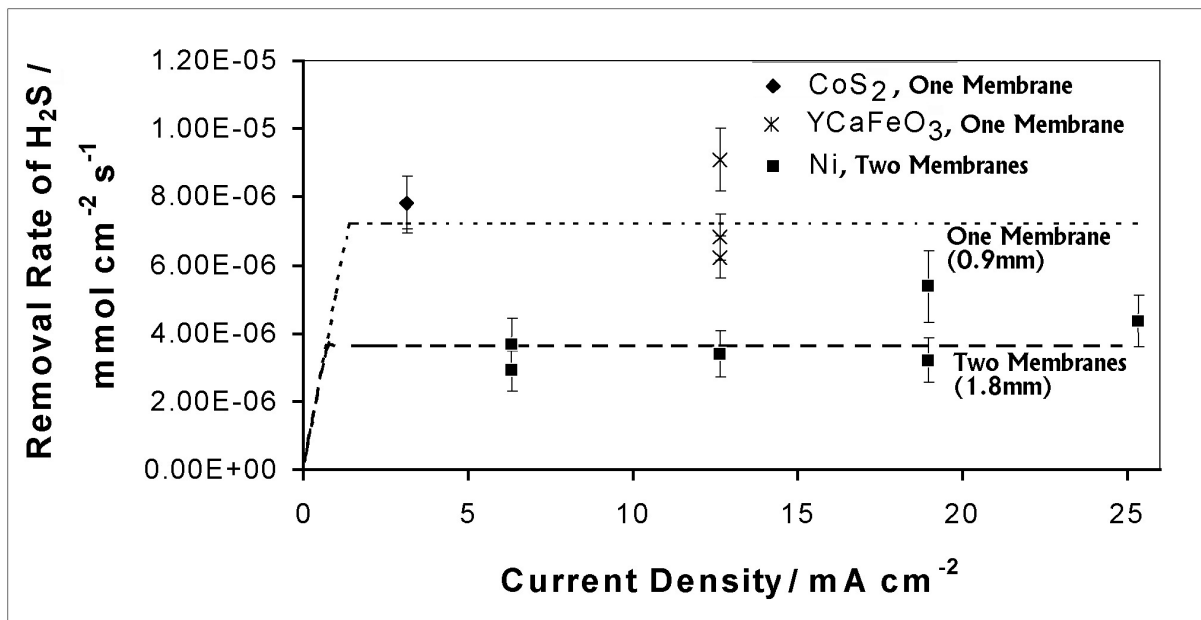


Figure 2.

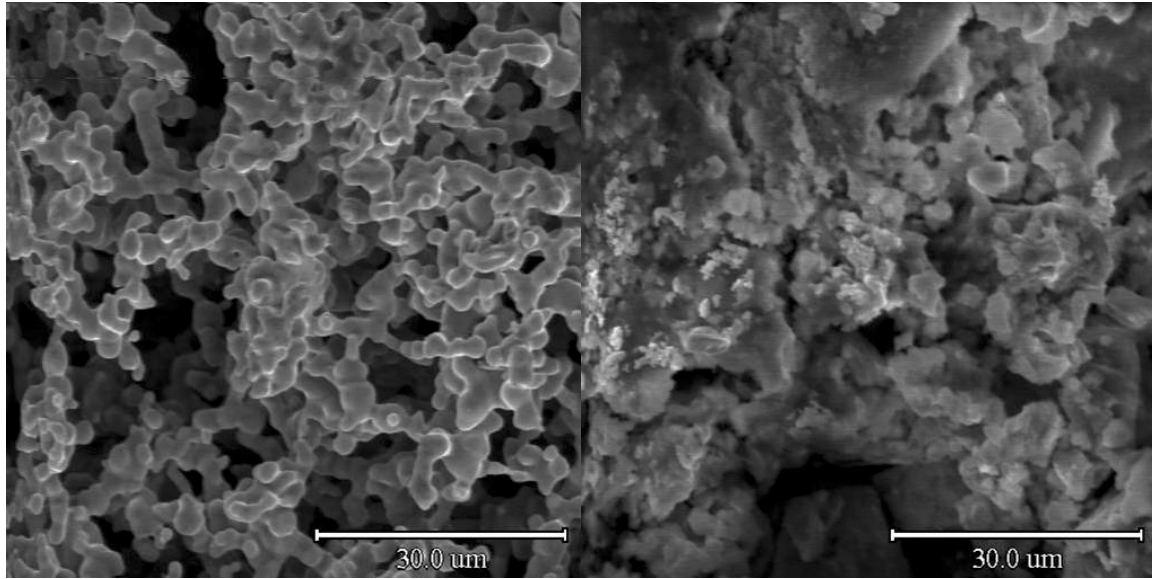


Figure 3. SEM of Ni cathode before and after use.

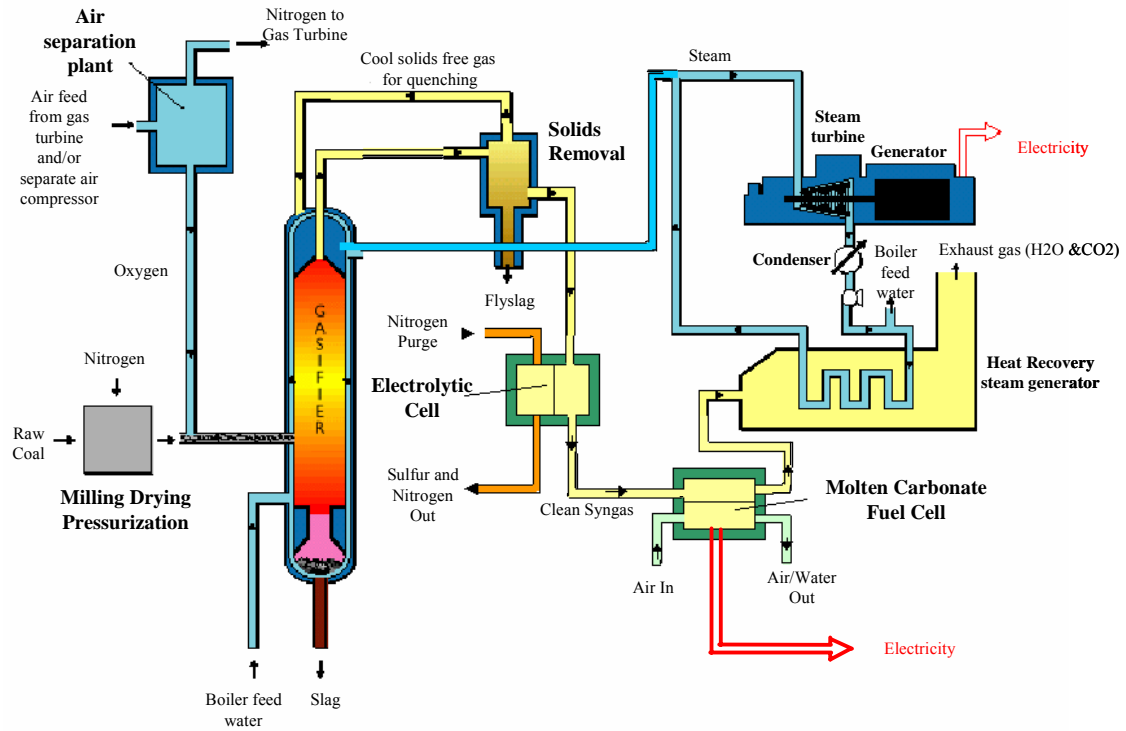


Figure 4.