

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_3 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

Work has continued on application of this technology to polishing H₂S from simulated coal gasification process streams. Both stainless steel and MACOR housings were successfully used, with 98% (100 ppmv H₂S to 2 ppmv H₂S) removal observed at a flow rate of 230 cc/min and a process temperature of 700°C with stainless steel housings (Run 57) and greater than 80% (11 ppmv H₂S to less than 2 ppmv H₂S) at a flow rate of 100 cc/min and a temperature of 650°C with MACOR housings (Run 65). Work has continued with attempts to increase removal efficiency by increasing the density of the membrane and slowing down H₂ diffusion from the cathode side to the anode side of the cell.

A. Experimental Run Results

Run 56

This experiment used lithiated Ni as both the cathode and the anode of the cell. The membrane was two tapes of MgO suspended within an acrylic binder layered with two mats of zirconia cloth. This was layered with a pressed electrolyte disk which used hydroxyethyl cellulose (HEC) as a binder material. These electrodes and membrane were loaded into a set of new 316 stainless steel housings which were painted with aluminum paint.

The cell was then heated to the binder burnout temperature of 350°C under pure O₂ at a rate of 200°C per hour. Once at the burnout temperature, N₂ was started to the cell and the cell was heated to 420°C. At this temperature, fuel gas (14.5% CO₂, 46.5% CO, 34.3% H₂, 6.1% H₂O, and 106 ppm H₂S after shift reaction at run temperature of 700°C) was started to the cell and the furnace was heated to 700°C. Under these conditions, the equilibrium sulfide level in the membrane should have been 0.6 mole%. The gas phase limiting current density was calculated as 1.22 Ma/cm² and the membrane limiting current density was estimated as 1.87 Ma/cm².

H₂S removal data (presented in Figure 1) and cross-cell potential data (presented in Figure 2) were recorded. While some H₂S removal was recorded, current efficiencies were unacceptably low (with stoichiometric current at this concentration and flow rate being only 3 mA applied current). Current efficiency was low due to H₂ cross-over and the presence of a possible alternative current path.

After cell shut-down, carbon build-up between the electrodes in the membrane was observed. This may have been caused by pyrolyzed HEC since this was not observed in runs which did not use HEC as an electrolyte binder.

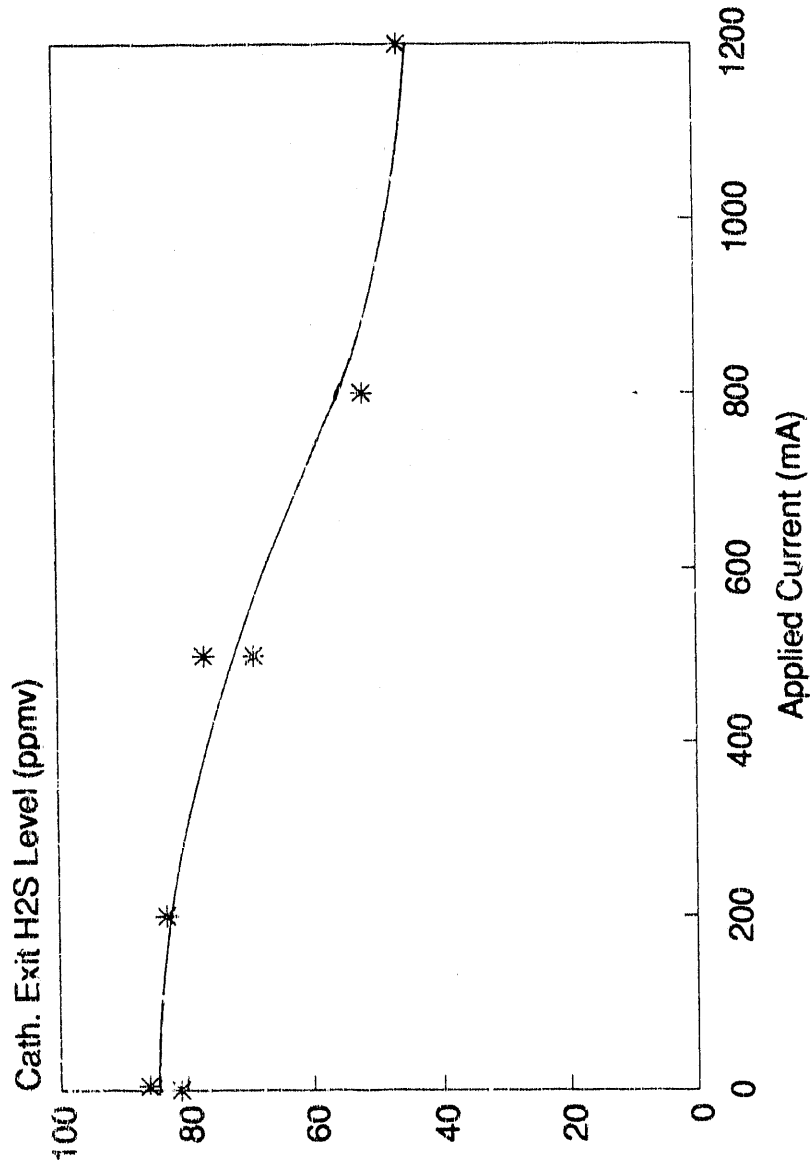
Run 57

Both electrodes in this experiment were lithiated Ni. The membrane was two tapes of MgO with two mats of zirconia cloth. One of the zirconia mats was cut with a wick extending out of the cell and resting in an electrolyte reservoir. This was to provide a continuous supply of electrolyte to the membrane in the event of electrolyte evaporation/reaction with the cell materials. The electrolyte loaded into the cell was 0.8 mole% sulfide in a carbonate supporting electrolyte. Eutectic carbonate electrolyte was loaded into the reservoir. The cell housings were 316 stainless steel painted with aluminum.

After binder burn-out and the cell had reached run temperature, fuel gas of final composition 14.4%CO₂, 45.1% CO, 6.2% H₂O, 34.2% H₂, and 113 ppmv H₂S was fed to the cell. This gives an equilibrium sulfide level in the electrolyte of 0.63 mole% sulfide. The gas phase limiting current density under these conditions was estimated to be 1.28 mA/cm² and the membrane limiting current density was estimated at 1.97 mA/cm².

H₂S removal data (presented in Figure 3). Removal of H₂S below 2 ppmv (GC detector limit) was recorded with only 5 mA (0.63 mA/cm²) applied to the cell and a cross cell potential of only -275 mV (cathode to anode). Upon shutting off applied

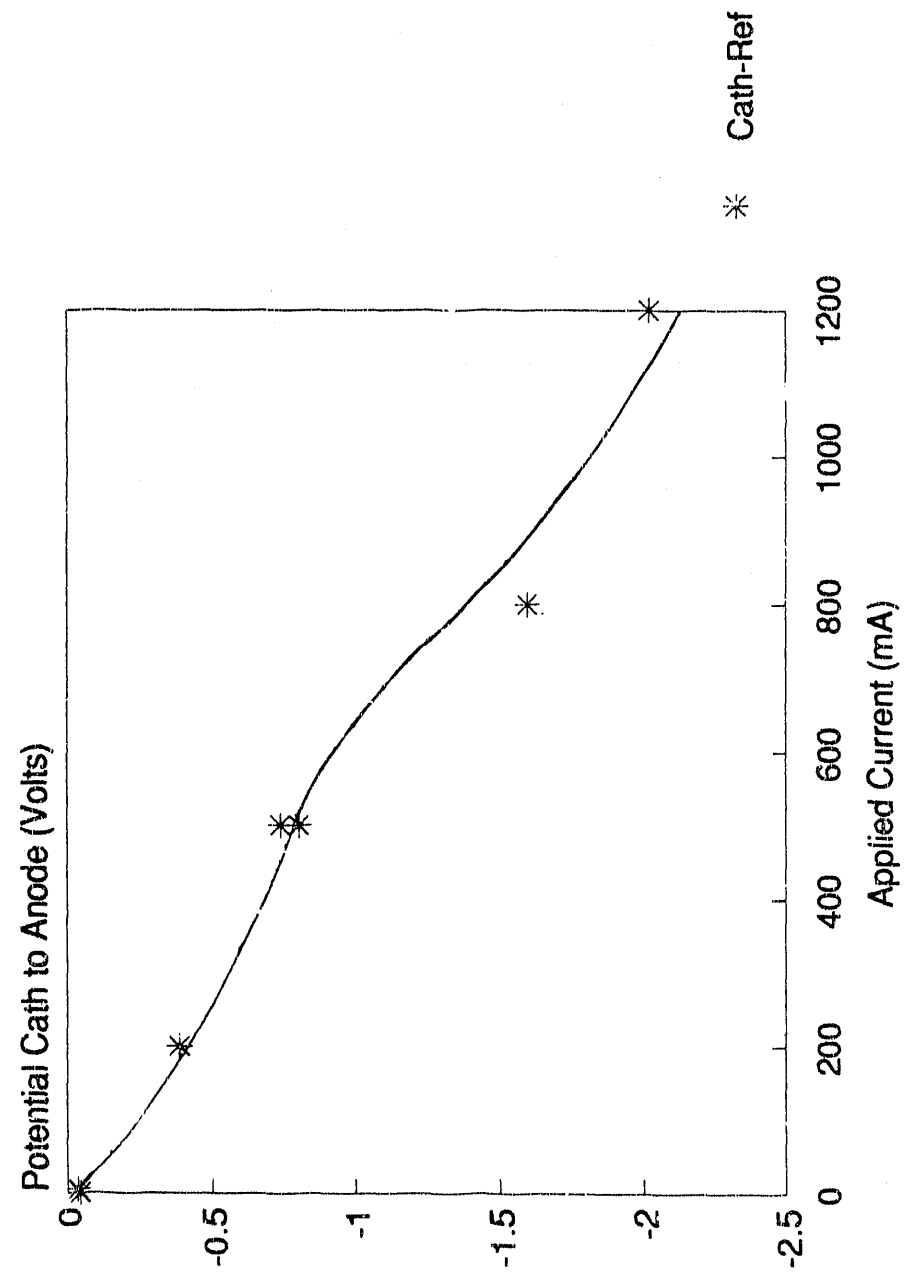
Exit H2S Level vs Applied Current Run 56



Inlet H2S = 96 ppmv
Cathode Flow = 235 cc/min
Temp = 700 C

Figure 1

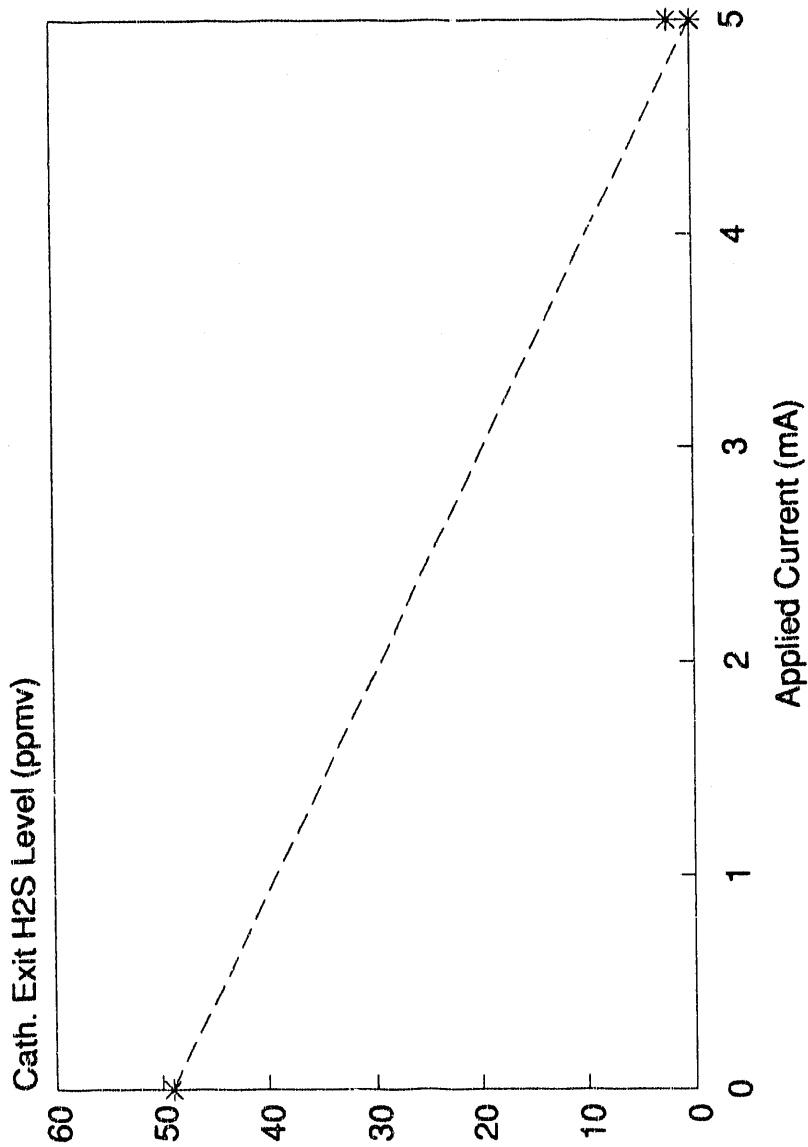
Cross-Cell Potential vs Applied Current Run 56



* Cath-Ref

Figure 2

Exit H2S Level vs Applied Current
Run 57



Inlet H2S = 110 ppmv
Cathode Flow = 230 cc/min
Temp = 700 C

Figure 3

current, exit H_2S levels only returned to 24 ppm (113 ppm entering the cell). The electrolyte reservoir was removed since it was a potential carbonate sink for reaction with H_2S in the gas. Cell cross flow started soon after this and the cell was shut down. Apparently, electrolyte was wicked out of the membrane onto the surface of the steel housings thereby depleting the membrane of electrolyte and allowing gas cross-over.

