Quarterly Progress Report:
High Temperature Membranes for
H₂S and SO₂ Separations
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by

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Purpose and Goals of Research

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification, H_2S has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion, SO_2 has been separated from the flue gas, with concentrated SO_2 produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the H_2S cell and the SO_2 cell require more efficient membranes and the H_2S cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

I. H₂S Removal Cell

Introduction

This electrochemical removal cell cleans a product gas of H₂S by electronating the most easily reduced component of the stream. In coal synthesis gas or natural gas, this is H₂S:

A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N₂ can be used at the anode to carry away oxidized sulfide ions as vaporous S₂:

Research Summary

The process has been successfully applied to the polishing of H₂S from simulated coal gasification streams. Removal of H₂S was shown at 700°C and flow rates varying from 88 cc/min to 600 cc/min. The maximum removal recorded was 89.1% (89.5 ppm to 9.7 ppm). Work has continued using type 316 stainless steel as a housing material and some marginal success has been shown.

Experimental Run Results

Run 49

This was the fifth experimental run using coal gas. It used two tapes of MgO and one mat of zirconia cloth as the membrane matrix material. The electrodes were both lithiated NiO. The acrylic binders in the tapes of MgO were burned out under an O₂ atmosphere and the Li/K eutectic-composition electrolyte was added with the cell at run temperature. MACOR machinable ceramic housings were used instead of stainless steel housings. The inlet gases were passed through a stainless steel shift reactor to allow them to come to their equilibrium composition before passing through the cell.

This experimental run was divided into three sections: the first confirmed ionic transport through the membrane by removal of CO₂ (and H₂O) from the syn-gas at 625°C (Run 49A), the second was an attempt at removal of H₂S from the syn-gas at 625°C (run 49B), and the third was an attempt at removal of H₂S from the syn-gas at 700°C (Run 49C). The results of these studies are presented below:

Run 49A

CO₂ removal from the process gas as a function of applied current was recorded and is presented in Table 1. Examination of this data shows that the removal of CO₂ from the cathode side of the cell and production of CO₂ at the anode side of the cell is stoichiometric across the range of applied currents examined.

Fuel gas flow was set at 75 cc/min and N₂ sweep was set at 63 cc/min. Seals were good and no cross-flow between the two process streams was observed.

Table 1.
Run 49A Recorded Data.

<u>Applied</u> <u>Current (mA)</u>	<u>Actual</u> <u>Cathode</u> <u>CO₂ Out</u>	<u>Calc.</u> <u>Cathode</u> <u>CO₂ Out</u>	<u>Actual</u> <u>Anode</u> <u>CO₂ Out</u>	<u>Calc.</u> <u>Anode</u> <u>CO₂ Out</u>
0	17.8%	17.8%	0.0%	0.0%
100	16.8%	16.8%	1.8%	1.2%
200	15.8%	15.7%	2.8%	2.4%
300	15.2%	14.7%	3.8%	3.7%

This data shows that the cell was functioning properly with respect to ionic transport of carbonate through the electrolyte.

After 2.65 hours with current applied, cross-flow between the cathode and the anode was observed, indicating that the ceramic matrix was damaged. Over the next 13.25 hours, 10.5 grams of electrolyte were added to the cell in order to stop this cross-flow by flooding any matrix cracks with electrolyte. Cross-flow between the two process streams was stopped in this manner and H₂S removal with applied current was then examined.

Run 49B

After 22.3 hours exposure to fuel gas at 625°C, an exit H₂S composition of 27.7 ppm was recorded. A current of 5 mA was applied to the cell (0.63 mA/cm², superficial electrode area = 7.92 cm²). After 27.7 hours with applied current, no

significant removal of H_2S was observed. Examination of the limiting current densities at these run conditions shows that at 625°C the gas phase limiting current density is only 1.1 mA/cm^2 while the membrane limiting current density is only 1.4 mA/cm^2 . This membrane limiting current density assumes an electrolyte diffusivity of $10^{-5} \text{ cm}^2/\text{sec}$. Once membrane porosity and tortuosity are taken into account, this estimate is in all probability too large. As an 'order-of-magnitude' estimate, however, it does show that the transport through the membrane is on the same order as the transport through the gas phase. It is probable that at these temperatures, the membrane cannot support the necessary flux of sulfide ion to significantly affect the exit H_2S concentration. Further study at these temperatures is required before this statement can be made with confidence.

