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 and SO_2 cells 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 toward these goals.

I. SO_x Removal Cell

INTRODUCTION

Successful removal of SO_x from flue gas depends on the development of a membrane able to achieve a current density of 50 mA/cm² at a total voltage of approximately 1V. Flooding of electrode has been identified as a problem, leading to increasing polarization over time. The resulting reduction of surface area also tends to limit the mass transfer flux, reducing the efficiency of the cell. To reduce flooding, new materials and techniques of manufacture will be investigated, in the attempt to produce a ceramic membrane of approximately 50% theoretical density. This membrane must have proper pore size distribution to ensure sufficient capillary force to prevent impregnated electrolyte from flooding electrodes, and subsequently drying the ceramic membrane. Various methods of matrix production were studied this quarter: tape casting, pressing and sintering, and slip casting. Each will be discussed in turn.

Electrolyte introduction to the cell is a continuing problem. The development of a method is still being investigated. Ideally, the electrolyte would be introduced as powder with binder in a green body. This binder would burn away at temperatures of approximately 300° C, leaving pure electrolyte to melt and complete the ionic path necessary for the electrochemical cell. The electrolyte used this quarter was, exclusively, a 90wt%K₂S₂O₇/10wt%V₂O₅ mixture.

Electrodes used this quarter were lithiated nickel oxide. These were obtained from National Standard (Fibrex) and the Energy Research Corporation (ERC) as Ni sheets. These sheets were cut, with a resulting superficial area of approximately 20.0cm². The cut Ni was placed in a 1-2M solution of LiOH, dried, and oxidized at 600° C prior to placement in the cell. This process creates a p-type semiconductor, exhibiting room resistivities on the order of 1.0-0.2Ω at room temperatures. Pore size of the National Standard Fibrex electrodes is approximately 1.0 μm. The pore size of the ERC electrode is proprietary. Other methods of manufacture of the electrodes were studied this quarter, and will be detailed as such.

Current is conducted through the cell from stainless steel 316L housings, to the electrolyte-wetted electrode, where the removal takes place. The current is then carried through the cell by the transporting species in the electrolyte. Oxidation of the transporting species occurs at the anode, and the current passes through the anode electrode to the anodic SS316L housing, and out of the cell.

MATRIX MANUFACTURE

Four methods of matrix manufacture were attempted this quarter, with varying success:

- (1) Pressing of VK-38 catalyst with and without electrolyte
- (2) Tape casting
- (3) Slip casting

(4) Pressing and Sintering

In addition, a sample of silicon nitride was obtained from the Oak Ridge National Laboratory, courtesy O.O. Omatete, and additional silicon nitride was obtained from Phillips Petroleum, courtesy L. Kallenbach. A sample of boron nitride was obtained from Carborundum, Inc.. The Phillips Petroleum silicon nitride was used exclusively this quarter, but testing of the Oak Ridge silicon nitride and the boron nitride will be pursued this quarter.

Pressing of VK-38

VK-38, a sulfuric acid catalyst obtained from Haldor-Topsoe, was crushed to a median particle size by weight of $90.67\mu\text{m} \pm 11.12\mu\text{m}$. This powder was then pressed at 4000 psig for 5 minutes in a 3" diameter die. The resulting disk crumbled easily. A second attempt was made, and after pressing, the disk was heated to 350° C before removal from the die. The heat was used in an attempt to allow the pyrosulfate present in the catalyst to melt and form a hard solid. The resulting disk was exceedingly fragile to the touch, and large portions of the disk broke before it could be tested in a full scale cell. This process was abandoned.

Tape Casting

Tape casting was attempted with very little success. As has been reported in the past, casting has been successful using the Phillips Petroleum 0.2 μm silicon nitride particles, in only a 30vol% loading level. This low loading level led to the mechanical inability to support any type of structure necessary for use as an electrochemical

membrane. Silicon nitride seemed to be turned into almost a slurry in the molten pyrosulfate, allowing easy gas passage.

The casting procedure used utilizes a polyvinyl butyryl binder, in a benzene/toluene solvent. This prepared mixture, including some dispersants and surfactants, was obtained from Metoramic Sciences. The binder is added in an appropriate quantity, such that, after burnout, the resulting ceramic and ash left will occupy 50% by volume of the apparent volume of the ceramic disk.

After binder mixing, additional solvent and surfactant is added as needed to keep the solution at an appropriate viscosity. No consideration of pH has been applied to this time. The slurry is mixed in an alumina ball mill, and is sonicated prior to casting.