Run 58

This experimental run also used lithiated Ni electrodes. In this experiment, the membrane was a hot pressed Molten Carbonate Fuel Cell (MCFC) membrane provided by Gas Research Institute (GRI). This structure is a 50/50 weight mixture of $LiAlO_2$ and eutectic Li/K carbonate. The housings were MACOR (with a stainless steel coil in the feed gas line to act as a shift reactor) and aluminum foil gaskets were used. Excess Li_2CO_3 (for reaction with the Al gaskets in conversion to $LiAlO_2$) was sprinkled on the membrane surface with enough Li_2S to bring the electrolyte to 0.8 mole% sulfide.

After the electrolyte was molten, fuel gas with composition 17.3% CO_2 , 42.2% CO , 3.3% H_2O , 37.1% H_2 , (after shift reaction) and 117 ppmv H_2S was fed to the cell. This gives an equilibrium sulfide level of 0.65 mole%. The calculated gas phase limiting current density at this temperature was found to be 1.31 mA/cm^2 and the membrane limiting current density was estimated to be 1.53 mA/cm^2 .

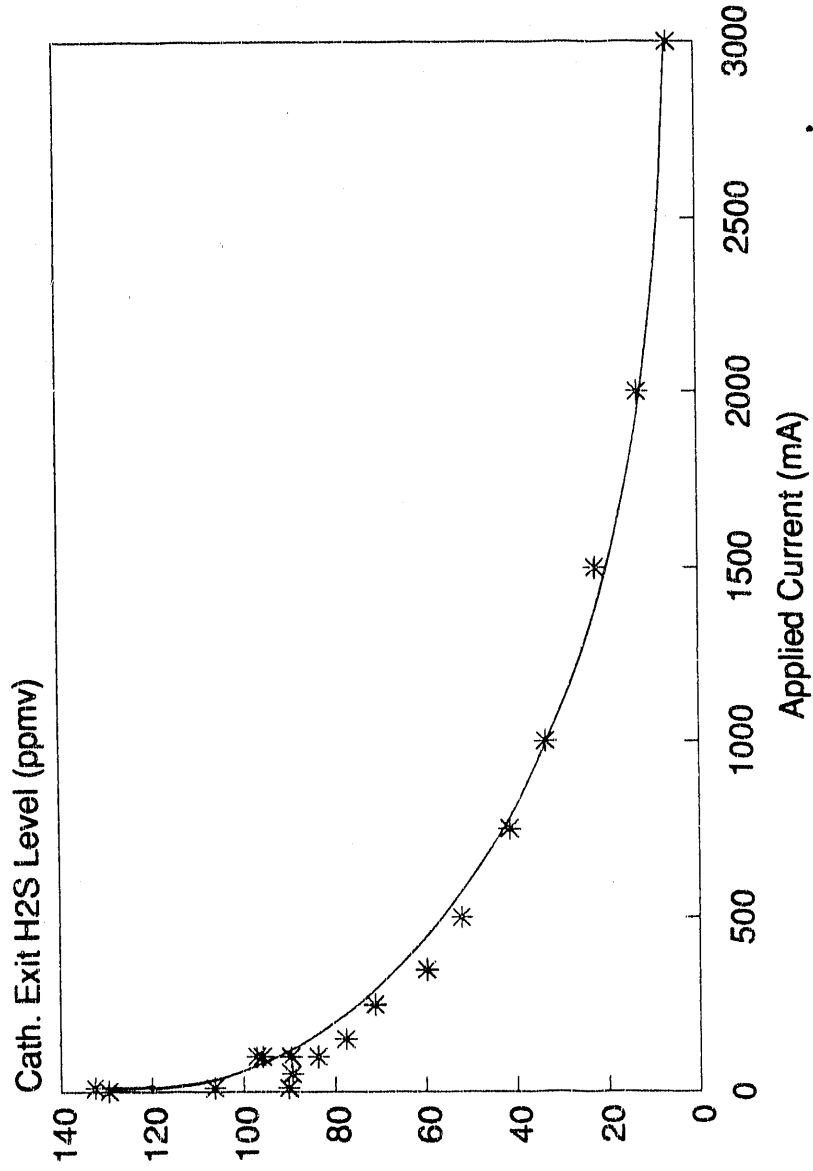
H₂S removal data (see Figure 4), anodic CO₂ production data (see Figure 5), and cross-cell potential data (see Figure 6) was taken. Examination of Figure 4 shows the most dramatic H₂S reduction takes place at currents less than 10 mA (1.23 mA/cm²). Beyond this, diffusion of H₂ across the cell decreases H₂S current efficiencies in favor of CO₂ production with applied current. Cross-cell potentials were very high at large applied currents (> 500 mA). This was due to concentration effects as the cathode gas was depleted of H₂O by the carbonate transport reaction. H₂S levels were driven as low as 6 ppmv even with H₂ cross-over.

Run 59

This experimental run used two mats of zirconia cloth that were densified from 83% voids to 72% voids by soaking in an ethyl alcohol slurry of LiAlO₂ (slurry 20 wt% LiAlO₂). Particles of LiAlO₂ were suspended within the ZrO₂ mesh after the water was evaporated away. No tapes of MgO were used in this experiment. The electrodes were both lithiated nickel. The electrolyte was pressed and loaded as a disk into the cell prior to heat-up. The electrolyte composition was 0.8 mole% sulfide and the balance was eutectic carbonate. The housings were MACOR and aluminum foil gaskets were used.

After melting the electrolyte into the matrix, fuel gas of composition 14.4% CO₂, 45.1% CO, 6.2% H₂O, and 34.2% H₂ (after shift reaction) with 85.7 ppm H₂S was started to the cell. This gives an equilibrium sulfide level of 0.48 mole %. The gas phase limiting current density was estimated to be 1.06 mA/cm² and the membrane

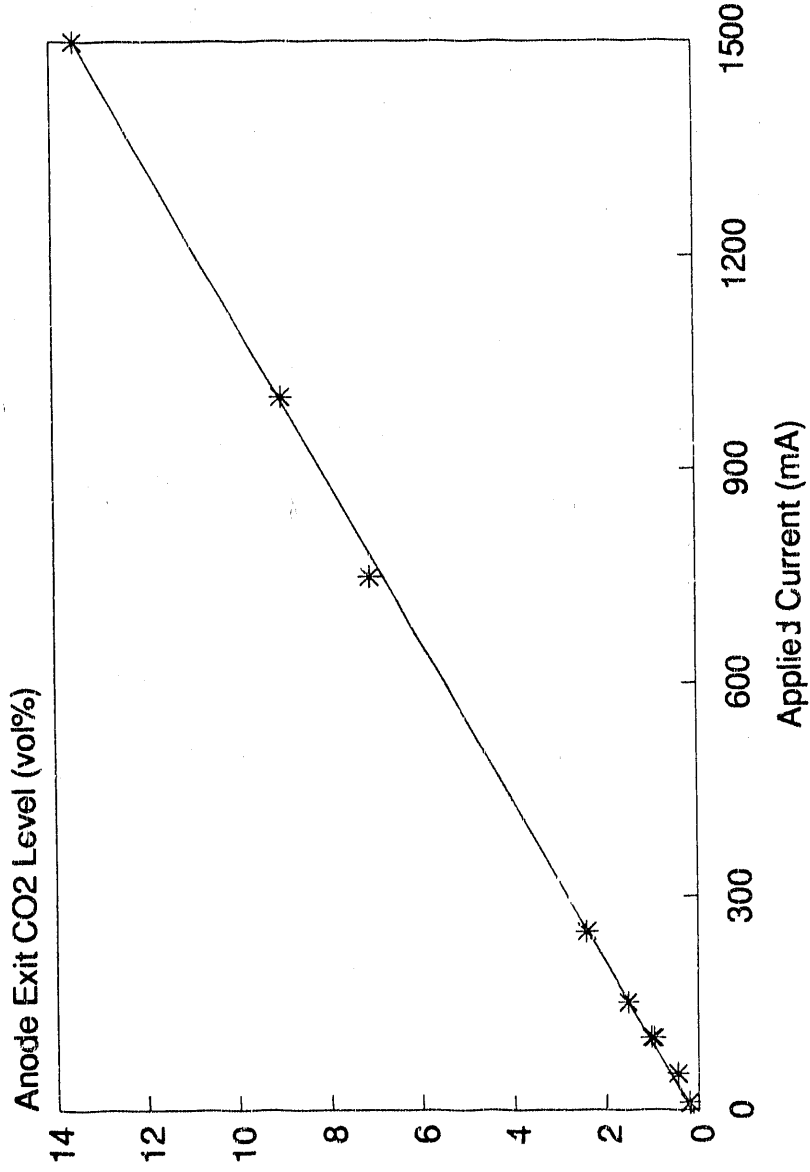
Exit H2S Level vs Applied Current Run 58



Inlet H2S = 117 ppmv
Cathode Flow = 200 cc/min
Temp = 700 C

Figure 4

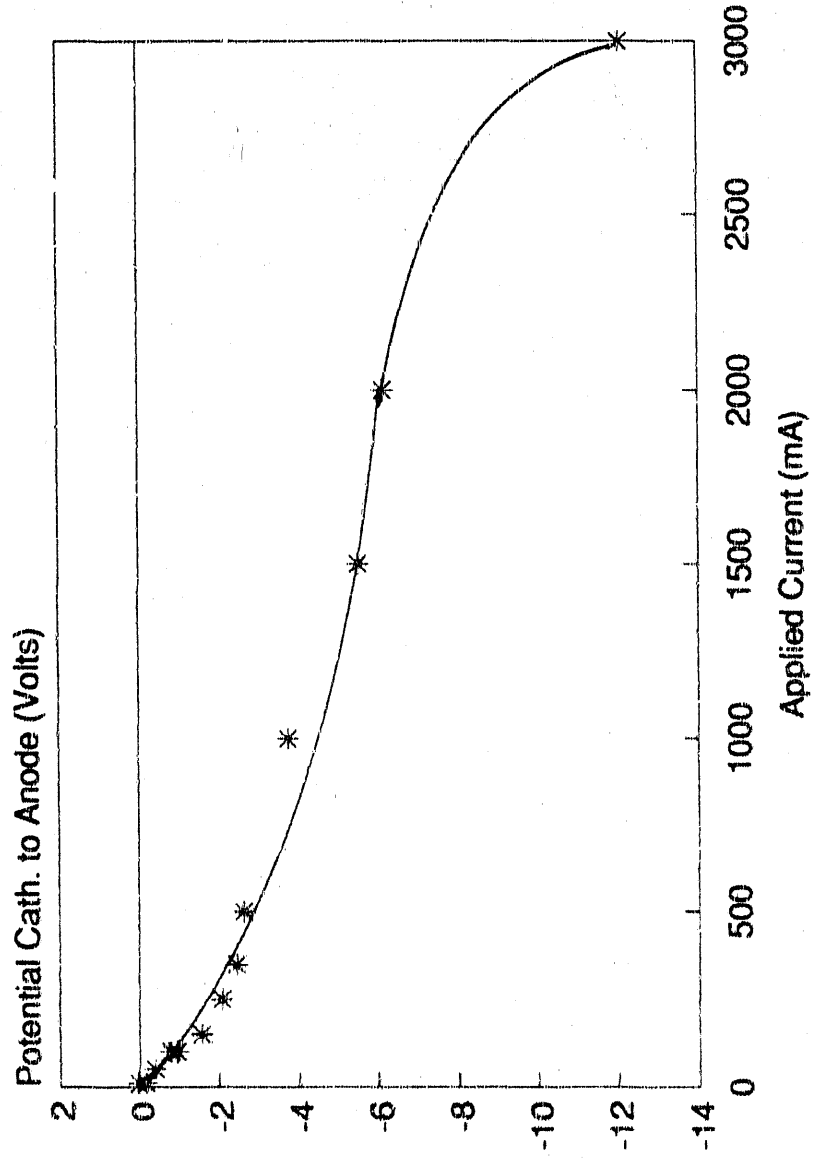
Exit Anode CO2 Level vs Applied Current Run 58



Inlet CO2 = 0 vol%
Anode Flow = 175 cc/min
Temp 700 C

Figure 5

Cross-Cell Potential vs Applied Current Run 58



Cathode Flow = 200 cc/min
Anode Flow = 175 cc/min
Temp = 700 C

Figure 6

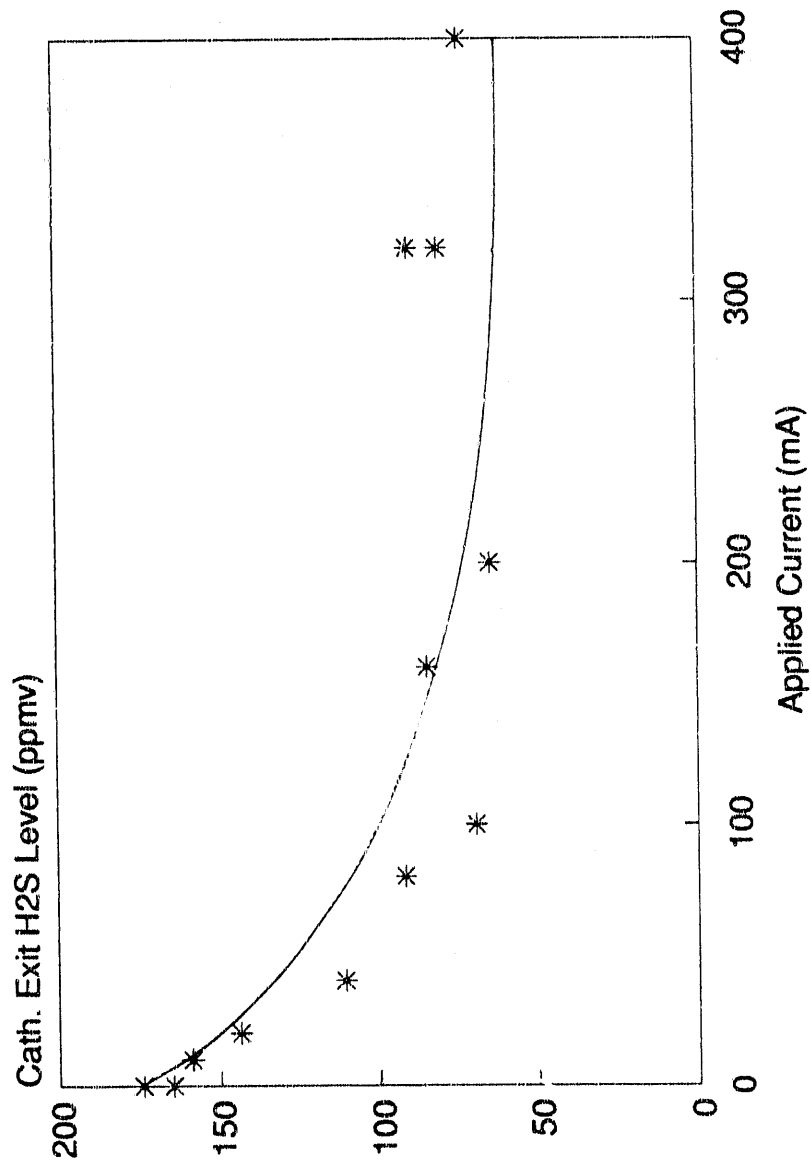
limiting current density was estimated to be 1.5 mA/cm^2 .