Run 49C

Cell temperature was increased to 700°C . At this temperature, analysis of limiting current densities within the system shows that the gas phase limiting current density is 1.15 mA/cm^2 while the membrane limiting current density is 3.29 mA/cm^2 . This shows that even if the electrolyte diffusivity estimate is in error, the membrane flux is three times greater at this temperature than at 625°C . H_2S removal at a variety of flowrates was observed and is tabulated in Table 2. The overpotentials reported here have not been corrected for IR loss. The measured cross-cell resistance by current interrupt was observed to be only around 1Ω . With the maximum current applied to the cell only 20 mA , this corresponds to only 20 mV of

ohmic loss. This is negligible compared to the overall cross-cell potential, which includes concentration effects, and potentials required to drive the electrochemical reactions.

Table 2.
Run 49C Recorded Data.

<u>Time</u>	<u>Applied Current (mA)</u>	<u>Cathode H₂S Out (ppm)</u>	<u>Cathode - Reference Overpotential</u>	<u>Anode - Reference Overpotential</u>
Cathode flow = 88 cc/min				
17:21 (2/16)	0	85.0	0.0	0.0
18:15	5	26.7	-0.007	0.159
19:48	5	16.0	-0.006	0.127
21:30	0	89.5	0.0	0.0
8:46 (2/17)	0	89.5	0.0	0.0
10:00	5	20.0	-0.030	0.149
12:02	1.2	42.0	N/A	N/A
12:35	2	51.5	-0.017	0.030
13:00	2	47.5	N/A	N/A
13:15	2	53.0	N/A	N/A
13:34	20	29.5	N/A	N/A
14:20	20	9.7	N/A	N/A
14:47	15	18.5	-0.023	0.099
15:07	10	25	-0.022	0.050
15:48	20	15.5	-0.033	0.106
Cathode Flow = 210 cc/min				
17:10	0	57	0.0	0.0
18:05	5	35.5	-0.014	0.127
19:00	5	30.6	N/A	N/A
20:09	10	31.5	-0.008	0.213
10:51 (2/18)	0	75.5	0.0	0.0
11:34	5	38.5	0.0	0.184
12:01	5	32	0.003	0.253
12:58	5	30	0.011	0.280
14:23	5	28.5	0.017	0.299

**Table 2 (con.)
Run 49C Recorded Data.**

<u>Time</u>	<u>Applied Current (mA)</u>	<u>Cathode H₂S Out (ppm)</u>	<u>Cathode - Reference Overpotential</u>	<u>Anode - Reference Overpotential</u>
Cathode Flow = 400 cc/min				
21:15	0	59.4	0.0	0.0
21:40	5	48.7	-0.093	0.004
21:55	5	44.5	-0.088	0.055
22:24	5	39.7	-0.081	0.099
22:48	5	39.7	-0.082	0.117
10:31 (2/19)	0	73	0.0	0.0
14:14	10	49	-0.007	0.150
14:55	10	37.3	0.002	0.280
15:34	10	38	0.007	0.293
16:16	15	37.5	0.009	0.333
17:08	15	38.3	0.014	0.343
17:55	20	38.7	0.012	0.326
Cathode Flow = 600 cc/min				
12:00 (2/20)	0	68	0.0	0.0
12:44	10	42	-0.001	0.208
13:15	10	43.3	0.0	0.273
13:45	10	48.3	0.006	0.249
14:30	20	46	0.001	0.318
15:00	20	40	0.003	0.310
15:30	20	45.3	0.003	0.365

The above data are presented graphically in Figures 1 through 4. The H₂S exit composition is plotted against run event for the 88 cc/min data in Figure 1. Note that initially, the membrane was showing process stream cross-flow. 1.5 grams of electrolyte were added to stop the cross flow and 5 mA were applied to the cell. This current level corresponds to five times the theoretical current required for complete H₂S removal. After driving the H₂S down to 16 ppm (81.2% removal, zero current

basis) the current was turned off. The exit H_2S level returned to 89.5 ppm. The lowest level to which the H_2S level was driven was 9.7 ppm (89.1% removal, zero current basis). This data shows good response of the system to applied current. The overpotential to accomplish this removal is shown by Figure 5 to be negligible.