Casting takes place on an appropriate surface, either glass, galvanized steel, or teflon, depending on the surfactant and dispersants used in formulation. Spacers are used so that a doctor blade may be drawn across the surface at a height of 1 mm relative to the surface. The mixture is poured across the surface, and the doctor blade is drawn across to produce a uniform height. The wet tape is then covered completely to slow down the evaporation of the solvent, allowing the tape to dry uniformly, without cracking or undue stress. Drying is done overnight, or as required.

The resulting green tape is then removed from the substrate, and cut to the proper form. It can be pressed, combined with other tapes, and generally used as desired, as it is extremely pliable at this point. As the tape is subjected to higher and higher temperatures, as in full cell tests, the organics volatilize with oxygen, and burn out

completely by 380° C, according to a Metoramic Sciences TGA, leaving only a small amount of ash. The resulting ceramic matrix is then impregnated with electrolyte.

Various problems have arisen in the application of this much-desired process. The attempt to tape-cast such a small particle size, with such a large surface area (80 m²/g), is somewhat unprecedented in a 50 vol% loading level. There is a constant problem of surface wetting by the polymer due to the large surface area. The natural alleviation of this problem is the addition of binder to the system. This will result, however, in the reduction of volume percent ceramic, which leads, as previously discussed, to a mechanically intolerable system.

Additional solvent is then the possible solution. The result, however, tends to choose one of two avenues: the large amount of solvent evaporation leads to a cracked green tape; or the mixture is not homogenous, with viscous and less-viscous phases present, resulting in a non-uniform green tape. Neither of these two results is at all desirable.

Additional surfactant has been tried in an attempt to reduce the amount of solvent required to obtain a homogenous mixture. This carries its own problems: solvent evaporation will be slowed down at the surface, as the surfactant increasingly inhibits easy solvent evaporation as it travels to the surface with the solvent and accumulates due to its lower vapor pressure. Again, internal stress may result, as solvent is trapped inside the drying tape, resulting in cracking of the tape.

Solutions to this problem have been discussed with Metoramic Sciences¹. Among the solutions discussed is the variation of solvents to from just ethanol and toluene to

include possibly acetone or MEK. Some of these may not be feasible, however, as the rate of evaporation would increase in some cases, possibly leading to cracking. Additional surfactants were also been discussed, including acetates, high carbon acids, and possible phosphoric acid, along with some amides, aminos, and polyesters. None of these suggestions has been attempted at this point, but will be should other methods of membrane manufacture prove unacceptable.

Slip Casting

As a unique method, slip casting of the silicon nitride was attempted. Slip casting, is the mixing of the ceramic into a slurry, and pouring the slurry into a mold. The solvent is drawn off by the mold, leaving the resulting ceramic in the desired shape. Thickness is controlled by the solvent/ceramic ratio, speed of casting, and relative solvent humidity conditions. The casting solution may contain only the solvent, or some mixture of solvent, binder, surfactant, or dispersant, all of which will affect the casting ability and resulting ceramic piece.

The attempt was made, again using the Phillips Petroleum silicon nitride, in conjunction with water as the solvent, and using Darvan C, courtesy Konrad C. Reiger of the R.T. Vanderbilt Company, Inc., as the dispersant, to slip cast a membrane. Darvan C has a low ash content on burnout, and has shown low foaming in Vanderbilt tests.

A slurry was mixed in a beaker, with DI-H₂O (18.3 Ω -cm), Darvan C, and silicon nitride in a, respectively, 48.3 wt%/0.3 wt%/51.4 wt% mixture, for a total of 20.570g. Mixture viscosity was visually estimated as correct. The slurry was then poured into the

full cell housings, with electrodes in place, and the top housing was pressed onto the slurry top to form a membrane of a thickness of approximately 1.5mm. Unfortunately, the electrodes and housings were dry, and the water was quickly absorbed into the electrodes, setting the slurry in a less-than-ideal configuration. It was felt, however, that despite the problems encountered, and the resulting thick membrane, the cell could be properly sealed when wet with electrolyte.

The cell never did seal, using an estimated amount of electrolyte, and the cell test was terminated. Upon post-mortem examination, however, the membrane was found to simply be deficient in electrolyte, and wetted only on the top. Had additional electrolyte been added, the cell might have succeeded. Further testing of this method will involve the saturation of the electrodes and housings with water prior to casting of the slip. This will hopefully allow thinner membranes, while still maintaining a high volume percentage ceramic.

Pressing and Sintering

Dry pressing, and sintering of ceramic membranes also took place this quarter. Dry powder was packed uniformly into a die of 3" diameter, to thicknesses of 1mm to 1.5mm. The die was then taken to a hydraulic press, with a applied pressure of 1132 psig. The resulting disk is then transferred to a firing plate, covered, and placed in an oven with a slow temperature ramping to 1150° C, held at that temperature for a period of time, and slowly brought back down to room temperature.