H_2S removal data (see Figure 7) and cross-cell potential data (see Figure 8) were taken. The inlet H_2S level was 85.7 ppm, but with zero current applied to the cell, the exit H_2S level was seen to be 165 ppm. This was due to excess sulfide initially present in the electrolyte. With application of current, H_2S levels were driven as low as 73 ppm with 400 mA applied to the cell (50.5 mA/cm^2). Hydrogen cross over hampered H_2S removal efficiency causing higher current levels to be needed to achieve removal. With higher currents came higher cross-cell potentials until the carbonate transport region was reached. Here, H_2S removal stopped due to the concentration preference for carbonate transport.

Run 60

This experimental run used two zirconia mats that were densified with sub-micron particles of ZrO_2 in aqueous solution purchased from Zircar, Inc. This rigidizer is composed of 44 wt% ZrO_2 , 8 wt% Acetic acid, 3 wt% Y_2O_3 , in an aqueous slurry. Mats were densified by soaking in rigidizing solution under a vacuum to pull air out of the woven cloth and facilitate complete wetting. These were then dried and soaked again. This process was repeated for three consecutive soakings. These mats were densified to 66 vol%. The electrolyte was 0.8% sulfide and was pressed into a disk and loaded into the cell to be melted in-situ. The electrodes were lithiated nickel and the housings were MACOR with aluminum foil gaskets.

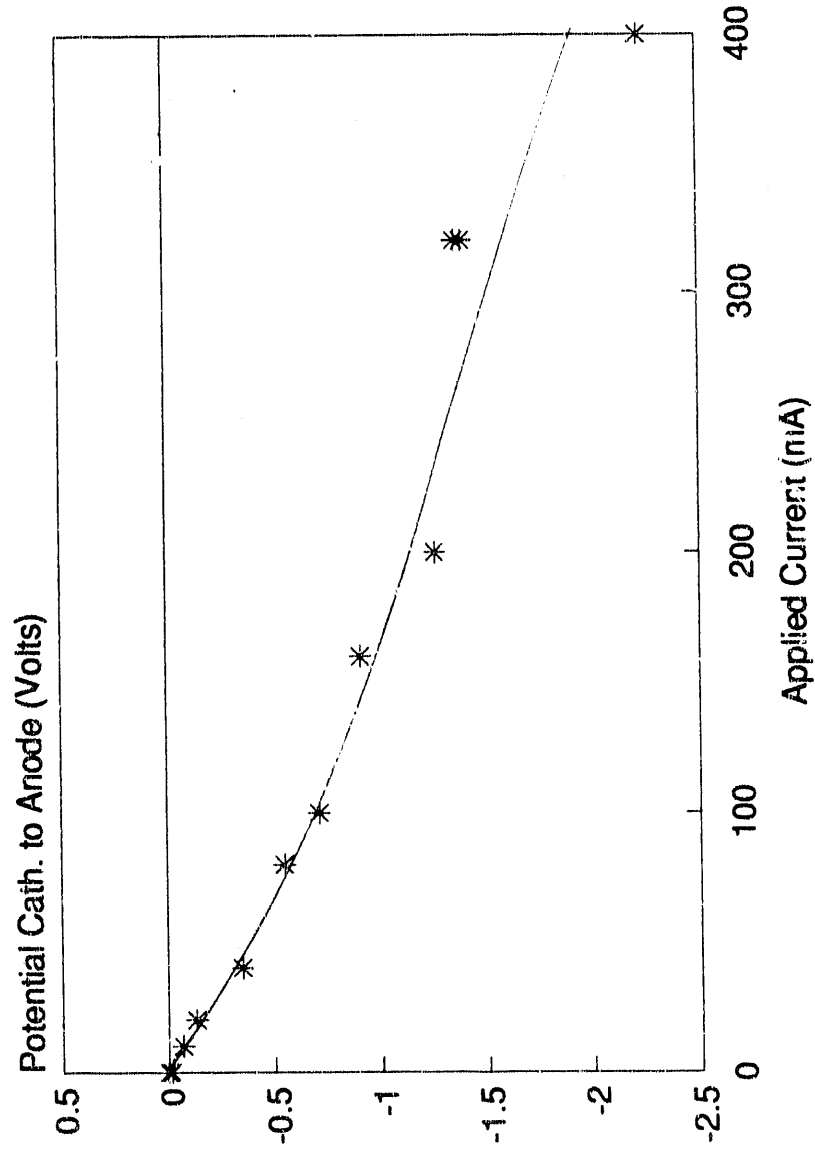
Exit H2S Level vs Applied Current Run 59



Inlet H2S Level = 85.7 ppmv
Cathode Flow = 237 cc/min
Temp = 700 C

Figure 7

Cross-Cell Potential vs Applied Current Run 59



Cathode Flow = 237 cc/min
Anode Flow = 100 cc/min
Temp = 700 C

Figure 8

Poor electrical contacts between the electrodes and the membrane lead to high cell resistance and high cross-cell potentials. The cell was shut down before any useful data was taken.

Run 61

This experimental run was identical in set up to run 60. Excess electrolyte was also added to accommodate reaction of Li_2CO_3 with the Al foil to form LiAlO_2 . The rate of this reaction is evidently slow, however, since the excess electrolyte flooded the anode channels and froze in the exit anode tube. This caused a pressure spike on the anode side of the cell which ruptured the membrane. The cell was shut down before any useful data was taken.

Run 62

This experimental run was also identical in set-up to run 60. The zirconia mats were densified to 64 void %. Only enough electrolyte was added to wet the membrane, extra electrolyte was slowly added after the cell had reached run temperature to react with the Al gaskets.

Once the electrolyte had melted, fuel gas of composition 14.4% CO_2 , 45.1% CO , 6.2% H_2O , 34.2% H_2 (after the shift reaction at 700°C) with 120.4 ppmv H_2S . H_2S removal data was taken at 216 cc/min and a temperature of 700°C . At this temperature and gas composition, the equilibrium sulfide level in the electrolyte is calculated to be 0.68%. The gas phase limiting current density is 1.33 mA/cm^2 and

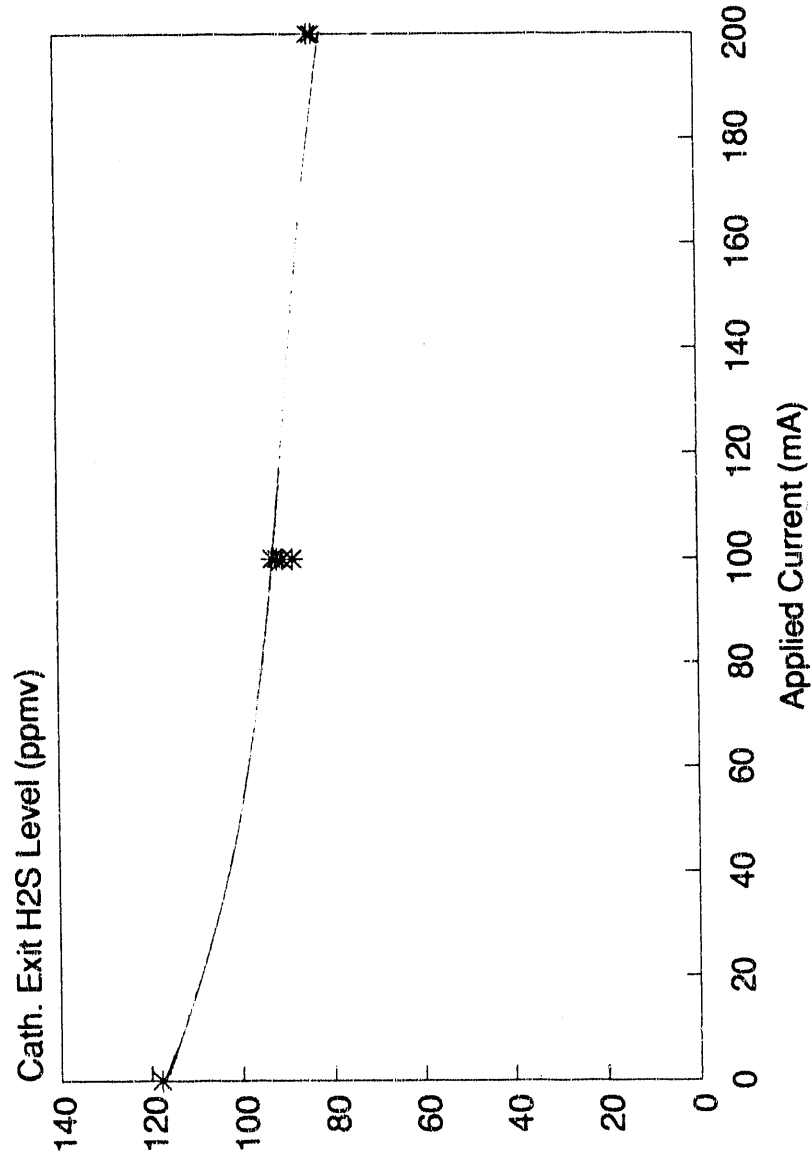
the membrane limiting current density is 2.10 mA/cm^2 . A second set of H_2S removal data was taken at a flow of 100 cc/min and a temperature of 750°C (gas composition $13.6\% \text{ CO}_2$, $45.8\% \text{ CO}$, $6.9\% \text{ H}_2\text{O}$, $33.4\% \text{ H}_2$ with $93.6 \text{ ppmv H}_2\text{S}$) (see Figures 9 and 10). At this temperature and gas composition, the membrane equilibrium sulfide level was estimated to be $0.91 \text{ mole\% sulfide}$. The gas phase limiting current density was estimated to be 1.15 mA/cm^2 and the membrane limiting current density 2.82 mA/cm^2 . Anodic CO_2 production was also monitored (see Figures 11 and 12) and cross-cell potentials were recorded for 100 cc/min and run temperature of 750°C (see Figures 13). Comparison of Figures 9 and 10 shows that H_2S removal efficiency is improved by lower flow rates (higher residence time) and higher temperatures (higher limiting current densities).

Run 63

This experimental run used Si_3N_4 tapes with vinyl binder as the membrane support material. Eutectic carbonate electrolyte was also added to the membrane by mixing in a 50/50 weight mixture with the same binder material and laminating the structure together under pressure. The electrodes in this experiment were both lithiated Ni and the housing was MACOR. No aluminum foil gaskets were used.

The cell was heated under O_2 to 520°C . Cross-flow between the cathode and the anode side of the cell indicated that the membrane had lost integrity. No amount of electrolyte added corrected the situation. The cell was shut down before any useful

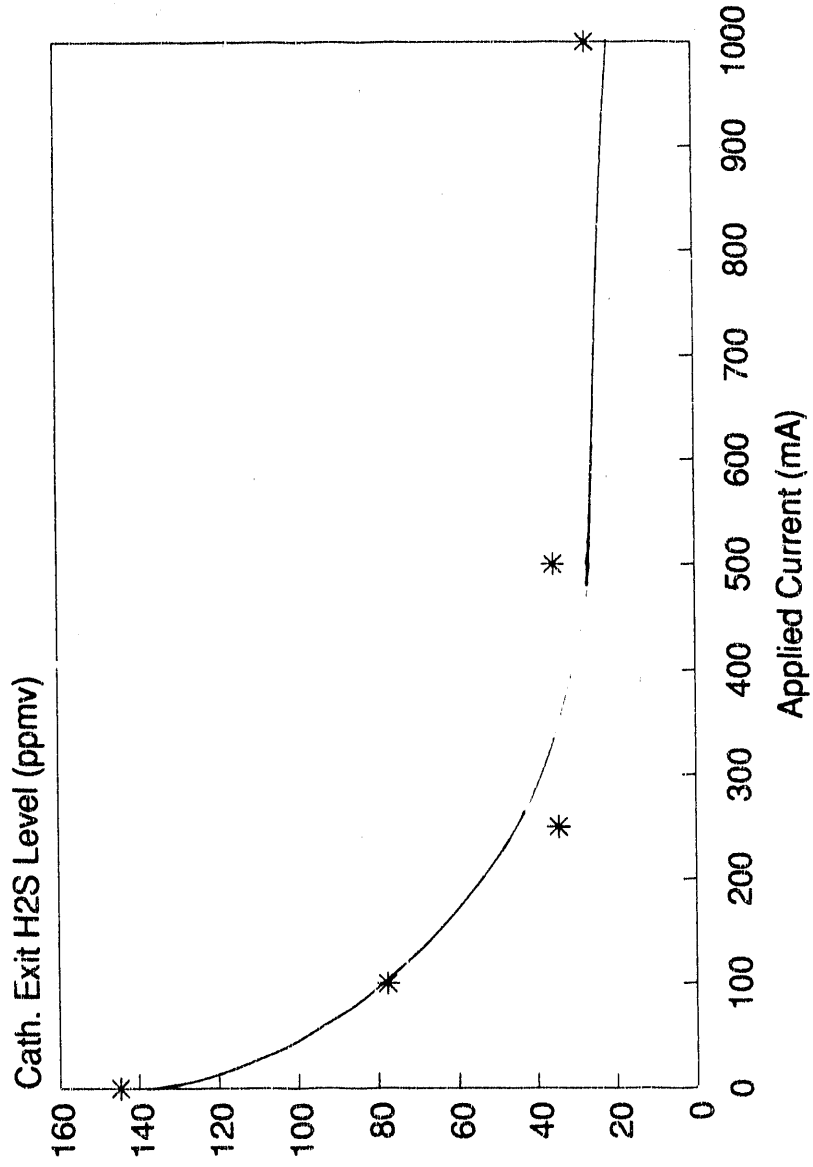
Exit H2S Level vs Applied Current Run 62