The H_2S removal versus run event for the 210 cc/min data is shown in Figure 2. This data still shows good response of the system to applied current. More electrolyte had to be added to repair membrane damage, and thus the initial exit H_2S cathode level with no current applied is down to 57 ppm. This is due to a build-up of carbonate caused by excess electrolyte which had been added to the system.

The data taken at a flowrate of 400 cc/min is presented in Figure 3 and the data taken at 600 cc/min is presented in Figure 4. Comparison of this data with the overpotential results presented in Figure 5 shows that the efficiency of the system dropped off with time. At several points through the run, as marked on Figures 1 through 4, electrolyte was added to stop cross-over between the cathode side of the cell and the anode side. The increase in anodic overpotential shows that this excess electrolyte had flooded the anode, thus decreasing the reactive surface area from the interfacial area of the electrolyte wetting the walls of the electrode capillaries to the superficial area of the electrode when the pores were fully flooded. This was verified in the post-mortem analysis of the cell when the assembly was taken apart and the components examined. The anode flooded because it is physically on the bottom of the assembly.

A total of 18.7 grams of electrolyte was added to the membrane during the

course of the run in addition to the 11 grams that were initially added to fill the ceramic matrix of the membrane. Post-mortem examination of the membrane showed a small fracture in the matrix around the edge of the electrodes. This fracture would be temporarily flooded with electrolyte to form a gas impermeable barrier. However, aggressive attack by the electrolyte on the MACOR housings would deplete the membrane of electrolyte and lead to gas cross-flow. This problem can be overcome by the use of stainless steel housings, which are more resistant to electrolyte attack.

The cell was terminated due to flooding of the anode and poor membrane integrity after 216 hours of operation.

Run 50

This was the sixth run with coal synthesis gas. The cell housings were 316 stainless steel that had been sputtered with a 20 micron thick Al coating. The electrodes were NiO and the membrane was two tapes of MgO and two mats of ZYW-30A. Binder burnout was at 350°C under an O₂ atmosphere. Once the binder was burned out, N₂ was started to both the cathode and the anode. The cell was heated to a temperature of 700°C. Once the cell was at run temperature, a total of 20 grams of eutectic Li/K carbonate electrolyte was added. Fuel gas was then started to the cathode side of the cell. Since the membrane did not support any back-pressure without cross-over, a total of 8.3 grams more electrolyte was added to the cell. H₂S was then added to the fuel gas mixture to bring the inlet H₂S concentration to 60 ppm. 13 hours later, the exit cathode H₂S level was only 15 ppm with no current

applied to the cell. The membrane damage appeared to be around the electrode wells on the reference electrode side of the cell. This is the area through which the electrolyte is added after heat-up. The density change caused by absorbing the electrolyte could be damaging the membrane. Future runs will use a pressed disk of electrolyte layered into the composite membrane structure.

The cell was shut down 48 hours later due to uncontrollable cross-flow. No useful data was taken, however this was the first run which used the new Teledyne UV H₂S analysis system. The UV analysis tracked the usual GC results to within a few ppm (usually > 5 ppm difference).

Run 51

This run used stainless steel housings that had been painted with 29wt% Al paint. The electrodes both started as lithiated Ni and were allowed to go to NiO in situ. The membrane was two MgO tapes with one mat of ZYW-30A. 10 grams of electrolyte were pressed into a disk and load into the cell with the membrane materials. The cell was heated under an O₂ sweep until the electrolyte melted and then fuel gas was supplied to the cell (temp approx. 500°C). Cell seals were initially good and the cell responded well with respect to CO₃²⁻ transport when no H₂S was in the fuel gas. Cross cell resistance was high (1.4 Ω) so two more grams of electrolyte were added. This excess electrolyte ran out of the membrane and into the anode flow channels where it was carried by the high sweep rate (200 cc/min N₂ flow) into the anode exit tube. Here it froze once it exited the furnace and clogged the anode exit

tube. This caused a pressure build-up in the anode side of the cell which ruptured the membrane and shut down the run.

