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High Temperature Electrochemical Polishing of H_2S From Coal Gasification Process Streams

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Abstract

An advanced process for the separation of hydrogen sulfide from coal gasification streams through an electrochemical membrane is being perfected. H_2S is removed from a synthetic gas stream, split into hydrogen, which enriches the exiting syn-gas, and sulfur, which is condensed downstream from an inert sweep gas stream. The process allows for continuous removal of H_2S without cooling the gas stream while allowing negligible pressure loss through the separator. Moreover, the process is economically attractive due to the elimination of the need for a Claus process for sulfur recovery. To this extent the project presents a novel concept for improving utilization of coal for more efficient power generation.

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Executive Summary

This quarter's research primarily focused on fabricating LiCoO_2 electrodes suitable for utilization as the cathode in full cell experimental runs. Appropriate sintering conditions have been established. However, electrode porosity and pore size distribution will need to be improved in order for this material to be successful as the cathode. The primary variables that were studied included: initial concentration of poreformer, initial concentration of binder, initial LiCoO_2 particle size, dry pressing times, and pressures. SEM, X-ray diffraction, and particle size analysis were three techniques that were employed to help characterize the fabrication process. Fabricated LiCoO_2 electrodes were utilized in full cell experiments at 650°C . The system successfully transported CO_3^{2-} , as expected, with clean fuel gas, and also transported H_2S from contaminated gas. However, the cathode showed inefficient porosity to allow mass transfer of the extremely dilute H_2S to the electrolyte interface. Thus, H_2S removal efficiencies were below theoretical. However, the electrodes did show the expected high electronic conductivity needed after equilibrating with the H_2S -containing gas.

Project Objectives

Coal may be used to generate electrical energy by any of several processes, most of which involve combustion or gasification. Combustion in a coal-fired boiler and power generation using a steam-cycle is the conventional conversion method; however total energy conversion efficiencies for this type of process are only slightly over 30%¹. Integration of a gas-cycle in the process (combined cycle) may increase the total conversion efficiency to 40%¹. Conversion processes based on gasification offer efficiencies above 50%¹.

H₂S is the predominant gaseous contaminant in raw coal gas. Coal depending on the type and area of extraction can contain up to 5 wt% sulfur, which is converted to gaseous H₂S during gasification. Problems arise due to the corrosive nature of H₂S on metal components contained in these cycles. Because of this, H₂S concentrations must be reduced to low levels corresponding to certain power applications. For example, an integrated coal gasification-combined cycle (IGCC) process producing electricity from coal at nearly 50% overall efficiency¹ incorporates gas turbines that cannot tolerate H₂S levels above 100 ppm. Coal gasification/Molten Carbonate Fuel-Cell(MCFC) systems, achieving conversion efficiencies around 60%², function properly only if H₂S is below 1 ppm.

An advanced process for the separation of hydrogen sulfide (H₂S) from coal gasification product streams through an electrochemical membrane is being developed using funds from this grant. H₂S is removed from the syn-gas stream, split into hydrogen, which enriches the exiting syn-gas, and sulfur, which is condensed from an inert sweep gas stream, Figure 1. The process allows removal of H₂S without cooling the gas stream and with negligible pressure loss through

the separator. The process is made economically attractive by the lack of need for a Claus process for sulfur recovery. To this extent the project presents a novel concept for improving utilization of coal for more efficient power generation.

Past experiments using this concept dealt with identifying removal of 1-2% H₂S from gases containing only H₂S in N₂³, simulated natural gas^{4,5}, and simulated coal gas⁶. Data obtained from these experiments resulted in extended studies into electrode kinetics and electrode stability in molten melts^{7,8,9}. The most recent experiments evaluated the polishing application (removal of H₂S below 10 ppm) using the Electrochemical Membrane Separator (EMS). H₂S removal efficiencies over 90% were achieved at these stringent conditions of low H₂S concentrations proving the technologies polishing capabilities.

Other goals include optimization of cell materials capable of improving cell performance. Once cell materials are defined, cell experiments determining maximum removal capabilities and current efficiencies will be conducted.