Inlet H2S Level = 120.4 ppmv
Cathode Flow = 216 cc/min
Anode Flow = 42 cc/min

Figure 9

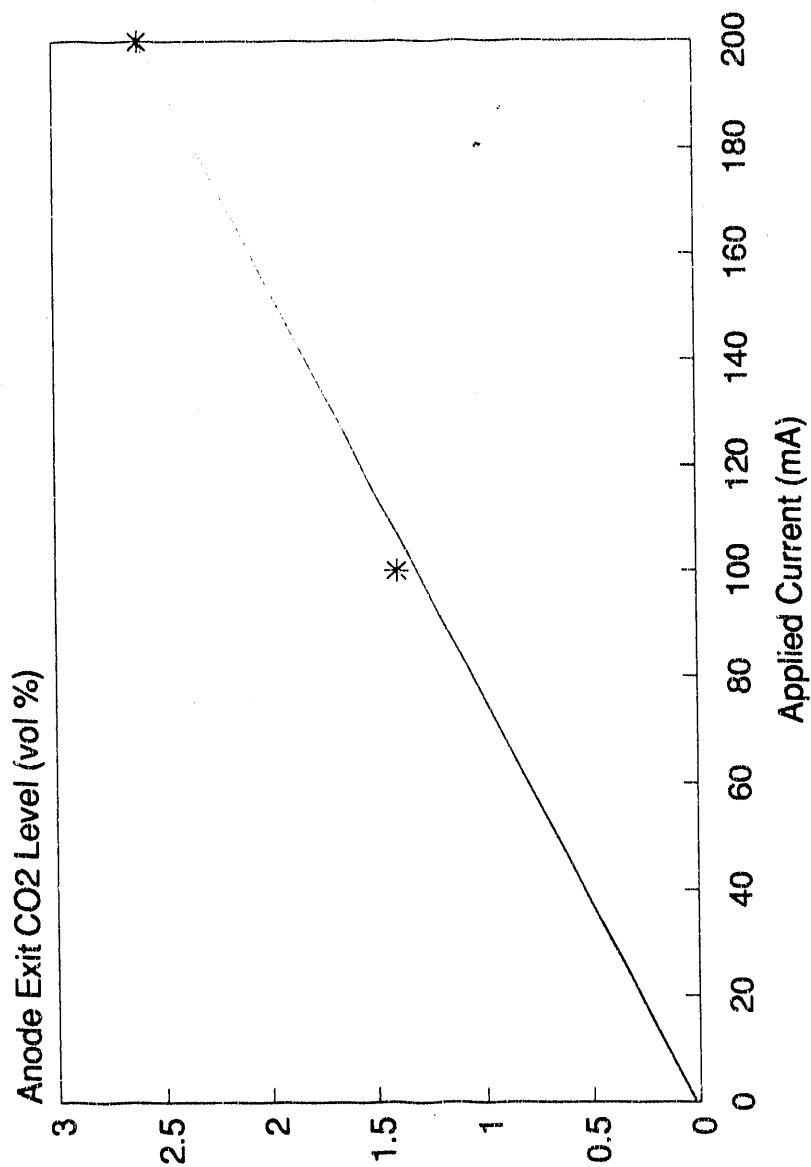
Exit H2S Level vs Applied Current Run 62



Inlet H2S Level = 93.6 ppmv
Cathode Flow = 100 cc/min
Temp = 750 C

Figure 10

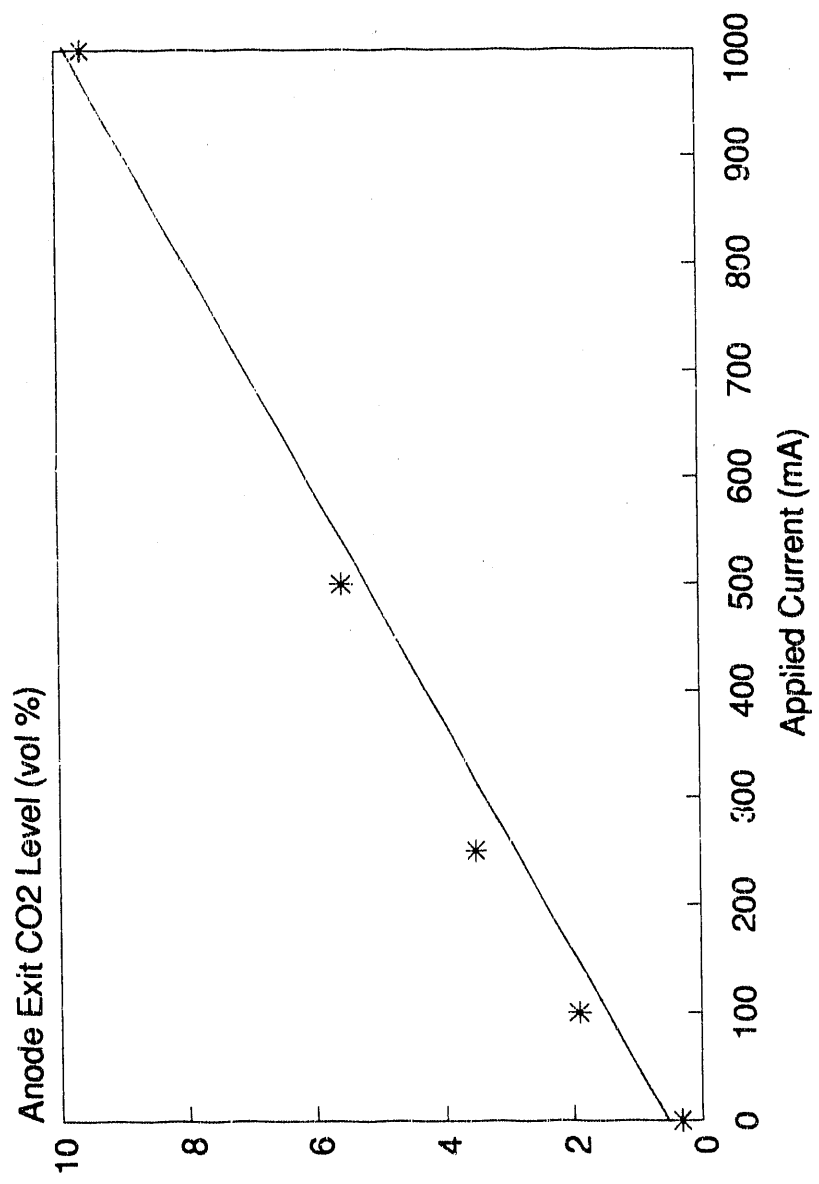
Exit Anode CO2 Level vs Applied Current Run 62



Inlet CO2 Level = 0%
Anode Flow = 42 cc/min
Temp = 700 C

Figure 11

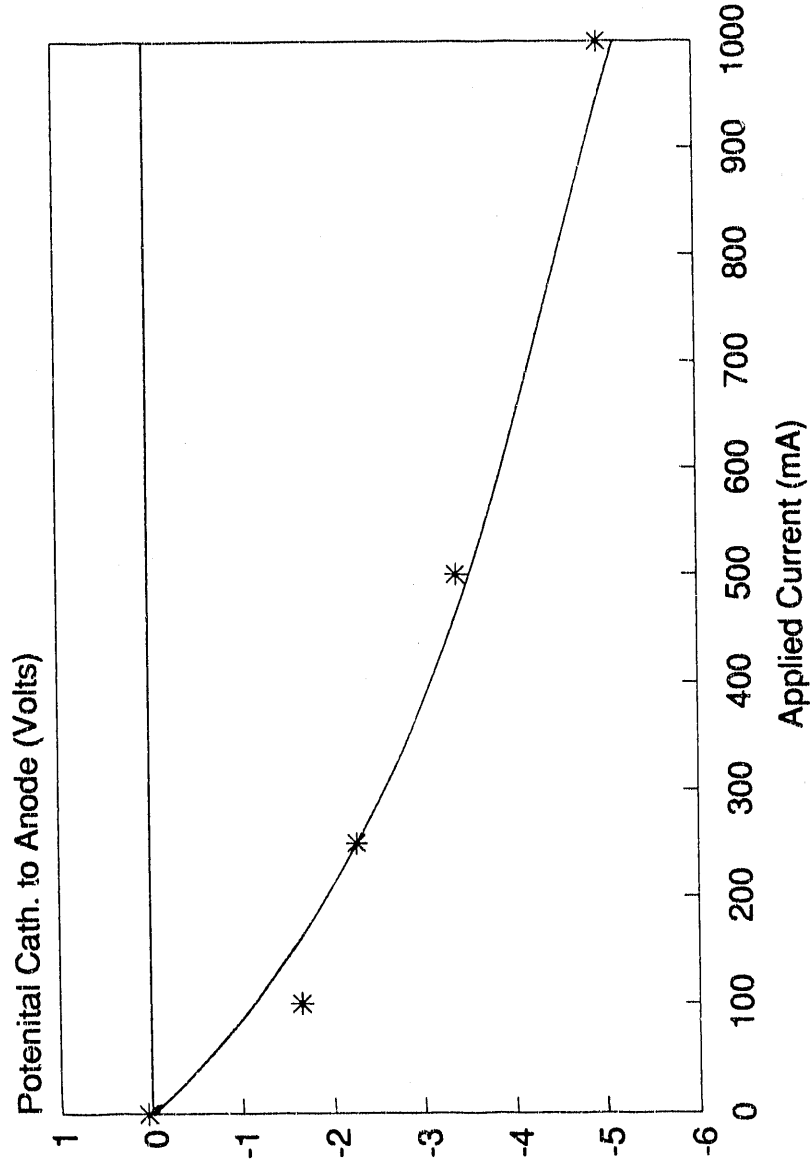
Exit Anode CO2 Level vs Applied Current Run 62



Inlet CO2 Level = 0%
Anode Flow = 58 cc/min
Temp = 750 C

Figure 12

Cross-Cell Potential vs Applied Current Run 62



Cathode Flow = 100 cc/min
Anode Flow = 58 cc/min
Temp = 750 C

Figure 13

data could be taken.

Run 64

This experimental used lithiated Ni as both the cathode and the anode. The membrane was a single mat of 15 mil thick zirconia cloth which was rigidized to 66 void%. This was layered with two tapes of MgO within the vinyl binder. The housings were MACOR and no gaskets were used. The electrolyte was soaked into the electrodes previous to run start-up. Since the electrodes could not hold all of the required electrolyte, the remainder was sprinkled onto the membrane before assembly.

The cell was heated under O₂ to 300°C over a 3 hour period and then switched to N₂ for the final heating to 600°C. No seals were formed on either side of the cell. Cross-flow between the cathode and the anode could not be controlled. When the cell was shut down, it was seen that carbon build-ups had formed the cell housings apart and damaged the membrane. This was from pyrolyzed binder material from incomplete burn-out. No useful data was taken.

Run 65

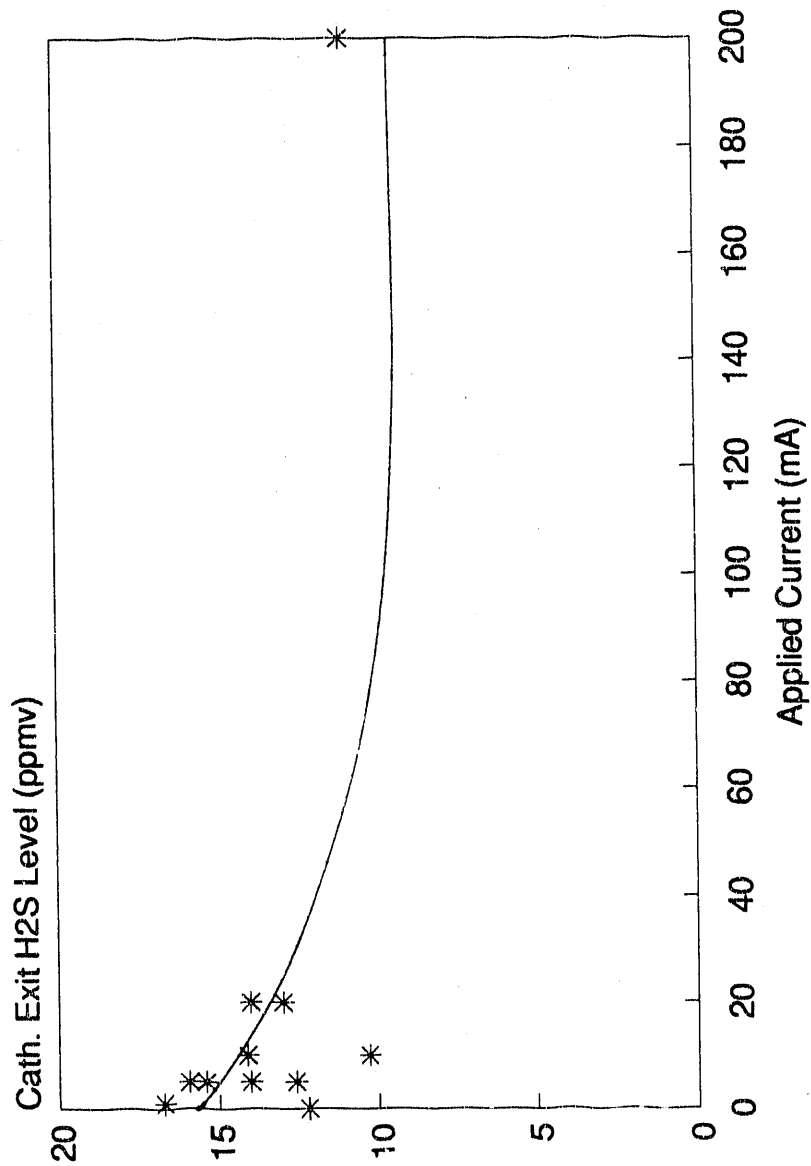
This experimental run used 1 mat of 30 mil zirconia cloth which was rigidized to 60.8% and two tapes of MgO/ZrO₂ in vinyl binder. The electrolyte was eutectic carbonate and was added to the cell as a pressed disk. the electrodes were lithiated

Ni. The housings were MACOR and Al foil gaskets were used. The run temperature was 650°C.