Run 52

This experimental run used lithiated NiO for both the cathode and the anode. The membrane was two tapes of MgO and two mats of ZYW-30A. The housings were identical to those used in run 51. Sixteen grams of electrolyte were pressed with 20 wt% HEC (hydroxyethyl cellulose) added as a binding agent. This pressed 'green body' of electrolyte was added to the membrane and allowed to heat up with the cell assembly as in run 51. The cell was heated with O₂ supplied to both sides of the cell. The cell was heated to 350°C and the exit CO₂ was monitored to mark the end of the binder burn-out. The cell was then heated to run temperature (700°C) but excess electrolyte once again clogged the exit anode tube. The cell was cooled to 200°C and the anode exit tube was replaced. Once the cell was reheated, no cross-flow was detected. Two hours later, the anode tube once again clogged with electrolyte. The cell was cooled down again and the anode exit tube replaced. The cell was then once again reheated. The membrane seemed to survive this temperature cycling, but the best current efficiency for CO₃²⁻ transport that could be observed was only 30%. While the membrane was able to prevent bulk process and sweep gas mixing, enough hydrogen cross-over and CO₂ back diffusion was present to offer no hope for successful H₂S removal. The cell was therefore shut down.

Run 53

This experimental run used Ni electrodes that were allowed to go to their equilibrium structures in-situ. The membrane matrix consisted of two tapes of MgO layered with two mat of ZYW-30A. The housings were identical to those used in run 52. Since the last run had excess electrolyte present in the initial electrolyte disk, only 13 grams of electrolyte mixed with 20 wt% HEC was pressed and added to this membrane. The cell was heated all the way to run temperature under an O₂ flow on both sides of the cell. The lack of CO₂ in the process or sweep gas caused the electrolyte to decompose by the following reaction:

A thermodynamic analysis of this reaction shows that the equilibrium coefficient of reaction 1 has the form:

$$K_e = \frac{P_{\text{CO}_2} a_{(\text{Li}_{0.62}\text{K}_{0.38})_2\text{O}}}{a_{(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3}}$$

However, since the activities of $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{O}$ and $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ are unity in this system, equation 2 reduces to:

$$K_e = P_{\text{CO}_2} \quad (3)$$

Thus, by analysis of the system at the run temperature of 700°C, at least 300 ppm CO₂ would have to be present in either the cathode or the anode stream to prevent the decomposition of the electrolyte.

The decomposition of the electrolyte led to matrix failure. The cell was shut

down due to this.

Run 54

This experimental run was used as a training run for the new graduate student. The housings were identical to those used in run 53. The membrane was two mats of ZYW-30A and two tapes of MgO with a pressed disk of 16 grams of electrolyte with 20 wt% HEC as a binding agent. Leaks in the tubes connecting the manometer across the cathode and the anode sides of the cell lead the student to believe that the membrane had blown and that there was bulk mixing of the process and sweep gas streams since no pressure difference across the membrane could be detected when flow on either side of the cell was throttled. The cell was therefore shut down.

Run 55

This experimental run used the same housings as in run 54. The electrodes were both lithiated Ni and were allowed to go to equilibrium composition in-situ. The membrane was two mats of ZYW-30A and two tapes of MgO with 13 grams of electrolyte with 20 wt% HEC pressed into a disk and layered into the initial structure. The cell was heated to 350°C under O₂ and allowed to remain at this temperature for 1 hour. Then fuel gas was started to the cathode side of the cell and N₂ sweep was started to the anode side. This was to prevent electrolyte decomposition as seen in run 53.

Once the electrolyte had melted, the cell carbonate transport efficiency was measured. Examination of the CO_2 removal showed that cathodic removal efficiency was close to 100% across the range of currents applied to the cell. Examination of CO_2 production at the anode showed that the production efficiency is less than 100% across the range of currents applied. This means that there was an alternative current path present at the anode. Since the housings were acting as the current collectors, if the Al coating on the anode side did not go to a homogenous layer of AlLiO_2 and thus insulate the housing wet seal area, it is possible that electrolyte which had seeped out into the wet seal area was being oxidized:

CO_2 from electrolyte oxidized in the wet seal area could escape to the furnace and would not be detected in the anode exit stream.