The first attempt resulted in an amalgamation of alumina and silicon nitride. The silicon nitride disk, after pressing, was fired on an alumina firing plate in an oxygen

atmosphere. Some unidentified liquid phase formed, resulting in warping of the disk, and the general defacing of the alumina firing plate. It was suggested² that the firing be done in an inert atmosphere of nitrogen, and on a surface of either silicon nitride or silicon boride. In addition, a solid-phase diagram was prepared, shown in Figure 1, to ensure the material obtained from the process was the material desired.

A reaction-bonded plate of silicon nitride was obtained from Norton Industrial Ceramics. A test disk of 1" diameter was pressed and fired under high purity nitrogen (Holox, 99.97 purity), with excellent results. The plate obtained, however, was not large enough to support a 3" diameter disk.

Discussion with Paul Kohl, Professor, Georgia Institute of Technology, revealed that the chemical vapor deposition (CVD) of pure Si_3N_4 onto Si wafers was common technology. Four such wafers were prepared by Martin Ceiler, Chemical Engineering, Georgia Institute of Technology, with $\sim 9000\text{\AA}$ of silicon nitride deposited onto the surface.

A 3" diameter disk was pressed at a pressure of 1132 psig, and fired under pure nitrogen, following the ramp seen in Figure 2. The resulting disk was found to be of sufficient mechanical strength, although this was not explicitly tested except in handling. It is known that the sintering of pure silicon nitride results in a final porosity of approximately 65% at a temperature of up to 2073 K³. The porosity of the sintered membrane is therefore estimated to be approximately 60%, with the sintering process actually incomplete at the low firing temperatures.

Si-O-N Phase Diagram

For Varying Temperatures

Figure 1: Silicon-oxygen-nitrogen phase diagram for the sintering of silicon at varying temperatures.

The disk was used in a full scale run. Cracking was heard upon cell assembly, but the test proceeded in the hope that the electrodes had broken, leaving the membrane intact. The introduction of electrolyte into the matrix was an unusually slow process, and consequentially, excess electrolyte was added, flooding the electrodes. The concern that, in a time period of 1 hour, the matrix had not been completely wetted was found to unjustified post-mortem, as the small capillaries seem to simply take a longer amount of time to properly wet. The additional electrolyte plugged the outlet tubes. They were immediately cleaned, but gas-crossover began in the interim. The disk, upon examination, was noted to have a few hairline fractures, possibly due to assembly rather than post-mortem examination.

The membrane can be tentatively considered a success. Its wetting capability, now better understood, should be carefully monitored, but the mechanical aspects of the matrix, fabricated in this manner, seem promising.

Temperature Ramp for Si₃N₄ Sintering In N₂ Atmosphere

P=1 atm, high purity N₂

Figure 2: Temperature ramp of the firing of a 3" diameter silicon nitride disk.

ELECTRODES

The electrodes used this quarter were obtained from ERC. Porosity experiments and measurements were performed with both the ERC electrodes and the Fibrex electrodes, used in previous quarters. The results of the ERC electrodes are proprietary in nature, but the results of the Fibrex electrodes will be reported.

It has been suggested⁴ that the electrodes be oxidized, and then lithiated, ex-situ. Presently, the oxidation and lithiation process is a co-current event; the electrodes are soaked in LiOH, and then ramped up to 600° C for simultaneous oxidation and lithiation. They are held at that temperature for a minimum of 8 hours.

Both Fibrex and ERC electrodes were oxidized at 600° C for 8 hours, lithiated in LiOH (saturated), and again placed in air at 600° C for an additional 12 hours. X-ray spectroscopy was performed to confirm lithiated NiO, noted by the slight shift of the peaks due to the incorporation of lithium into the NiO lattice, seen in Figure 3. Porosity experiments were then performed on five samples of each type of electrode, according to ASTM Standard Designation C 373-72. The results of the Fibrex electrodes are shown in Figure 4, along with the formulae used. The electrodes were heated to 150° C for 30 minutes to obtain the dry weight, boiled in water for 5 hours and then let sit overnight to get 25° C water. The saturated specimens were then carefully weighed, according to the standard, to obtain the saturated and suspended weights. These numbers are accurate to at minimum of 2% deviations. Higher accuracies may have been attained.

Sample: LiNiO ERC File: LINIOE.DI

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Figure 3: X-ray of oxidized and then lithiated ERC electrode.