Also, a model theoretically describing the preferred reduction of H₂S, the transport of S²⁻, and the competing transport of CO₂ will be investigated. The model should identify the maximum current efficiency for H₂S removal, depending on variables such as flow rate, temperature, current application, and the total cell potential.

Introduction

The Electrochemical Membrane Separator (E.M.S.), the focus of experimental work, purges a fuel gas contaminated with H₂S. This is done by reducing the most electro-active species in the gas stream. In this case, H₂S is reduced by the following:

A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H₂ diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.

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^{10,11}.

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds¹² or inefficient molten salt sorbent processes¹³ 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. Single-Cell View of the Electrochemical Membrane Separator

Results and Discussion

A majority of this quarter was spent fabricating LiCoO_2 electrodes. One of these electrodes was utilized in a full cell run. Beforehand, one electrode was subjected to sulfurizing conditions in a molten carbonate environment to study the conversion of the LiCoO_2 electrode to its sulfided state. In addition, one full cell run was attempted with stainless steel cell housings. All of these results will be discussed in detail below.

LiCoO_2 Electrode Fabrication

LiCoO_2 was produced from the calcination reaction of CoCO_3 and Li_2CO_3 at 700°C . The LiCoO_2 powder was then properly identified by X-ray diffraction and was ready for future use. Dry pressing proved to be the most feasible way to fabricate electrodes, thus this method was chosen. Four electrode batches were attempted; conditions are indicated in Tables 1 - 4. For all electrode fabrication attempts, the hydraulic ram pressure and sintering conditions were consistent. Disks were pressed at 11500 psi for approximately 10 minutes. The sintering program is as follows: ramp of $1^\circ\text{C}/\text{min}$ to 500°C for 4 hours, ramp of $1^\circ\text{C}/\text{min}$ to 850°C for five hours, ramp of $2^\circ\text{C}/\text{min}$ to room temperature. The diameter of the die was 1.25" in all cases.

The first batch, shown in Table 1, had three electrodes with moderate (75%) amounts of LiCoO_2 and three electrodes with extremely high (95%) amounts of LiCoO_2 . It is obvious from the resulting porosities that there must be significant amounts of binder and poreformer to fabricate an adequate electrode. Disks pressed with 95% LiCoO_2 resulted in less than 35% porosity. Higher porosities (66%) were observed when 25% poreformer was combined with 75% LiCoO_2 . Upon sintering, however, the resulting disk crumbled to the touch and was

Table 1. Conditions for LiCoO₂ Electrode Fabrication, Batch #1

Electrode #	Composition	Weight before sintering (g)	Weight after sintering (g)	Area (cm ²)	Thick-ness (cm)	Porosity (%)	Sintering Plate Code
1	1% MC 4% PF 95% LiCoO ₂	1.518	1.350	5.31	0.074	32	5
2	1% MC 4% PF 95% LiCoO ₂	1.508	1.285	N/A	N/A	N/A	5
3	25 % PF 75% LiCoO ₂	1.257	0.664	4.45	0.086	66	5
4	1% MC 4% PF 95% LiCoO ₂	1.300	1.252	5.35	0.071	35	3
5	25% MC 75% LiCoO ₂	1.417	1.003	4.83	0.075	45	3
6	25% MC 75% LiCoO ₂	1.400	0.983	4.52	0.100	57	2

Notes: MC = Methyl cellulose

PF = Carbon poreformer

Plate Codes:

2 = 5 cm diameter alumina disk

3 = 2.5" x 2.5" thin alumina plate

5 = 5" diameter alumina plate

Table 2. Conditions for LiCoO₂ Electrode Fabrication, Batch #2

Electrode #	Composition	Weight before sintering (g)	Weight after sintering (g)	Area (cm ²)	Thick-ness (cm)	Porosity (%)
1	15% MC 10% PF 75% LiCoO ₂	1.551	N/A	N/A	N/A	N/A
2	15% MC 10% PF 75% LiCoO ₂	1.488	N/A	N/A	N/A	N/A
3	15% MC 15% PF 70% LiCoO ₂	1.525	N/A	N/A	N/A	N/A
4	15% MC 15% PF 70% LiCoO ₂	1.562	N/A	N/A	N/A	N/A
5	20% MC 10% PF 70% LiCoO ₂	1.662	N/A	N/A	N/A	N/A
6	20% MC 10% PF 70% LiCoO ₂	1.468	N/A	N/A	N/A	N/A
7	20% MC 5% PF 75% LiCoO ₂	1.5	N/A	N/A	N/A	N/A

Notes: Electrodes failed upon sintering (none were in disk form).

Table 3. Conditions for LiCoO₂ Electrode Fabrication, Batch #3

Electrode #	Composition	Weight before sintering (g)	Weight after sintering (g)	Area (cm ²)	Thick-ness (cm)	Porosity (%)	Sintering Plate Code
1	15% MC 5% PF 80% LiCoO ₂ ($\mu=2\text{ }\mu\text{m}$)	1.463	1.041	5.853	0.108	67	1
2	15% MC 5% PF 80% LiCoO ₂ ($\mu=2\text{ }\mu\text{m}$)	1.486	1.139	5.228	0.085	49	2
3	15% MC 5% PF 80% LiCoO ₂ ($\mu=14\text{ }\mu\text{m}$)	1.493	1.109	5.147	0.072	41	3
4	15% MC 5% PF 80% LiCoO ₂ ($\mu=14\text{ }\mu\text{m}$)	1.480	1.166	5.067	0.085	46	4
5	15% PVA 5% PF 80% LiCoO ₂ ($\mu=14\mu\text{m}$)	1.425	1.072	4.909	0.081	47	3
6	15% PVA 5% PF 80% LiCoO ₂ ($\mu=14\mu\text{m}$)	1.518	1.123	4.988	0.084	47	4

Notes: MC = Methyl Cellulose PVA = Polyvinyl alcohol PF = Carbon poreformer
Plate Codes:

- 1 = 3" x 3" porous cell housings
- 2 = 5 cm diameter alumina disk
- 3 = 2.5" x 2.5" thin alumina plate
- 4 = 3" diameter ceramic disk

Table 4. Conditions for LiCoO₂ Electrode Fabrication, Batch #4

Electrode #	Composition	Weight before sintering (g)	Weight after sintering (g)	Area (cm ²)	Thick-ness (cm)	Porosity (%)	Sintering Plate Code
1	20% MC 10% PF 70% LiCoO ₂ ($\mu=4.29\text{ }\mu\text{m}$)	1.432	0.945	N/A	N/A	N/A	3
2	20% MC 10% PF 70% LiCoO ₂ ($\mu=4.29\text{ }\mu\text{m}$)	1.503	0.974	4.87	0.109	64	2
3	17% MC 8% PF 75% LiCoO ₂ ($\mu=4.29\text{ }\mu\text{m}$)	1.530	1.068	4.99	0.093	54	3 on top of 1
4	17% MC 8% PF 75% LiCoO ₂ ($\mu=4.29\text{ }\mu\text{m}$)	1.459	1.061	4.91	0.095	55	2

Notes: MC = Methyl cellulose

PF = Carbon poreformer

Plate Codes:

1 = 3" x 3" porous cell housings

2 = 5 cm diameter alumina disk

3 = 2.5" x 2.5" thin alumina plate

4 = 3" diameter ceramic disk

cracked in half. Disks pressed with only 25% methyl cellulose and 75% LiCoO_2 resulted in compact disks after sintering, but porosities were too low (45% and 57%). SEM of Electrode #6, which contained 25% methyl cellulose, revealed pore sizes on the order of 10 microns. A photograph of this electrode is shown in Figure 2. This photograph shows that adequate porosity was achieved, but increased porosity is desired. Therefore, it was concluded that the next batch should have a significant amount of binder and poreformer.