Once cathodic removal efficiency had been determined, H_2S was started to the cell at a level of 122 ppm. The cell spent the next four days accumulating enough sulfide in the electrolyte to carry current necessary for H_2S removal. Some current effect of H_2S was observed (cathode exit H_2S level of 35 ppm with no current applied dropping to a level of 28 ppm with 200% stoichiometric current applied). However, the shift reactor, which allows the simulated fuel gas to reach its equilibrium composition through the water/gas shift reaction:

began to clog with carbon. The reverse of the coal gasification reaction could occur at these conditions if the water level in the gas is too low:

It was thought that this reaction was happening before the water/gas shift reaction could build up sufficient water vapor to prevent the carbon monoxide from decomposing to deposit carbon. This problem was solved by hydrating the gas to a level of 3% water vapor (saturated at room temperature) before sending it into the shift reactor. To clear the shift reactor of carbon build up, air was blown through both the cathode and the anode side of the cell until the exit flow rate matched the inlet flow rate and the pressure drop through the shift reactor dropped to only a few mm of H₂O. Unfortunately, seal integrity was lost on the cathode side of the cell during this process. Seals became so bad that all gas entering the cathode side of the cell was blown into the furnace and no analysis samples could be taken. The seals were lost due to aggressive corrosion on the cathode side of the cell. It is thought that a small leak formed during the carbon clean up process. Gas exiting this leak ignited in the furnace and raised the cell housing temperature locally. This led to an increased local corrosion rate which only led to poorer gas seals and increased leakage. The cell was shut down for this reason.

Summary

Polishing application of this technology to coal gasification synthesis gas has been demonstrated with H_2S removals as high as 89.1% recorded (Run 49C). Work has proceeded with the stainless steel housings, though no successful runs demonstrating H_2S removal have yet been achieved. However, since stoichiometric CO_2 removal has been achieved with the stainless steel housings, H_2S removal will not be far behind.

Planned Work for Next Quarter

Work will continue in the polishing application of this process to coal synthesis gas. Work with the stainless steel housings will also continue. Since the key to successful use of stainless steel housings seems to be insulating the wet seal area to stop carbonate corrosion of the steel and alternative current paths by having the conductive surface of the steel housing in contact with the electrolyte. This will be accomplished by forming an intimately bound layer of Al metal on the wet seal surfaces of the stainless steel housings and then allowing the Al to go to the non-conductive and protective $LiAlO_2$ in-situ.

Figure 1.
H₂S Concentration vs Applied Current and Time, 88 cc/min, Run 49C.

Figure 2.
H₂S Level vs Applied Current and Time, 210 cc/min, Run 49C.

Figure 3.
H₂S Concentration vs Applied Current and Time, 400 cc/min, Run 49C.

Figure 4.
H₂S Concentration vs Applied Current and Time, 600 cc/min, Run 49C.

Figure 5.
Overpotential vs Applied Current and Time, Various Flow Rates, Run 49C.

II. SO₂ Removal Cell

Introduction

The key to the successful application of this removal method is the development of a membrane capable of achieving a current density of 50 mA/cm² at total voltages of approximately 1 Volt. Flooding of the electrode pores has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce a homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrode from flooding.

The technique used for construction of the ceramic membranes or 'tiles' is tape casting. The matrix material is mixed with an organic binder in a solvent. This mixture is poured at a constant thickness, maintained by an overhead doctor blade. The solvent is then allowed to evaporate, leaving the 'green' tape. This flexible tape is cut to the desired shape and pre-burned: placed in an oven at relatively low temperatures (<170° C), the tape is heated to remove a large amount of the solvent that is present before it is placed into a cell. There is far less organic binder having the possibility of being entrained within the cell as the full scale cell is brought to 400°C. The organic material is burned off in an oxygen atmosphere, leaving the desired rigid body of the porosity needed for the final tile. Electrolyte is then added at operating temperature. Pore size for the matrices used this quarter has been determined to be approximately 0.2µm.

The electrodes are Fibrex Ni sheets, commercially available, cut to a diameter of approximately 20cm^2 area. Before placement into the cell, they are oxidized to NiO, and lithiated to become a p-type semiconductor, in which conductivity increases with temperature. Resistivity at room temperature has been measured at approximately $2\ \Omega$. Current travels from the stainless steel housings to the electrode through contact made with the housing. Pore size of the electrodes used this quarter was approximately $1.0\mu\text{m}$. The electrolyte is made of a mixture of 10wt% V_2O_5 and 90wt% $\text{K}_2\text{S}_2\text{O}_7$ in all cases. The gas mixture run over the cathode (reducing) side of the cell is composed of 0.3% SO_2 , 3% O_2 , and 96.7% N_2 , except in noted cases, and all SO_2 is oxidized by platinum pellets to SO_3 prior to cell entry.