After binder burnout and electrolyte melting, fuel gas of composition 15.2% CO₂, 44.2% CO, 5.4% H₂O, 35.0% H₂ with 18.8 ppmv H₂S was put through the cell. This gas composition and temperature gives an equilibrium membrane sulfide level of 0.06 mole% sulfide. The gas phase limiting current density is estimated to be 0.18 mA/cm² and the membrane limiting current density is 0.34 mA/cm².

H₂S removal data was taken at cathodic flow rates of 200 cc/min and 100 cc/min (see Figures 14 and 15). Cell polarization data was also take at these flow rates (see Figures 16 and 17). Anodic CO₂ production data was also taken at cathodic flow of 100 cc/min (see Figure 18).

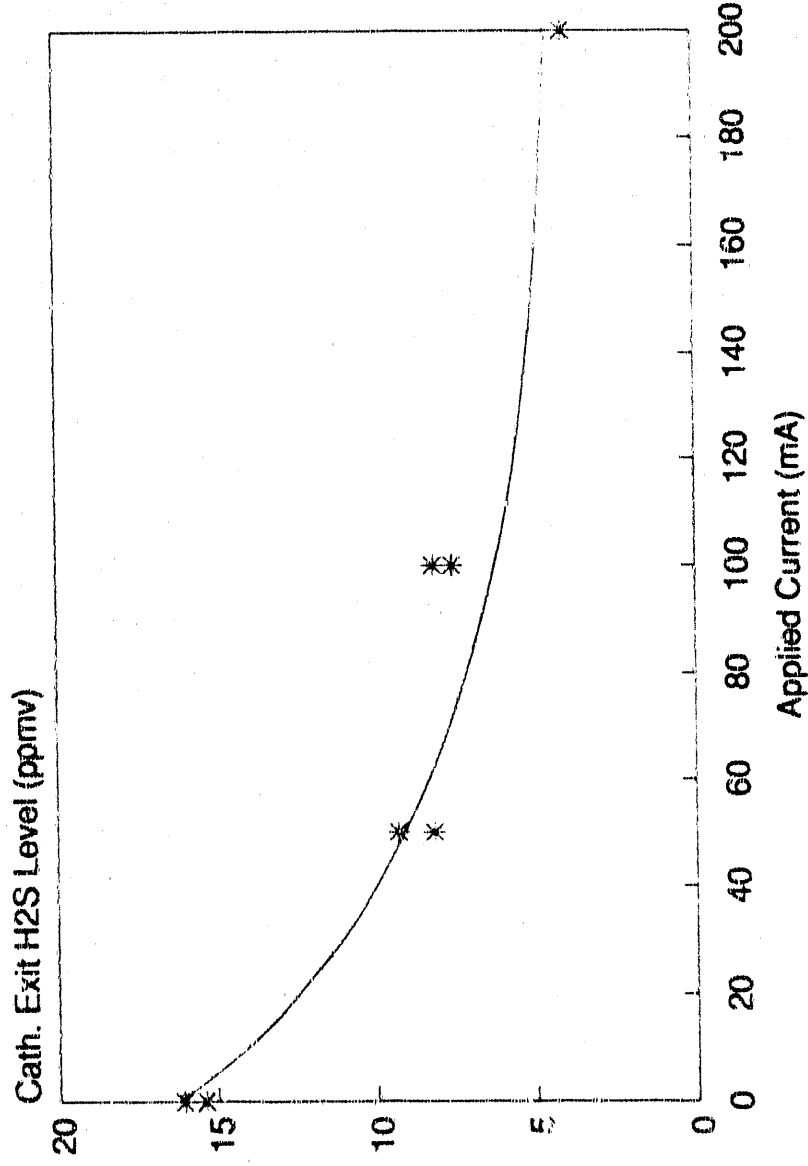
Exit H2S Level vs Applied Current Run 65



Inlet H2S Level = 18.8 ppmv
Cathode Flow = 200 cc/min
Temp = 650 C

Figure 14

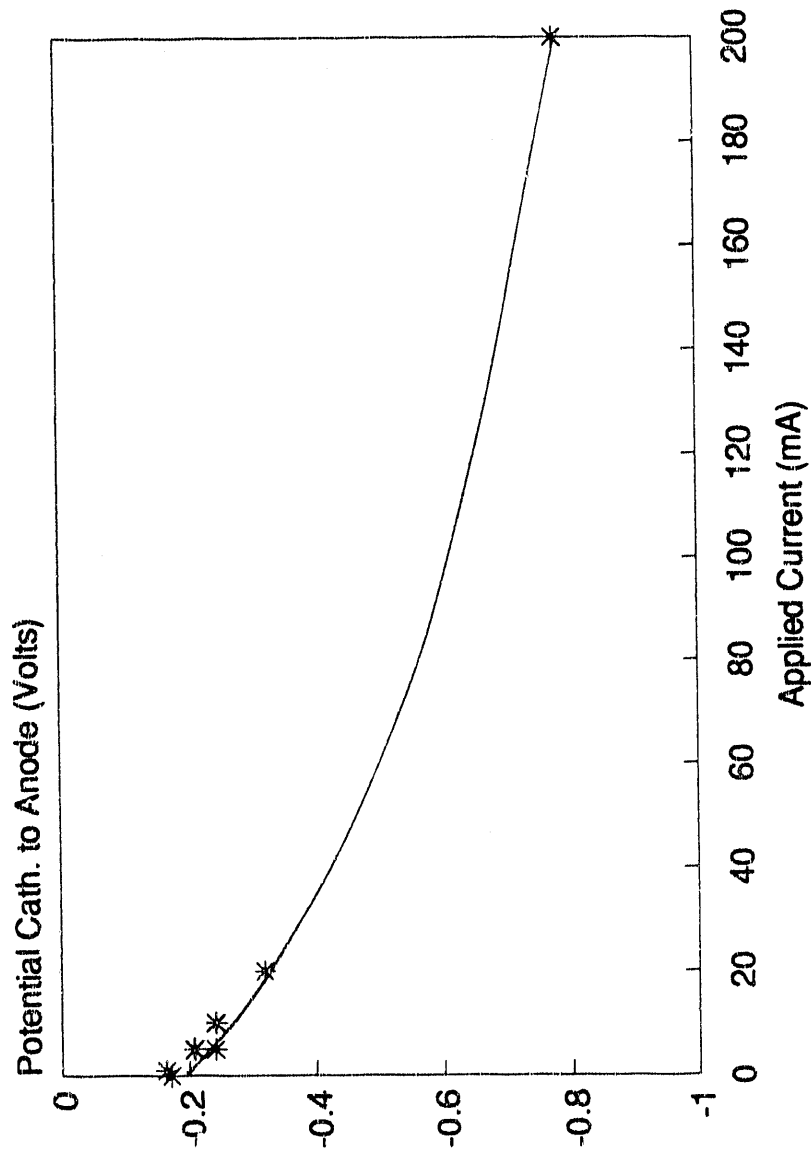
Exit H2S Level vs Applied Current Run 65



Inlet H2S = 27 ppmv
Cathode Flow = 100 cc/min
Temp = 650 C

Figure 15

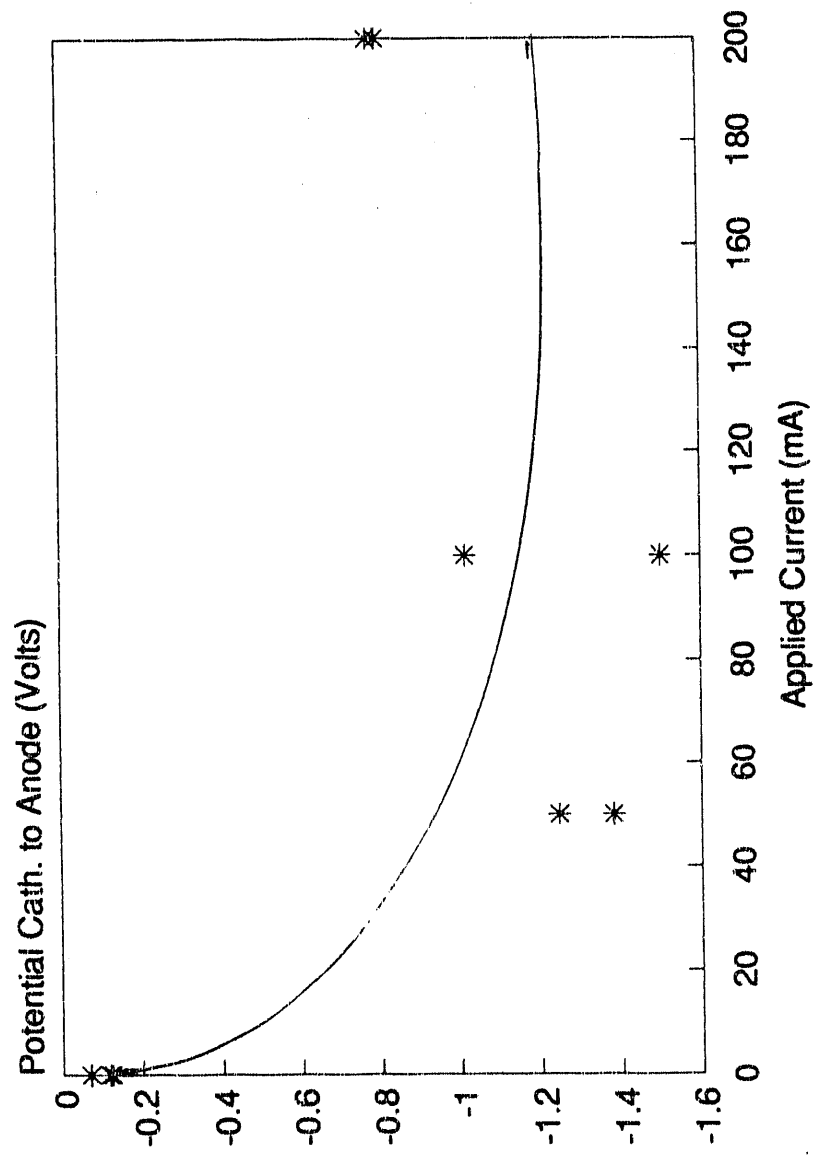
Cross-Cell Potential vs Applied Current Run 65



Cathode Flow = 200 cc/min
Anode Flow = 100 cc/min
Temp = 650 C

Figure 16

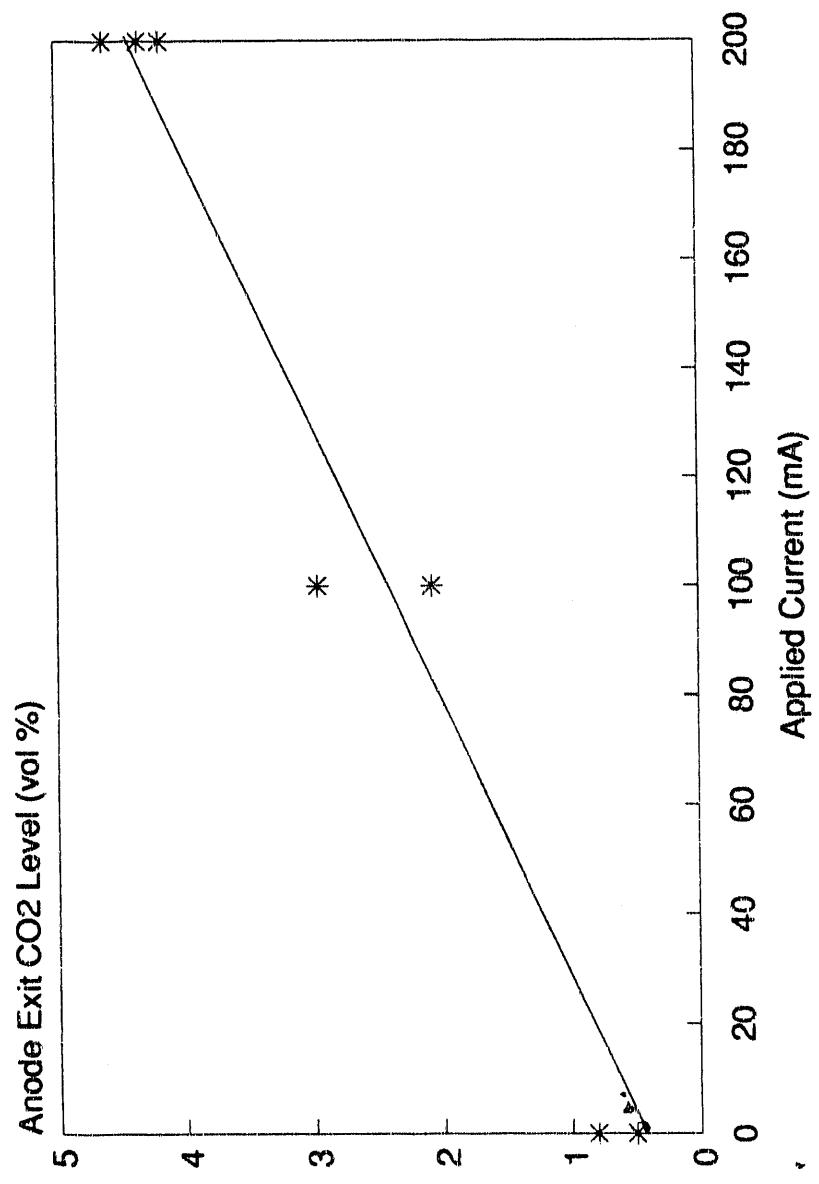
Cross-Cell Potential vs Applied Current Run 65



Cathode Flow = 100 cc/min
Anode Flow = 100 cc/min
Temp = 650 C

Figure 17

Exit Anode CO2 Level vs Applied Current Run 65



Inlet CO2 Level = 0 %
Anode Flow = 100 cc/min
Temp = 650 C

Figure 18

Summary

Polishing application (100 ppmv H₂S to less than 5 ppmv H₂S) of this technology to coal gasification synthesis gas has been repeated with both MACOR and 316 Stainless Steel housings. Polishing application has further been demonstrated at removing H₂S to below 5 ppmv with only 16 ppm entering the cell.