Fibrex Nickel Electrodes
Starting porosity of 86% (Fibrex)

January 13, 1993	Sample number-->	1	2	3	4	5	Averages	Standard Deviation
Measurement	Formula							
Dry Weight, g	D	1.466	1.674	1.945	1.152	2.045	1.656	0.324
Saturated Weight, g	M	2.644	2.967	3.585	2.159	3.698	3.011	0.577
Suspended Weight, g	S	1.274	1.454	1.661	1.013	1.792	1.439	0.277
		density = 1 g/cc						
		T(water) = 25C						
Exterior Volume, cc	$V = M - S$	1.370	1.513	1.924	1.146	1.906	1.572	0.304
Volume of open pores, cc	$M - D$	1.178	1.293	1.640	1.007	1.653	1.354	0.255
Volume of Impervious Portions, cc	$D - S$	0.192	0.220	0.284	0.139	0.253	0.218	0.050
Apparent Porosity, %	$P = (M - D)/V * 100$	85.99%	85.46%	85.24%	87.87%	86.73%	86.26%	0.96%
Water Absorption, %	$A = (M - D)/D * 100$	80.35%	77.24%	84.32%	87.41%	80.83%	82.03%	3.50%
Apparent Specific Gravity	$T = D/(D - S)$	7.635	7.609	6.849	8.288	8.083	7.693	0.496
Bulk Density, g/cc	$B = D/V$	1.070	1.106	1.011	1.005	1.073	1.053	0.039

Figure 4: Results of porosity standard on lithiated NiO electrodes (Fibrex).

Mercury porosimetry was also performed on both Fibrex and ERC lithiated NiO samples, courtesy Westvaco. The pore size distribution in the Fibrex electrode was found to vary widely, primarily from 32.8 μ m to 0.642 μ m. The incremental volume per gram can be seen in Figure 5. These values, however, should not be taken literally. Mercury porosimetry has a number of flaws associated with it, including accurate correction for the phase behavior at critical pressures, seen in Figure 6, contact angle determination⁵, rate effects⁶, sample destruction⁷, and the model used⁵.* Scanning Electron Microscopy is currently being performed on similar samples to determine the relative accuracy of the porosimetry measurements.

Finally, the electrode resistance was measured while the electrode was subjected to temperature cycling. The electrode was attached to gold and platinum leads on either side, and the resistance between these leads measured. Corrections were made for the resistance of the leads, but not for the subsequent oxidation of the alligator clips used. It can be seen in Figure 7 that there is an initial large drop in resistance with increasing temperature. This is believed to be the effect of incomplete lithiation, with completion occurring in the first cycle. The resistance then follows the same curve, but tends to rise slightly. This is believed to be the effect of oxidation of the stainless steel alligator clips used in connection. P-type semiconducting behavior is definitely exhibited, with a resistance of approximately 1 Ω at 400° C.

* A good review of available mercury porosimetry data and limitations can be found in *Powder Technology*, 29(1981), including a bibliography of available literature.

Mercury Porisometry Readings

Figure 5: Incremental pore volume obtained from Mercury porosimetry for Fibrex electrodes.

Phase Behavior of Hg at 298.15K

Calculation by Peng-Robinson E.O.S.

Figure 6: Mercury phase behavior with pressures used in mercury porosimetry.

E.R.C. Electrode Resistance

p-type semiconductor

1/21+/92, E.R.C. Lix(NiO)y

Figure 7: Cyclic resistance of a p-type semiconductor, LiNiO, with temperature.

FULL SCALE TESTING

There are no definitive results this quarter from full scale tests. The problems encountered with materials have been mentioned. Full scale testing and analysis is currently ongoing with pressed and sintered silicon nitride disks, and initial results do look promising.

FUTURE WORK

Future work will concentrate on full scale testing, with emphasis on the chemistry involved. Poor long term removal may be due to poor oxygen transport to the vanadium pentoxide catalyst present in the electrolyte. Reduced vanadium (V_2O_4) may be the cause for the SO_2 generation noticed at higher currents and flow rates.

ENDNOTES

1. Mark Wesselman, Electro Scientific Industries, personal communication.
2. D.N. Hill, Professor, Ceramic Engineering, Georgia Institute of Technology, personal communication.
3. Chin G.Y., Advances in Powder Technology, American Society for Metals, 1982, p.293.
4. D.M McHenry, personal communication.
5. Good, R.J., and Mikhail, R.S., "The Contact Angle in Mercury Intrusion Porosimetry," *Powder Technology*, **29**(1981) 53-62.
6. Moscou, L., and Lub. S., "Practical Use of Mercury Porosity in the Study of Porous Solids," *Powder Technology*, **29**(1981) 45-52.
7. Brakel, J.V., Modry, S., Svata, M., "Mercury Porosimetry: State of the Art," *Powder Technology*, **29**(1981) 1-12.