The second batch, shown in Table 2, tried to address the problems which were discovered in the first batch. Three different initial concentrations were attempted - 15% methyl cellulose, 10% poreformer; 15% binder, 15% poreformer; and 20% binder, 10% poreformer. Upon sintering, all disks failed (powder was spread throughout with no cohesiveness). Before this batch, the particle size of LiCoO_2 had not been measured. It was determined that the failure of the second batch may have been due to the large particle size of the LiCoO_2 . Particle size analysis revealed that the 50% median particle size was 22 microns. To achieve proper disk strength, particle size distribution, and porosity, initial LiCoO_2 particle size needs to be smaller. Therefore, samples of LiCoO_2 were ball milled for 24 - 36 hours for future sintering experiments.

The third sintering batch (Table 3) had binder and poreformer concentrations similar to the second batch, but the particle size of LiCoO_2 was reduced. Four disks had 15% methyl cellulose, 5% carbon poreformer, and 80% LiCoO_2 , with two of these disks having an $\mu_{50\%}$ of 14 microns and the other two with $\mu_{50\%}$ of 2 microns. The resulting sintered disks all appeared solid. The two disks with the smaller initial particle size (2 microns) had much larger porosities (67% and 49%) compared with the larger initial particle size (14 microns), whose porosities were 41% and 46%. Two other disks were attempted - with 15% polyvinyl alcohol and 5% poreformer.

121501 #6

Figure 2. SEM of Electrode #6, Batch #1: Porosity = 57%

The resulting sintered disks were cohesive, but not qualitatively as good as the other four. Slight cracks and non-circular shapes plagued the two disks. Resulting porosities were 47% for both disks. This batch led us to conclude that smaller LiCoO_2 particle size was important in a resulting sintered disk's strength and porosity. The success of methyl cellulose over polyvinyl alcohol dictated that methyl cellulose be the designated binder in future sintering experiments.

The fourth batch of LiCoO_2 electrodes this quarter (see Table 4) consisted of four pressed disks. In order to increase porosity, the poreformer and binder concentrations were increased. Two electrodes had 20% methyl cellulose, 10% carbon poreformer, and 70% LiCoO_2 while the other two electrodes consisted of 17% methyl cellulose, 8% carbon poreformer, and 25% LiCoO_2 . The resulting electrodes were more porous, with porosities ranging from 55 to 64%. Progression is being made in LiCoO_2 electrode fabrication. Further work in this area will attempt to increase electrode porosity even further without sacrificing electrode strength and durability.

LiCoO_2 electrode test in sulfurizing and molten carbonate conditions

A fabricated LiCoO_2 (from Batch #1, Electrode #4, 35% porosity) disk was subject to a cell run which mimicked the conditions that it would encounter as the cathode in a full cell run. A MACOR ceramic housing was utilized to hold the disk in place. Gold wires running through alumina tubes connected to the MACOR cell housing terminated at the LiCoO_2 disk to measure the conductivity of the material. A Zircona membrane which was impregnated with $(\text{Li}_{0.68}\text{K}_{0.32})_2\text{CO}_3$ was placed on top of the LiCoO_2 -containing MACOR cell housing. A 3" diameter alumina plate was placed on top of this and a 1.6 kg weight was added to ensure no gas leakage. This apparatus was placed in a furnace and the temperature was gradually increased to

650 °C. Then, process gases were introduced to one of the alumina tubes. The inlet gas concentrations were approximately: 7.7% H₂O, 3.6% CO₂, 1.1% CO, 5.0 % H₂, 3000 ppm H₂S, and balance N₂. The LiCoO₂ was subject to these conditions for 50 hours. X-ray diffraction (see Figure 3) of the resulting sample revealed peaks for Co₃S₄, Co₄S₃, and Co₉S₈, which are highly conductive compounds. A crude conductivity analysis demonstrated that the conductivity fell from over 100 ohms at the beginning of the experiment to less than 2 ohms at the end when the electrode had been totally sulfided. These results lead us to believe that LiCoO₂ can be utilized as a successful cathode material if the pore size and porosity are manipulated correctly.