Planned Work for Next Quarter

Work will continue with the stainless steel housings. Priority will be placed on improving H₂S removal efficiency by developing even more H₂ impermeable membranes.

II. SO_x 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. 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, unless otherwise stated, are Fibrex Ni sheets, commercially available, cut to a diameter of approximately 20 cm² 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. Resistance at room temperature has been measured at approximately 2Ω . 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.

Summary

Experiments performed this quarter were attempted with new materials and methods. Fabrication of electrolyte tapes was attempted upon the evaluation of Run 3. The seal formed with the electrolyte 'in situ' was found to be superior to past experiments. Fabrication of tapes and disks for introduction of the electrolyte to the cell 'in situ' have been explored.

The electrodes obtained from the Energy Research Corporation (E.R.C) were also used in a full scale experiment. The past problem of flooding due to the relatively small interstitial electrode pore size was addressed through the use of smaller ceramic particles in constructing the ceramic matrix. These attempts were not successful, but did reveal various properties of the components used.

Finally, density and surface tension experiments were performed on the electrolyte. The density experiment provided an estimate of $1.997 \text{ g/ml} \pm 0.05 \text{ g/ml}$.

This number was then utilized in two separate attempts at determining the surface tension of the electrolyte at operating temperature. The surface tension experiments agreed within 33%.

Full Scale Testing

The first full scale test this quarter is a continuation of the last reported

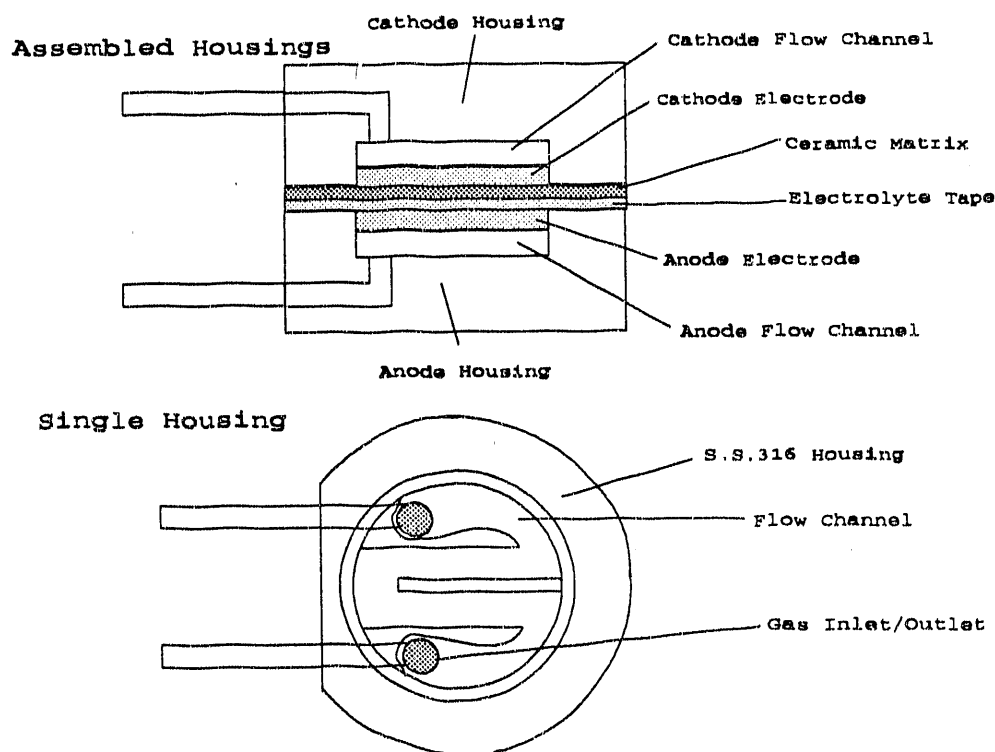


Figure 19: Housings used for full scale testing, with the placement of electrolyte disks noted.

test, Run 3. It was reported the inability to achieve mass balances might be due to the presence of organics from the binder volatilization in the electrolyte tape incorporated into the cell¹ as shown in Figure 1. Upon voluntary shutdown and

evaluation of the membrane, it was determined that the strong seal (gas crossover of 0.5 cm² every 2-5 seconds at a back pressure of 2 in. H₂O) developed during the run was not due to organics. No organic material or discoloration of any part of the system was observed, indicating that the strength of the seal was due entirely to the electrolyte.

Analysis of the polarizations yielded an average exchange current density (i_0) of 0.0792 mA/cm² for varying O₂ partial pressure. Exchange current densities varied inversely with O₂ partial pressure as seen in Table I.

Run 4, the next full scale test, attempted to confirm the sealing ability of the electrolyte tape, with 78% of the

Table I: Run 3

P(O ₂) [atm]	i_0 [mA/cm ²]
0.12	0.0498
0.06	0.0821
0.03	0.135

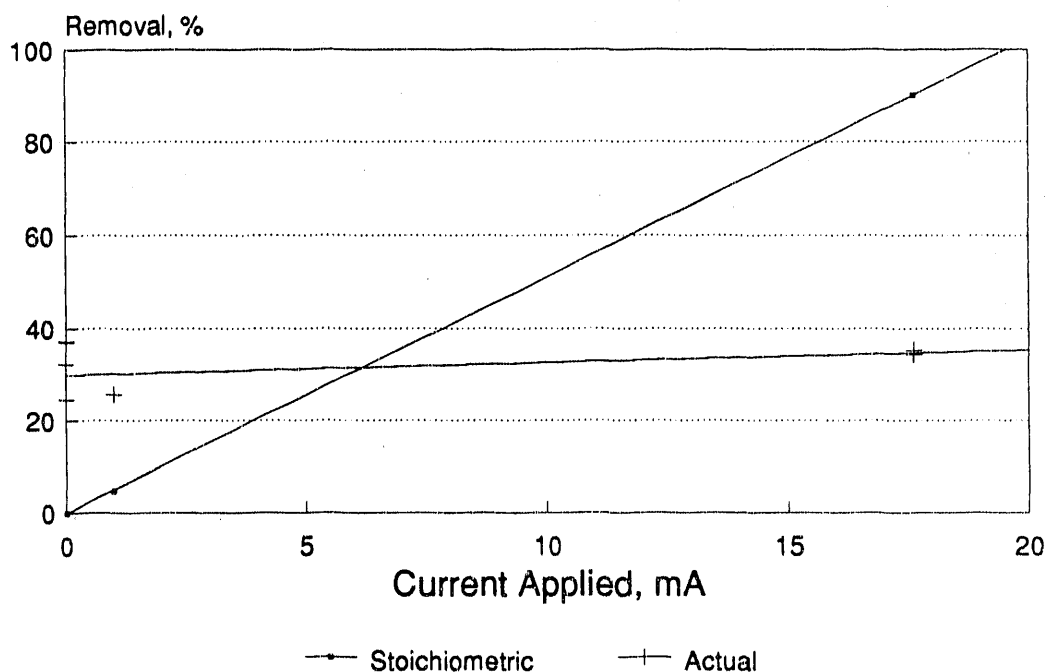
electrolyte needed in the cell being introduced in the tape. One change made to the system was the introduction of "Liquid Steel," a commercially available product distributed by Loctite Corporation, to the cell in an attempt to ensure conductivity between the electrodes and the housing. The "Liquid Steel" had been previously tested to verify conductivity at the high cell temperatures.

Run 4 exhibited inhibiting resistances, despite conformation of the conductivity of each individual part of the cell. Attempting to resolve this crisis resulted in the rupturing of the cell and the ceramic membrane; the test was terminated. Evaluation revealed the "Liquid Steel" had not performed as expected, exhibiting a resistance of

12-20 k Ω . This could be due to the resins present, eliminating a current path. Further use of "Liquid Steel" was discontinued.

Run 5 used electrolyte 'in situ,' in the form of a hot-pressed disk consisting of 66.7 wt% electrolyte and 33.3 wt% polyethylene oxide (MW=900,000). Further details

SO₂ Removal - Run 5



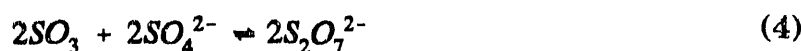
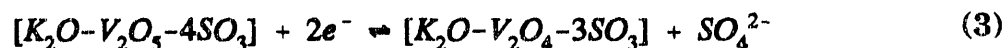
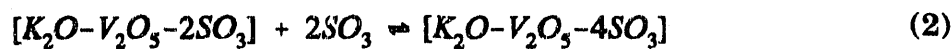
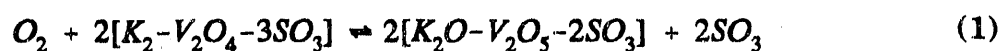
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Figure 20: Removal rates for Run 5 versus stoichiometric removal at various applied currents.

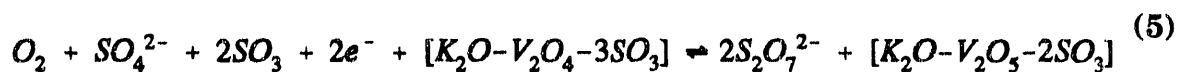
on electrolyte disk manufacture will be discussed later in this report. Heating of the cell proceeded under an oxygen atmosphere. Seals in the cell were determined to be excellent, holding 1.5-2.5 in.H₂O back pressure. Cell performance, however, was unsatisfactory; apparent removal was below stoichiometric levels (see Figure 2). Cell

polarization (see Figure 3) shows a total cell potential of 0.5 V at low applied currents. As the current across the cell was increased to 150 mA, corresponding to a 61.7% stoichiometric removal level, the galvanostat overloaded. Anodic voltage was observed to reach levels as high as 15 V, with the IR drop being virtually equivalent to the voltage as shown in Figure 4. The cell was shut down due to the large anodic resistance.

One possible explanation for the low removal is the removal of O_2 and SO_2 to form pyrosulfate through a complex of reactions utilizing complexes of vanadium



pentoxide. The sum of the reactions contained in equations (1) through (4) is shown

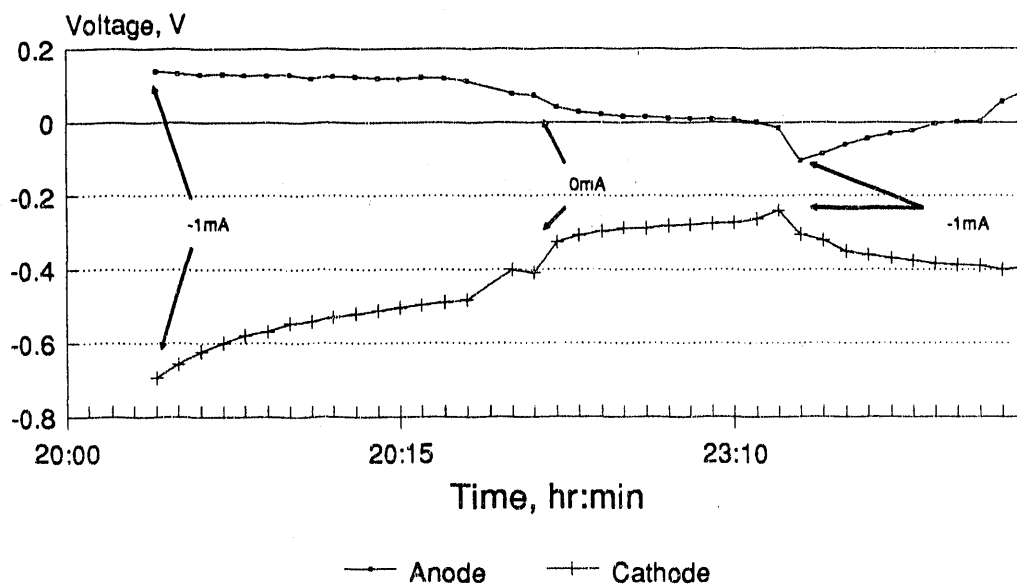


in equation (5). The net result is the formation of pyrosulfate and a vanadium oxide complex through the utilization of oxygen, sulfate, and sulfur trioxide, and the use of two electrons. This mechanism is suggested by McHenry², and could explain the

apparent difference between the stoichiometric removal levels, and the actual removal levels.