Research Summary

The production of SO_2 on the cathode side of the cell has been identified as a problem at high currents. The elimination of this side effect is of paramount interest. Research this quarter centered on the elimination of this SO_2 production in full scale cell testing. An attempt was also made to introduce the electrolyte into the cell insitu by tape casting. Three full scale tests were done with SS316 housings, at cathodic flowrates of approximately 500 cc/min.

The first run incorporated eleven pellets into the flow channel of the cathode housing. The Haldor Topsoe VK38 pellets are commercially used to oxidize SO_2 to SO_3 . They were cut and ground to fit into the flow channels, and attached to the housing with small amount of cement. It was felt that the presence of such a catalyst might reform SO_2 generated into SO_3 , allowing the chemical mechanisms of the cell

to remove this SO_3 from the stream.

The run was initiated with O_2 flow on both sides to facilitate the burnout of the polymer from the ceramic matrix. Upon initiation of the simulated flue gas flow over the cathode side, and a N_2 purge over the anode, the seal of the matrix was evaluated to be of poor quality, allowing for stream mixing, and poor cell performance. After attempts to revive the test with additional electrolyte failed, the run was terminated. Evaluation upon cooling revealed that the ceramic membrane had been fractured, thereby negating a seal. This cracking was felt to be due to mechanical difficulties rather than chemical or electrochemical. The VK38 pellets were intact and showed little color change.

The second run was of the same type, also incorporating eleven VK38 Haldor Topsoe pellets into the flow channel of the cathode housing. The ceramic matrix thickness was doubled (two tapes were pressed together) in an attempt to prevent mechanical stress fracture. In doing this, no pre-burning of the matrix was possible with the present polyvinyl butyral binder. After three failed attempts to pre-burn the 'green' tape, it was placed directly into the cell with no pre-burn. This may contribute to errors in mass balances due to the organic mixture possibly residing within the cell structure where it cannot be removed.

The cell was run with the simulated flue gas over the cathode side of the cell at a 500 cc/min flowrate, and a pure N_2 sweep over the anode side of the cell. Removal data at this flow rate can be seen to be higher than that of stoichiometric removal rates in Figure 1. This may be due to the absorption of the gas into the cell

Removal Data

Flowrate = 500 cc/min
 $I \text{ (limiting)} = 196 \text{ mA}$

Figure 1: The removal rate for the second run of the quarter.

in an attempt to reach a solubility equilibrium, or to the method of mass flow evaluation. High flow rates have presented a problem in the past, and continue to do so. New methods of evaluation of the mass flows must be developed.

As in the past, it was noticed that the polarity of the cell increased over time as seen in Figure 2, possibly due to the formation of a large, insoluble amount of sulfate at the surface of the electrode. The addition of 1g of electrolyte to the system decreased the polarity of the cell by approximately 65% at virtually constant stoichiometric removal rates. Should the reason for the increased cell polarity be the

Time vs. Potential

I (applied) = 100 mA

Figure 2: The general increase of the polarity of the cell dropped by 65% with the addition of 1g electrolyte.

formation of a layer of sulfate, such a response would be expected, as the addition of the pyrosulfate/pentoxide mixture would tend to dissolve the sulfate formation, and place fresh pyrosulfate at the gas/molten salt/electrode interface. SO_2 production at the cathode was observed as the total applied current increased.

To evaluate the SO_2 production at the cathode, the chemistry of the cell need to first be considered on the cathode side. Franke¹ shows the electrochemical

reduction of the pyrosulfate as shown in Equation (7). This reaction must occur at the electrode/electrolyte interface due to the electron transfer required.