Full-Cell Experimental Run with a LiCoO₂ Cathode

There were two attempts at full cell H₂S removal experiments this quarter utilizing LiCoO₂ as the cathode. Run #45 was plagued by connection problems between the current collector and the cathode. The cathode, which was in the top cell housing, was too thin and did not have proper contact between the membrane and the gold current collector. Therefore, this run was terminated before any data collection. Run #46 attempted to alleviate the contact problem by placing the LiCoO₂ cathode in the bottom cell housing and the nickel anode in the top cell housing. Initially, however, there were still cathode-current collector-membrane contact problems. Therefore, the cell was cooled to room temperature. Then, additional and thicker gold current collector was added inside the cell housings. Also, the LiCoO₂ cathode and Zircar membrane, which cracked upon cooldown, were replaced. Table 5 summarizes the conditions for the two full-cell runs.

Figure 3. LiCoO_2 after 50 hours in sulfurizing conditions.

Table 5. Full Cell Runs with LiCoO₂ Cathodes Attempted this Quarter

Run #	Temp (°C)	Cathode	Anode	Membrane	Housings	Passivation
45	650	LiCoO ₂ Batch#4,#3 55%porosity	Lithiated Ni	Fabricated ZrO ₂	MACOR	None
46	650	LiCoO ₂ Batch#4,#3 54%porosity & LiCoO ₂ Batch#3,#4 46%porosity	Lithiated Ni	Fabricated ZrO ₂	MACOR	None

Carbonate Transport

Before the addition of H₂S to the cell, it is necessary to evaluate the electrochemical membrane separator's ability to transport carbonate across the cell. This is accomplished by CO₂ removal from the process gas (cathode coal syn-gas) (3):

and anode CO₂ evolution due to carbonate oxidation (4):

This is the first test performed during a full-cell run which displays the EMS cell's performance. Based on 2 Faraday's of charge transferred per mole of species reduced or oxidized, the actual carbon dioxide removed/produced can be compared to theoretical amounts. A current step method is utilized to determine the carbon dioxide removal, carbon dioxide production, as well as cell potential at varying applied currents. Due to a faulty IR analyzer, CO₃²⁻ transport data was

not taken at this stage of the experiment. However, the machine was fixed and used to measure anode CO_2 levels during H_2S removal experiments.

Removal of H_2S from Sour Coal Gas

Once carbonate transport across the cell was demonstrated, H_2S was added to the process syn-gas. The process gas was equilibrated by the following two reactions:

via a stainless steel shift reactor before entering the cell housing. Once process gases entered the cell housings, they equilibrated with the molten electrolyte by:

which creates a conversion of carbonate ions to sulfide ions depending on the concentration of H_2S in contact with the electrolyte as well as the temperature of the cell. Increased temperatures result in higher molten sulfide concentrations which facilitate sulfide oxidation. Typically, at least twenty-four hours is necessary for this reaction to reach equilibrium.

The goal of full-cell experiments is to validate the removal capabilities of the EMS system while maintaining economically feasible current efficiencies (high current efficiencies at high inlet H_2S concentrations). H_2S current efficiency is calculated by:

$$\eta_{\text{H}_2\text{S}} = \frac{\% \text{H}_2\text{S Removal}_{\text{actual}}}{\% \text{H}_2\text{S Removal}_{\text{theoretical}}} \quad (8)$$

which represents the ratio of H_2S actually removed to the amount that should be removed at a

specified applied current. The following equation calculates the amount of H₂S removed from the process syn-gas:

$$\% \text{ H}_2\text{S Removal} = \frac{\text{Inlet H}_2\text{S} - \text{Outlet H}_2\text{S}_{(I_{app})}}{\text{Inlet H}_2\text{S}} \times 100 \quad (9)$$