Upon breakdown of the cell, it was noted that both the anode and cathode electrodes exhibited excellent conductivity; $0.6\text{-}1\Omega$ at room temperature on both sides. The conductivity from the anode electrode to the anode housing, the cause of the

Polarization Run 5



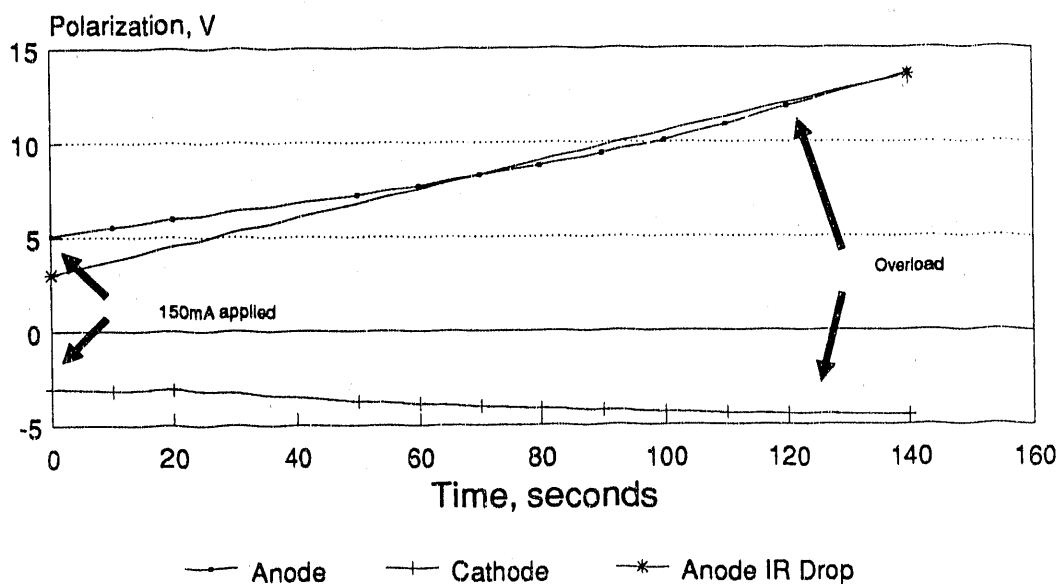
1 mA, 0 mA, 1 mA at 50 cc/min
7/2/92

Figure 21: Polarization performance of Fibrex electrodes with applied current variations between -1 mA and 0 mA.

large polarization, was on the order of $13\text{ M}\Omega$. Housing conductivity was 0.015Ω , except at the points where the electrode was supposed to come in contact with the housing; resistance readings obtained were on the order of megohms. The

membrane appeared well wetted, and the seal appeared excellent as the both electrodes and the membrane adhered to the cathode housing when opened. Corrosion and pitting of the 316L housings has been suggested as the cause for the loss of conductivity³. While additional avenues are being investigated, it is noted that the housings have oxidized to an appreciable extent.

Polarization - Run 5 150mA applied



Overload, 63.7% stoich removal
7/2/92

Figure 22: Polarization leading to galvanostatic overload at 150 mA.

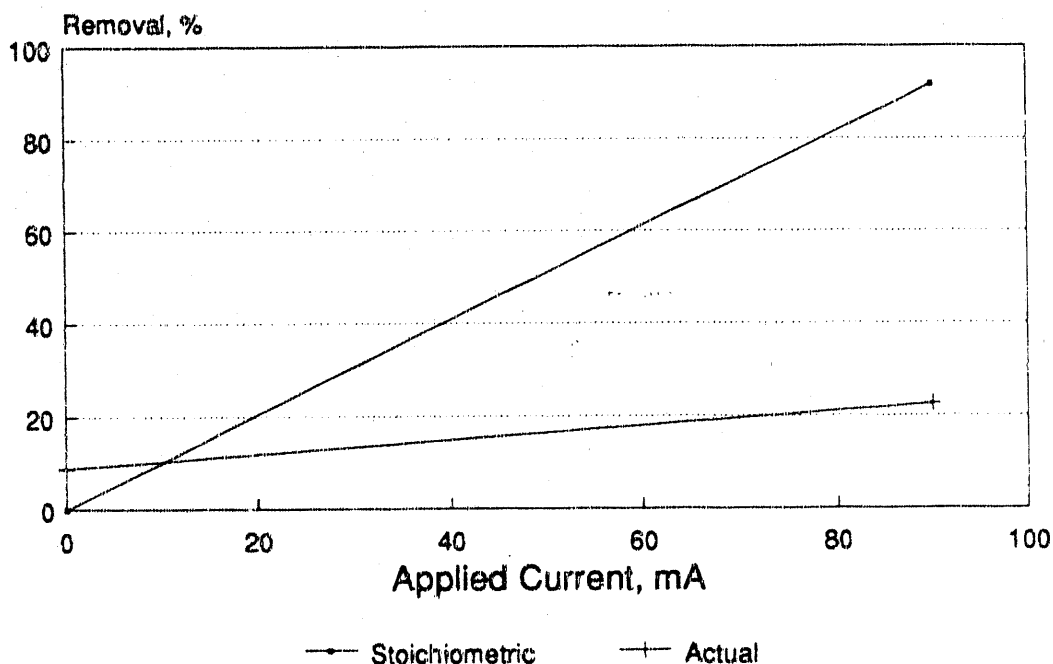
In the attempt to alleviate any short-term conductivity losses, the anode and cathode housings were well cleaned to expose fresh material, and the anode side was painted with platinum paint. Gold wire was also placed between the electrode and the housing on each side to assist in conduction. While the gold withstands the

environment well⁴, excess electrolyte could reduce its effectiveness should the electrode flood and the direct housing-wire-electrode contact be interrupted by electrolyte. Care was thus taken to maintain the minimum amount of electrolyte needed by the cell. Electrolyte addition to the cell was done indirectly through the reference hole.

For verification of the hot-pressed electrolyte/polymer disk viability, the disk was placed above the ceramic matrix and below the cathode electrode. This disk was 33 wt% electrolyte. Other changes in the cell included the use of an 11 vol% ceramic tape for the matrix. The ceramic was the Phillips Petroleum Company Advanced Ceramics experimental powder SC-P. This silicon carbide has a particle size of 0.2 μ m, and a surface area of 25 m²/g. This particle size is ten times smaller than the SN-P particles used in the previous trials. One tape of 11 vol% ceramic was used in this cell. The smaller particles may provide a smaller interstitial pore size. The ceramic was cast in an acrylic binder, available from Metoramic Sciences, Inc. Attempts to cast SC-P in polyvinyl failed at various loading levels of the slurry.

In anticipation of smaller interstitial pore sizes in the ceramic matrix, the E.R.C. electrodes were used in this run, both at the anode and cathode. The 0.75 mm thick E.R.C. electrodes also availed themselves readily to the placement of the gold wire. Both electrodes were lithiated and oxidized prior to use. Upon cell assembly, a crack was heard. It was assumed that one of the brittle E.R.C. electrodes had broken, but to what extent was unknown. Full scale testing continued.

SO₂ Removal for Run 6

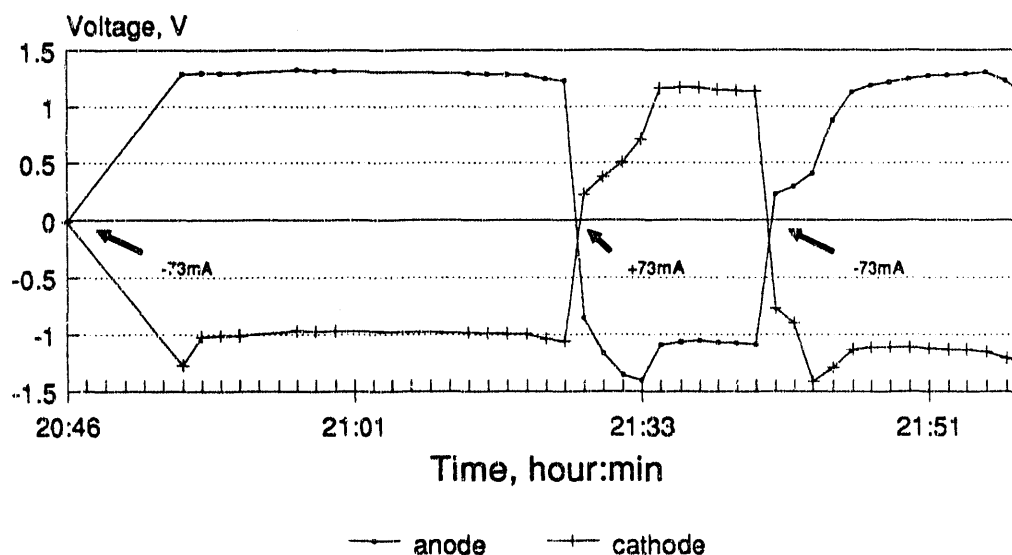


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Figure 23: SO₂ removal levels versus those of stoichiometric removal at the same applied current.

Due to the large amount of polyethylene oxide in the electrolyte disk in the cell, the temperature ramping proceeded at a slow rate, holding at 275° C for 4 hours under a pure oxygen atmosphere. Upon reaching operating temperature of 400° C, the membrane was noted to have virtually no seal, allowing free gas passage from cathode to anode and the reverse. Removal performance was below stoichiometric as seen in Figure 5, and mass balances did not converge during this run. This was not unexpected, with virtually no seal in the cell; the gas flows and cell reactions could not be properly analyzed.

Polarization Performance Run 6 85.3% Removal



ERC electrodes; 90%K₂S₂O₇/10%V₂O₅
 $I = \pm 73 \text{ mA}$ or 85.3 stoich% removal
 7/12/92

Figure 24: Polarization performance of the E.R.C. electrodes under a varying current of -73 mA to +73 mA.

Polarization performance of the cell was found to be excellent, however. Figure 6 shows excellent response of the electrodes at relatively high current levels. Response indicates that these electrodes might be preferable to the Fibrex electrodes. The total potential of 1.4 V was also excellent and consistent. The run was terminated due to the large crossover and unacceptable removal.

Upon examination of the cell, the ceramic membrane was virtually non-existent. A residue of white powder with electrolyte indicated that the 11 vol% ceramic matrix did not have the density required to maintain a membrane in a cell. In addition, there existed a residue, containing electrolyte, that had flowed out of the

cell, presumably the polyethylene oxide disk. This flow may have led to further degradation of the ceramic membrane, and the lack of sufficient electrolyte in the cell may have added to thermal or mechanical shock absorbed by an unimpregnated membrane.

The electrodes exhibited flooding, similar to that noted by McHenry², and both electrodes were broken, due probably to the force required to separate the cathode and anode housings from one another. The cell was not well-wetted, but there was evidence of an electrolyte path between the anode and cathode electrodes. The perimeter of the cell, however, showed no evidence of an electrolyte presence. Most of the electrolyte appeared to have availed itself to the electrodes and the space in between the electrodes.

Electrolyte Management

It has been found that the 'in situ' placement of electrolyte has led to excellent seals in full scale testing of the SO_x removal cell. A search has begun for a method of management allowing the placement of electrolyte into the cell prior to binder burnout and cell heating. The presence of the electrolyte is believed to stabilize the ceramic matrix, making it less susceptible to thermal and mechanical shock than an unimpregnated matrix.

The first attempt at this management was the tape casting of the electrolyte in a 78 vol% mixture with polyvinyl binder. The result, reported last quarter, was an inhomogeneous mixture that yielded varying tapes. The slurry itself also

presented difficulties, forming a jelly-like substance that was unmanageable. Only additional solvent allowed the mixture to be poured and cast.

A second attempt to tape cast the electrolyte in a 55.6 vol% mixture with the polyvinyl was made. The slurry was again unmanageable, and only the addition of 30 ml solvent (doubling the total volume) after 24 hours of milling allowed recovery of the slurry. The resulting tape cracked and adhered to the casting surface.

Attempts were then made to cold and hot press a disk of pure electrolyte. The cold-press was carried out with 2.5 g electrolyte and 1050 psig for 5 minutes. The resulting disk was fragile and crumbled to the touch. Subsequent attempts at pressures of 1680 psig and 10 minutes produced the same results.

The hot press technique is somewhat arbitrary in this application. The presence of bisulfates in the pyrosulfate exposed to humidity greatly reduced the melting point; while bisulfates will melt and decompose to pyrosulfate upon heating, that melting is not desirable in the hot pressing process. Hot pressing requires pressing the material at a point 10-15° C below its melting point. If that melting point is not well known, the procedure will tend to be ineffective. The melting point of the electrolyte was determined to be approximately 300-350° C, and a pressing temperature of 275° C was chosen. Three times, the die was baked in the oven for 5-10 minutes, and then pressed at 1050 psig for 1 minute. The resulting disk, while showing a slightly stronger mechanical strength than the cold pressed disk, still fell apart during handling.

Table III. Table of attempted electrolytic disk with the electrolyte in the pressing.

#	wt% Elect.	T(oven) (° C)	cycles	Oven Time	MW polymer	Mill Time (hr)	Results
6	66.7	155	3	7	900000	0.5	usable disk
7	81.4	100	3	10	900000	0.5	15% usable
9	66.7	165	3	10	900000	0.5	20% usable
10	50.0	155	3	15	900000	0.5	40% usable
11	33.3	162	6	16	900000	0.5	usable disk
12	66.7	156	1	7	100000	1.0	25% usable
13	66.0	158	2	10	100000	1.0	usable disk
15	85.7	158	2	10	100000	1.0	usable disk
16	80.0	158	2	10	100000	1.0	90% usable
17	75.0	158	2	10	100000	1.0	usable disk
18	85.7	158	2	10	100000	2.0	10% usable
19	75.0	158	2	10	900000	2.67	70% usable, but brittle
20*	69.4	-----	1	---	30000	1.0	60% usable
21*	71.4	-----	1	---	30000	1.0	85% usable
22*	62.5	-----	1	---	300	1.0	90% usable
23	85.7	158	3	20	100000	1.0	75% usable
24*	55.5	-----	1	---	300	1.0	90-95% usable
25*	69.4	-----	1	---	300	1.0	70% usable

* - denotes the use of hydroxyethyl cellulose, courtesy Union Carbide Corporation, which was cold-pressed.

All others use polyethylene oxide.

Polyethylene oxide was first milled with electrolyte for a minimum of 1/2 hour before placement between two cut aluminum foil circles in the pressing die. The die was then alternated between an oven and the press, for various numbers of cycles and at various temperatures. Pressing occurred at 1900 psig in all cases. This technique was tried with two different molecular weights of polyethylene oxide: 900,000 and 100,000. The results are shown in Table II. Also shown in Table II are the results of the use of hydroxyethyl cellulose, courtesy Union Carbide Corporation, in combination with the electrolyte. The hydroxyethyl cellulose has been shown to burn out completely at a temperature of 350° C. Work has just begun on a hot pressing technique with hydroxyethyl cellulose. Up to this time, the cellulose has been cold pressed only, also at 1900 psig.