II. H₂S Removal Cell

Introduction

This electrochemical cell purges a fuel gas contaminated with H₂S. This is done by reducing the best Lewis acid in the gas stream. In this case, H₂S is electronated 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.

Research Summary

Experiments this quarter dealt with application of an electrolyte filled tile. During start-up the electrolyte filled tile relieves the process of pre-pressing an electrolyte disk and in-situ electrolyte infiltration. Also the appropriate amount of electrolyte needed to saturate the tile should already be present, making the tile mechanically favorable. Therefore, alleviating the concern of over or under addition of electrolyte for the tile. If too much electrolyte is introduced to the membrane, flooding of the electrolyte occurs, causing inadequate pore area for electronation of H₂S. Also, clogging of the flow tubes has been evidenced due to superfluous addition of electrolyte. Under addition, on the other hand reduces the flow path needed to transport the sulfide ions across the membrane. A laboratory replicated membrane along with a Zircar manufactured membrane were also used in other experiments.

MACOR housings were used for runs #6-#9, while stainless steel materials were used in run #10. Electrodes consisted of Ni which transformed to NiO in-situ.

Replication of past experiments which selectively removed 100 ppm inlet H₂S concentrations, below 10 ppm, were attempted. The start-up problems negated the application of H₂S to all but run #10. H₂ cross-over prevented any removal data from being collected due to the initial problem of cross-over. This was attributed to lack of stability in the

membranes structure.

In the electrolyte filled tiles the instability of the membranes at molten conditions failed to prevent H₂ cross-over. The high porosity of the replicated membrane also allowed for gas cross-over. The Zircar membrane, however, did provide adequate defense against H₂ crossover. Discussion of individual runs are in the following paragraphs.

Run #6

This experimental run used a rigidized, electrolyte filled membrane, which becomes molten around 550 °C. Seal development was attempted using aluminum foil gaskets, coupled with an electrolyte-water solution. Seals never developed, but the major problem of hydrogen cross-over caused the shut-down of the run after 166 hours. This cross-over originated because of the lack of structural support once the membrane became molten. Once the cracks developed salvaging the cell became impossible.

Run #7

Thermal stress caused by thermocouple damage resulted in immediate cracks in the electrolyte filled tile. Shut-down proceeded after 15 hours.

Run #8

Aluminum paint cooked in an oxygen environment provided the seals in this experiment. The seals never formed to proposed expectation due to the lack of bonding with the MACOR material. The electrolyte filled tile once again weakened under molten conditions, causing cracks in the membrane. Cross-over due to these cracks, progressively worsened the cells performance. Shut-down occurred 24 hours after start-up.

Run #9

A replication of the Zircar manufactured membranes was produced for this experiment. The optimum porosity should be comparable to that of the manufactured membrane, 66%. Previous successful replicated membranes were 65% porous. An attempt to use an 80% porous membrane in this experiment failed due to a lack of structural support, similar to that of the electrolyte filled tiles. Cross-over resulted, causing shut-down after 24 hours.

Run #10

A Zircar manufactured membrane provided the support mechanism for the electrolyte. Seals were developed by initially cooking the housing after coating with aluminum paint. A layer of alumina formed which made available the reaction forming, lithium aluminate, on contact with the electrolyte. Seals developed immediately, but a miscalculation in the amount of water needed for the water-gas shift caused carbon formation in the inlet flow tubing. Once the problem was cured, H_2S was sent to the cell. Sulfide equilibrium never occurred due to a consistent lack of electrolyte. Continuous addition of electrolyte should have caused flooding of the electrodes, but reaction with the aluminum paint exceeded the small estimates of required electrolyte. Shut-down occurred after 140 hours.

Summary

Use of the electrolyte filled tile was inadequate for our research. The instability of the tile, resulting in H_2 cross-over prevented the removal of H_2S . The Zircar manufactured membrane performed well in the molten environment as expected and will continue to be a focal point of our research. Replication of the Zircar membranes is effective if the porosities are around 65%. The 80% porous membrane produced for in run #9, lacked the stability of a more dense membrane. H_2 cross-over must be stopped to selectively remove H_2S .

Planned Work for Next Quarter

The Zircar membranes will be the focus of next quarters experiments. Replication of these membranes will also continue. If the porosities are controlled the stability of the membrane should follow. Work with sealing the MACOR housings will also continue using aluminum paint.

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