Run #46 was tested for H₂S removal at two flow rates for H₂S inlet values around 2500 ppm, which will be subtitled Run #46a and #46b. Both runs occurred at 650 °C. Run #46a had a cathode inlet flow rate of 181 cc/min, with a corresponding outlet flow of 90 cc/min. The process gases equilibrated to: 4.9% CO₂, 2.20% CO, 7.1% H₂O, 7.1% H₂, 2500 ppm H₂S, and balance N₂. The molten salt equilibrium concentration was estimated at 83% M₂CO₃ and 17% M₂S, where M represents the lithium/potassium eutectic. The gas phase limiting current density was estimated at 29.6 mA/cm², while the membrane limiting current density was estimated at 170 mA/cm². With an electrode area of 5.07 cm², the limiting current density for these conditions was 150 mA. Applied current approaching this level will result in severe mass transfer limitations. Anode inlet and outlet flow rates for this run were approximately 208 and 109 cc/min, respectively.

Run #46b had an increased cathode flow rate of 297 cc/min with an inlet H₂S concentration of 2200 ppm. The cathode inlet gas was estimated as follows: 4.35% CO₂, 1.65% CO, 7.34% H₂O, 6.20% H₂, 2200 ppm H₂S, and balance N₂. Limiting current densities in the gas phase and membrane were estimated at 26.1 and 166 mA/cm², respectively. Molten salt equilibrium was estimated at 84.3% M₂CO₃ and 15.7% M₂S.

A current step was applied to determine the H₂S outlet levels, %H₂S removal, current efficiency, and the electrode overpotentials. Figure 4 demonstrates that H₂S outlet levels fall with increasing cell current for the two different flow rates. Figure 5 shows H₂S removal as a function of applied current. H₂S removal was observed at both flow rates for this run. However,

H₂S Outlet Levels vs. Applied Current

Figure 4. Run #46. H₂S Outlet Levels vs. Applied Current

H₂S Removal vs. Applied Current

Figure 5. Run #46. H₂S Removal vs. Applied Current

Current Efficiency vs. Applied Current

Figure 6. Run #46. Current Efficiency vs. Applied Current

Cell Potentials vs. Applied Current

Figure 7. Run #46. Cell Potentials vs. Applied Current

CO₂ Production vs. Applied Current

Figure 8. Run#46. CO₂ Production vs. Applied Current

the H_2S removal was not stoichiometric. Figure 6 illustrates this by showing the decreasing relationship between H_2S current efficiency and applied current. Figure 7 compares cell potentials with applied current. Overpotentials are within reasonable bounds. Ohmic resistance for this entire run was unreasonably high; this was probably due to poor contact between the anode current collector, nickel anode, and electrolyte-filled membrane. The linear relation of the anode-reference potential with applied current implies that there is significant ohmic loss here. Figure 8 shows that CO_2 is produced at the anode with increasing applied current. This is a certain sign that carbonate transport is occurring rather than desired sulfide transport. The lack of porosity in the cathode limits the amount of surface area available for reduction. Since H_2O and CO_2 are much more abundant than H_2S , they will be preferred for reduction when the reaction is mass transfer limited. This results in CO_3^{2-} formation, which is consequently oxidized at the anode to form CO_2 . The run was eventually stopped after 11 days due to cathode failure (as observed from cathode-reference potentials and lack of H_2S removal). Figure 9 is an SEM photograph of the LiCoO_2 electrode after the full cell run.

LiCoO_2 was successful as the cathode at removing 2500 ppm H_2S at two different flow rates. While desired removal levels were not achieved, it is presumed that this is purely a lack of electrode optimization. The LiCoO_2 cathode porosity of 46% needs to be increased. The highly porous (~90%) nickel electrodes from ERC which have been successfully used in the past at 580°C provide ample pores and surface area to allow for H_2S diffusion from the bulk phase into the electrode where it is then reduced at the electrode/electrolyte interface. LiCoO_2 is preferred over nickel since it can operate at a temperature of 650°C , well above the operating range of nickel. However, ultimate success of the LiCoO_2 electrode can only be achieved with a higher porosity and proper pore size distribution.

Figure 9. Run #42. SEM Photograph of cathode after experiment.