Future work in electrolyte management will include the development of tape casting techniques, should the pressed-disk methods proved unsatisfactory or inconsistent. Preliminary results have shown that for the same mixtures and processing, two very different disks can be obtained. Method must be improved if this type of processing is to prove to be viable. Tape casting of the electrolyte and ceramic matrix is a relatively well-developed method of electrolyte management in the molten carbonate fuel cell^{5,6}, and will be considered as an option, should it be found that the addition of electrolyte will not increase the interstitial pore size of the ceramic matrix.

Electrolyte Experiments

Before any type of model for electrode wetting can be developed, the transport properties of the molten electrolyte must be known. While much data is available for potassium sulphate, little is known about potassium pyrosulfate, and even less about a mixture of potassium pyrosulfate and vanadium pentoxide. An experiment was performed to determine the density of the molten salt at 400° C.

A Pyrex graduated cylinder was used to determine the density. The coefficient of linear thermal expansion for Pyrex is listed as 0.033×10^{-6} up to 300° C. The expansion of the cylinder due to the increase in temperature was therefor assumed negligible. The cylinder was loaded with a known weight of electrolyte, covered to maintain a constant SO_3 partial pressure, and heated. Readings were taken over a 4 hour period. The loss of weight was found to be $0.083 \text{ g} \pm 0.005 \text{ g}$ possibly due to SO_3 formation or vaporization of any water present on the surface of the cylinder. This small loss was considered negligible. The beginning and end weights were averaged, and the density at 400° C was calculated as $1.997 \text{ g/ml} \pm 0.05 \text{ g/ml}$. Error in this experiment may result from an inaccurate reading, or solidification of the molten salt when the oven was open to read the height.

An attempt was then made to calculate the surface tension of the electrolyte using capillary tubes (see Figure 7). The Pyrex housing was marked at known

$$\gamma = \frac{r h \rho g}{2} \quad (6)$$

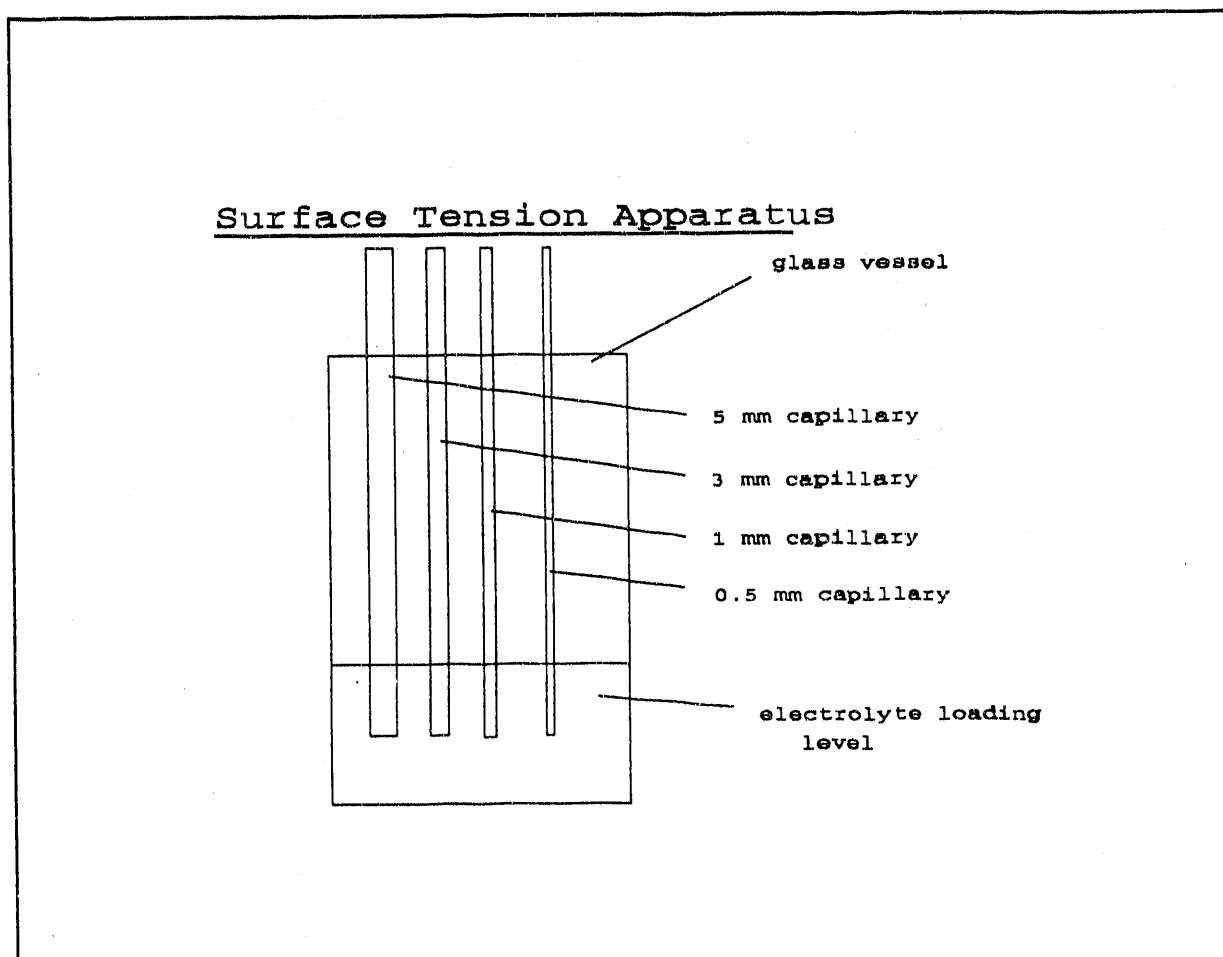


Figure 25: Capillary apparatus used in an attempt to determine the surface tension of molten electrolyte.

intervals for visual height measurement. The capillary tubes used were of inner diameter 5 mm, 3 mm, 1 mm, and 0.5 mm, and also of Pyrex. The multiple tubes eliminated the absolute need to know the height of the molten electrolyte in the housing. Using the capillary equation (6), and taking the differences in height for the different size capillaries, the surface tension could be determined independently of the height of the molten electrolyte.

The result, however, was not readable. Electrolyte level was only readable in the 0.5 mm capillary; the larger ones all had plugs of electrolyte at various levels,

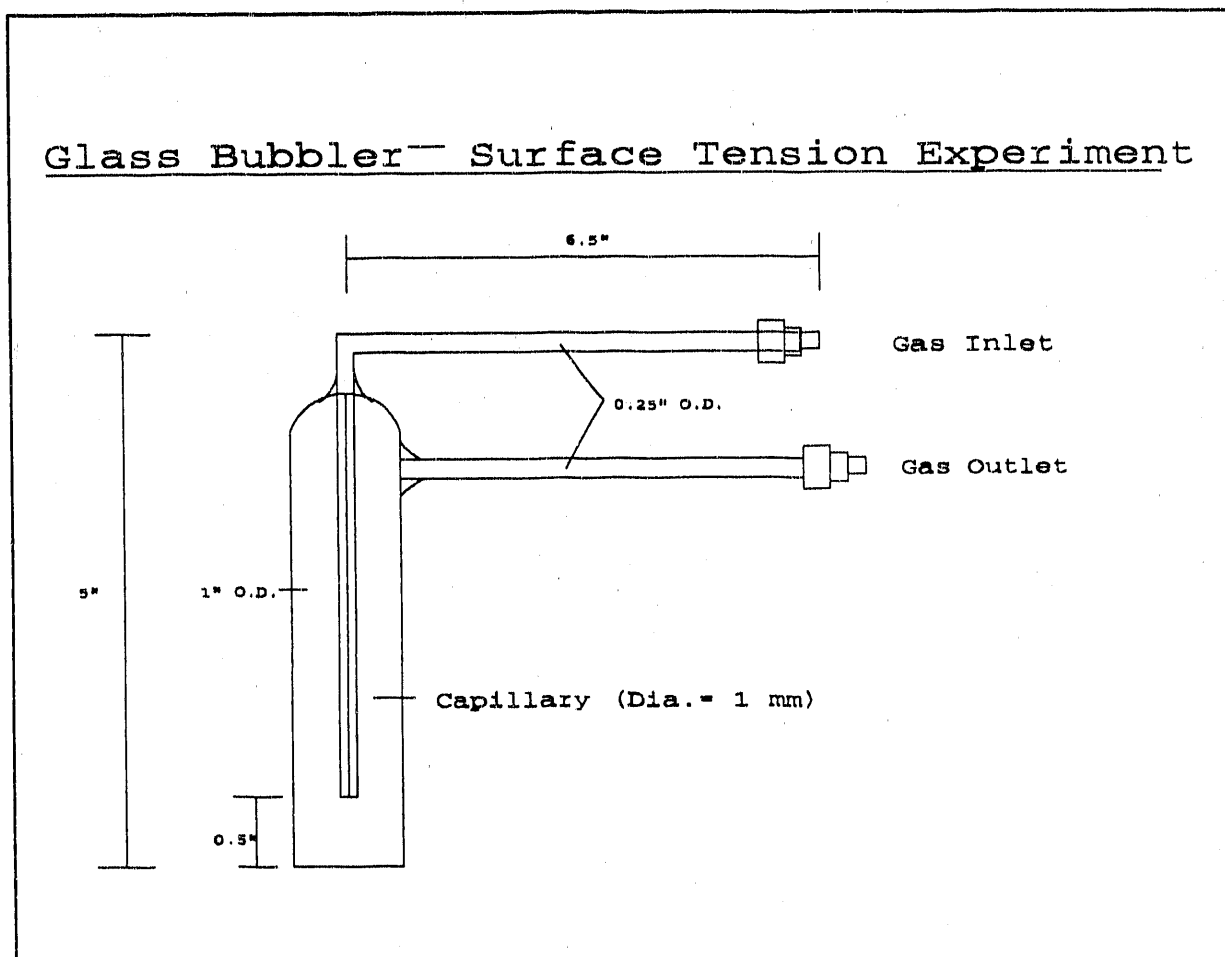


Figure 26: Bubbling apparatus for use as described in Jaeger's maximum bubble pressure method.

leading to the questioning of the validity of any reading with the slight partial pressure differences that must exist between plugs of electrolyte. The level of the molten electrolyte was measure in the housing and in the 0.5 mm capillary. From these readings, a reading of 93.69 dynes/cm \pm 6.85 dynes/cm at 400° C was obtained.

Lovering⁸ has suggested Jaeger's⁹ maximum bubble method as an excellent technique with which to measure the surface tension of a molten salt. The method

$$p = \rho gh + \frac{2\gamma}{r} \quad (7)$$

requires the ability to measure the pressure required to force one N₂ bubble out of an opening at a known depth. This pressure is assumed to be due to the depth of the liquid and the force required to overcome the surface tension of the liquid, forming a bubble. The equation used is shown as Equation (7), where p=pressure, h=depth of immersion for tip of capillary, r=radius of the capillary opening, g=gravitational constant, ρ=density of the melt, and γ=surface tension. An apparatus was then developed for the experiment (see Figure 8), and a mercury manometer was used to measure the pressure difference.

The result is encouraging, although the range is large. The manometer read only a 6 mmHg difference. The pressure reading is the largest source of error, and was treated as such in the analysis. The final value for surface tension from the maximum bubble pressure method was 138.8 dynes/cm ± 33.4 dynes/cm. The two values stand almost in agreement with one another, yet neither is felt to have the desired accuracy. In the next attempt to measure the surface tension, the Hg manometer will be replaced with a H₂O manometer for accurate pressure measurement. In addition, SO₂ and SO₃ will be bubbled through as well as N₂. This

may aid in allowing the electrolyte to maintain a constant SO_3 partial pressure, although this is not a major concern.

Ceramic Membrane Development

Various schemes have been tested this quarter in an attempt to develop a ceramic membrane with a pore size less than $0.2\mu\text{m}$. Phillips Petroleum Silicon Nitride, SN-P, had been used in previous runs, and found by McHenry² to have an interstitial pore size of $0.2\mu\text{m}$. Smaller pore sizes would enable the use of the E.R.C. electrodes, which flood when used with a SN-P membrane. Tape casting, as described previously has been the method of membrane manufacture, allowing the development of 0.30 mm membranes for used in full scale testing.

Attempts have been made to develop a membrane using particles with a diameter (d_p) of $0.2\mu\text{m}$, an order of magnitude smaller than SN-P particles. Phillips Petroleum SN-R, a silicon nitride, and SC-P, a silicon carbide, have both been considered. Both have $d_p=0.2\mu\text{m}$. The binders available at this time are provided by Metoramic Sciences, Inc.: B73305, a polyvinyl, and K565-4, an acrylic. Modifiers for casting on glass (M-1111) and galvanized steel (M-1114) are also available. The results of various attempts can be seen in Table III. The one SC-P membrane that did cast (#3, Table III) was used in Run 6, and was shown to have inadequate ceramic volume to maintain the matrix. A higher volume percentage ceramic is needed.

Future membrane work includes the development of a tape casting technique for the SN-R and SC-P particles. At this point, there are various combinations to still

Table III: Ceramic Tape Casting

#	Ceramic	Vol% ceramic	Binder	Modifier	Results
1	SN-R	50.0	Vinyl	M-1114	Would not flow despite sonication
2	SN-R	48.3	Vinyl	M-1114	Additional solvent; cracked upon drying
3	SC-P	11.0	Acrylic	M-1111	Cast well; pliable tapes
4	SC-P	50.0	Acrylic	M-1111	Did not cast well; cracked upon drying
5	SC-P	30.0	Acrylic	M-1111	Not homogenous; cracking
6	SC-P	40.0	Acrylic	M-1111	Cracked on drying

be tried, and new binders must also be considered. A membrane of approximately 50 vol% ceramic is desirable, although a more dense membrane will also be considered. Less dense membranes do not have the physical ability to maintain the matrix.

Future Research

The E.R.C. electrodes have demonstrated excellent polarizability. Before they can be used, however, a ceramic matrix with a smaller interstitial pore size must be developed. The development of an electrolyte membrane has proven to be crucial in consistently developing and maintaining gas seals.

It is also crucial that a full scale test exhibit converging mass balances to verify results from previous runs. A working full scale test with the new materials is also needed to see the effect of new materials on the problem of SO₂ generation.

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