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{x_{SO_4^{-2}} \gamma_{SO_4^{-2}}}{P_{SO_2} P_{O_2}} \right) \quad (11)$$

The SO_2 then reacts with the superoxide ion according to Equation (10) and also with sulfate ions present. For the SO_2 to enter the gas stream, it must diffuse through the electrolyte, and into the gas stream. This mass transfer action is in direct opposition to the diffusion of SO_3 from the gas stream to the electrolyte where it reacts. (SO_3 dissolves in the electrolyte, and quickly reacts with the sulfate ion to form the pyrosulfate ion.) Should the superoxide ion not be present (due to the reduction of the vanadium pentoxide) in high enough concentration at the interface, the SO_2 can escape the cell, possibly the cause of the SO_2 production. The overall cathodic cell reaction can be written as seen in Equation (8). The Nerstian potential for this reaction can be written as in Equation (11), where the activity for the gaseous species is approximated as the partial pressure in atmospheres, and the activity of the solvated species is the mole fraction times the activity coefficient. E° is the standard reversible potential, and E is the equilibrium potential. It would be

suspected that increasing the partial pressure would have the effect of pushing the equilibrium to the right, thus producing more sulfate ions, reducing the amount of SO_2 production. while lowering the equilibrium potential.

The anodic overall reaction can be written as in Equation (12), so an increase in the dissolved O_2 would increase the reaction resistance unless the availability of the SO_4^{-2} is relatively high.

After taking a reading of the cell at 100 mA and a 500 cc/min flowrate, the partial pressure was doubled, and a measure of the SO_2 generation was taken. Figure 4 shows the extrapolated values obtained. It was not known, however, how much of this change in SO_2 generation was due to the electro-chemistry of the cell, and how much was due to the oxidation (and possibly increase in activity) of the VK38 pellets in the channel. The cell was then run for an additional 24 hours to determine the long term effects of doubling the O_2 partial pressure, and additional electrolyte was added. Figure 4 shows that the effect of the doubling of the O_2 was effective in reducing the SO_2 generation by 73%, with continuing decrease as time progressed, for a relatively constant cathodic potential of -6.2 Volts. The effect of the addition of electrolyte to the potential has already been established, but the SO_2 generation was again lowered, this time initially by about 50%. As the cathodic potential began to increase, the SO_2 generation also increased. This would suggest that the theory that the formation of the SO_4^{-2} on the surface of the electrode over

SO₂ Generation Under O₂ Pressure Increase Run2

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Figure 3: The change in both the cathodic potential and SO₂ generation with the increase in P(O₂) and the addition of electrolyte.

time might be partially responsible for inability of the electrolyte to internally utilize the SO₂, as the decreasing surface area available for the dissolving of the O₂ could force the equilibrium in Equation (8) to the right-hand side in a perpetuating cycle.

Upon breakdown, the relative color of the VK38 pellets in the channel showed a change in color only for the pellets nearest the exit, suggesting that any in-channel conversion of SO₂ to SO₃ was taking place primarily at the exit, at approximately 0.36 micromoles/min based on one pellet. However, the change due to the partial pressure of O₂ present was not known. It was therefore determined that a full-scale cell test

SO₂ Generation Run 2

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Figure 4: The extrapolated SO₂ generation for Run 2 with a change in the partial pressure of O₂ from .03 atm to .06 atm.

should be implemented without the VK38 pellets in the flow channels.

Incorporated into this third test which is currently ongoing, was a 'green' tape of electrolyte, placed below the ceramic tape, for the efficient introduction of the electrolyte into the cell. This tape was made with the electrolyte comprising 78% by volume of the mixture (versus the usual 50 vol% in matrix tape-casting). The high percentage insured the a high density of electrolyte, and therefore a thinner tape to wet the matrix and pores of the electrodes. In addition, the high percentage of electrolyte minimized the amount of solid left residually by the binder in the burnout

process. The mixture turned out to be problematic, and multiple additions of solvent were needed to insure any mixing whatsoever. Additional surfactant was also added due to the tendency of the agglomerate to stick to the mixing vessel. In the actual tape casting procedure, it was difficult to maintain the homogeneity of the mixture, thus resulting in a variety of different tapes being cast from one batch. Tapes obtained varied from a very thin rubbery film to a thick, crumbling tape. The tape placed into the cell comprised of four separate castings: two somewhat flexible tapes, and two thin rubbery tapes, all cut to the cell size and pressed together.

The temperature of the cell was brought up slowly under pure O_2 on both the cathodic and anodic sides in the attempt to insure the full burnout and removal of the organics from the two ceramic and four electrolyte tapes. This may not have been achieved. As the run continued, the wet seal was determined to be virtually perfect, having the ability to withstand large pressure gradients. Furthermore, the mass flow measurements did not converge throughout the experiment, suggesting the absorption or adsorption of the gas into the organic present. Organic was observed in the exit tubes, and was cleaned. This process was to no avail as the mass balances continued to be in error, and more organic material streamed out of the cell. Measurements should therefore be considered relative only to this cell, and not compared against previous data.