Full Cell Run with Stainless Steel Cell Housings

One full cell run was attempted this quarter with stainless steel cell housings. The conditions for the run are in the following table:

Table 6. Full Cell Run Conditions for Experiment #44

Run #	Temp (°C)	Cathode	Anode	Membrane	Housings	Passivation
44	580	Lithiated Ni	Lithiated Ni	Fabricated	Stainless	All areas
		Thickness:	Thickness:	ZrO ₂	Steel (316)	aluminum
		1.12 mm	1.12 mm			passivated

This experiment also had gold current collectors designed to enhance the contact area between the stainless steel and the electrodes.

Like past experiments with stainless steel cell housings, the EMS was successful at carbonate transport across the cell. Stoichiometric CO₂ reduction at the cathode and production at the anode was observed. However, once H₂S is added to the cathode inlet gas mixture, the EMS is plagued by several problems. The primary problem is lack of equilibration between the H₂S cathode inlet and outlet levels. At least three days are typically required for the outlet H₂S values to come within 60% of the inlet values with stainless steel cell housings. For example, in this experiment, the inlet H₂S value was ~2400 ppm. It took four days for the outlet value to reach 1300 ppm. This can be attributed to H₂S adsorption onto stainless steel. Shvartsman and Petrova¹⁴ demonstrated that H₂S adsorption depends on the mean grain size of the metal and the ratio of P_{H₂S}:P_{H₂} in the gas phase. Our experiment has 8 inch stainless steel tubes leading into and out of the stainless steel cell housing. Therefore, there is abundant stainless steel surface area for H₂S adsorption.

Another interesting observation utilizing stainless steel cell housings should be noted. Previously utilized cell housings that had been subject to H_2S for long periods of time still contained the H_2S on the stainless steel surface. When subject to a cathode inlet containing only H_2 , H_2O , CO , CO_2 , and N_2 , the resulting cathode outlet contained at least 400 ppm H_2S . It is assumed that H_2 in contact with the sulfided stainless steel forms H_2S . It is obvious that this occurrence can have detrimental effects for H_2S removal. Any removal that occurs will be offset by the adsorbed H_2S downstream, which will react with H_2 to reform H_2S . Thus, limited or no removal will be observed at the cathode outlet. One technique to deter this occurrence is a ceramic cathode tube outlet. This will eliminate some potential H_2S adsorption as well as prevent downstream H_2S reformation.

Conclusion

$LiCoO_2$ has been proven to be a successful alternative to the nickel cathode. In addition, it can operate at 650 °C, which is favorable because this is the common gasifier temperature. Moreover, for our flow conditions, higher temperatures result in higher sulfide concentrations in the molten electrolyte. However, full cell runs employing $LiCoO_2$ as the cathode have been plagued by low current efficiencies. This is due to low cathode porosities, which will hopefully be increased in the near future.

Full cell H_2S removal runs with stainless steel cell housings may be limited by H_2S adsorption onto the cell housings as well as the stainless steel inlet and exit tubes. This has deleterious effects in two ways. First, cathode H_2S outlet levels require long periods of time to reach cathode inlet levels. Second, the adsorbed H_2S reacts with hydrogen in the presence of

lower non-equilibrium H_2S levels to reform H_2S . Therefore, removal experiments are more difficult to quantify.

Projected Work

This quarter, full cell runs with alumina (Al_2O_3) plasma coated stainless steel cell housings will be performed. The alumina is being plasma coated by Plasma Coatings, Inc., the same company who previously plasma coated aluminum onto the cell housings. The alumina should provide a totally nonconductive layer so that no current is lost to undesired side reactions. The outlet tube from the stainless steel cell housing will be ceramic, which is nonreactive with H_2S . Therefore, the detrimental downstream effects of H_2S adsorption can be avoided.

$LiCoO_2$ porosity will be enhanced by increasing the initial concentration of binder and poreformer. This will be accomplished without sacrificing the strength of the resulting electrode. H_2S removal full cell removal runs at $650^\circ C$ will be continued with high porosity electrodes. SEM and X-ray diffraction will be utilized to characterize the $LiCoO_2$ electrodes before and after the cell runs.

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