Data was evaluated at $P(O_2)$ of 0.03, 0.06, and 0.12 atm, at flowrates of 500cc/min to 545cc/min. Increases from 500cc/min were due solely to the addition of O_2 . Figure 5 shows a limitation, probably due to mass transfer, on the cathode side

Tafel Plot for Varying Partial Pressures O₂

Flowrates = 500 cc/min + x% O₂, ln(i_{lim}) = 2.3

Figure 5: The variance of Overpotential (Volts) with $\ln i$ (mA/cm²). 1, 2 refers to $P(O_2) = 0.03$ atm, 3 to $P(O_2) = 0.06$ atm, and 4 to $P(O_2) = 0.12$ atm.

increasing with the partial pressure, while the anode shows a decrease in limitations with increasing partial pressure. The data is consistent at low overpotential, leading to an exchange current density (i_0) of approximately 1.28 mA/cm². This is an order of magnitude higher than determined by McHenry², but the removal rates obtained are far from stoichiometric as seen in Figure 6. The one varying line was the first data taken, suggesting that an equilibrium had not yet been established.

With the inability of the mass flows to balance, the error involved is substantial. On average, the mass balances were 50% in error. Examination of the

Applied Current vs. Removal (Based on Cathode SO_x)

Flowrate = 500 cc/min
 $I(\text{limiting}) = 196 \text{ mA}$

Figure 6: Removal rates based on cathode SO_x for varying O₂ partial pressures.

rate of SO₂ production shows a definite decrease from a partial pressure of 0.06 atm to 0.12 atm, but, for this same cell, the initial partial pressure of 0.03 has a lower production rate in the high current region, despite a large slope in the low current region (see Figure 7). The error in the mass balances denies any qualitative analysis of the effects of the O₂ partial pressure on the cell. The exceedingly high cell polarizations seen in Figure 5 at high current densities may come from the inability of the cell to remove SO₃ from the cathode stream, thus channeling the current into internal reactions. This inability of the cell to achieve lower SO₂ production may be

Applied Current vs. SO₂ Production

flowrate= 500 cc/min
 $I(\text{limiting}) = 195 \text{ mA}$

Figure 7: The production variance of SO₂ on the cathode side with various $P(\text{O}_2)$ for a constant flowrate.

due to organics present from the burnout, reducing the surface area available for mass transfer. In addition, the SO₄²⁻ formation at the surface may further reduce the available surface area, and lead to further formation of SO₂ over time. The increasing polarization of the cell over time may explaining the conflicting SO₂ production at low partial pressures, as the initial runs were done at low partial pressures, without addition of electrolyte at any point during the run. Testing of this cell is currently ongoing. Further results will be published in future reports.

Future Testing

As the formation of SO_2 probably occurs at the electrode/electrolyte interface, the possibility exists of a limitation due to an inadequate surface area. To further increase the surface area, an electrode with smaller pore size will increase the surface area, but will, at this stage be a problem due to capillary action in both the electrodes and matrix. A new matrix will need to be developed to insure the flooding of the matrix while maintaining only a wetted surface in the electrodes.

Further testing and modification of an electrolyte membrane will also be performed. Options for the membrane include changing the binder and solvent, and the volume percent of the electrolyte in such a mixture. The possibility also exists for a cold or hot pressed membrane of electrolyte. A pressed membrane is developed by pressing of loose powdered electrolyte at a pressure of approximately 1200 psi, forming a packed disk of electrolyte. A crumbling disk resulted with the first attempt at this process, possibly due to mechanical shock. A membrane of this type would have no inherent residue, thus reducing any possible reduction of surface area due to organic burnout. Further testing of this process need be done.

Modification of the mass flow analysis needs to be revised. For substantive readings to be taken, the mass balances need to converge close to or at the expected values. A measurement system needs to be developed in which the mass flows can be determined with greater precision and confidence. The high flowrates needed to achieve a current density of 50 mA/cm^2 , requires the ability to accurately read high mass flows.

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2. McHenry, D. J. Development of an Electrochemical Membrane Process for Removal of SO₂/NO_x from Flue Gas, Ph. D. Thesis, Georgia Institute of Technology, 1992.

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