1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

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

Professor Jack Winnick
Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100

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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.

Membrane Manufacture

Matrix manufacture this quarter used Si₃N₄ powder of 0.5 μm diameter, with a surface area of approximately 10.9 m²/g. This ceramic, as mentioned in earlier reports, was obtained from Oak Ridge National Laboratory courtesy of Dr. O. O. Omatete. This low surface area material tape cast with greater ease than did the SN-R Si₃N₄ courtesy Phillips Petroleum (d_p=0.2μm, SA=90m²/g). The binder used for tape casting was a

polyvinyl butyryl from Metoramic Sciences, along with appropriate surfactants and de-agglomerates. This system had been previously successful with large particle sizes of silicon nitride.¹

Multiple casts of this system to yield a 50 vol% ceramic structure upon binder burnout were successful. Scrap was tested in air at 400° C to insure that the structure did in fact wet properly, and capillary action would carry the electrolyte through the ceramic structure. Preliminary Scanning Electron Microscope (SEM) analysis has verified a pore match with the electrode.

One of the purposes of the construction of a new ceramic membrane was the desire to use an electrode with a smaller interstitial pore size to increase the area available for mass transfer. The drawback was that previously membranes were of such large pore sizes that capillary action drew the electrolyte from the ceramic matrix to flood the electrode, breaking the wet seal and diminishing the path for migration of the transport species.

Membranes used in full cell testing generally consisted of two tapes, cut to appropriate size, and pressed together at approximately 9000 psig. These tapes were then placed in the cell under O₂ flow and allowed to burn out at 350° C. Electrolyte was introduced to the cell at this point, and the cell was sealed. Thickness of the membranes used this quarter averaged 0.50mm.

Results varied, but look encouraging. One run suffered from incomplete wetting of the membrane. Upon post-mortem observation, it was discovered that the membrane was, in fact, non-uniform, due to an oversight in the casting process. Other runs

developed various problems; one membrane was wet completely, but seemed to leave burned material, possibly unremoved organic material trapped by the infused electrolyte, which allowed gas cross-over. Overall, non-wetted portions or non-uniformly wetted portions of the membrane caused gas cross-over and overall cell leakage.

Membrane manufacture for the desired system is very much a reality. The present system must be perfected to produce, consistently, homogenous membranes, but the outlook is very positive.

Full Cell Runs

Membrane seals are a very important aspect of the full cell run, and the overall seals have generally been found to be excellent this quarter. Failure has occurred, in some cases, with the cross-over seal. In addition, a building electrical failure made a promising run unrecoverable.

Three areas have been the focus of the research this quarter: the membrane, the electrodes, and the housings, in particular, the anodic housing. The membranes are discussed above, but the electrodes became a particular concern this quarter, due to the physical set of the cell. The housings used are machined to hold electrodes of approximately 1.1mm thickness, and place those electrodes in direct contact with the membrane, facilitating the wetting of the electrode by electrolyte, and good wet contact between the electrodes, housings, and matrix. The electrodes used this quarter from E.R.C. are of 0.98 mm thickness. This leaves a gap on between either the housing and

electrode, or the matrix and electrode, depending upon the orientation of the electrode in the cell.

When it was discovered that flat electrodes were losing this crucial contact, two actions were taken in an attempt to alleviate the problem. The first was the incorporation of additional electrode layers for the express purpose of contacting the housing. Three thin strips of electrode material were cut from the green body, and placed at intervals corresponding to the current collectors in the flow channels, on the electrode to be used. This assembly was then pressed slightly so as to bring the separate parts into full contact upon burnout. The resulting electrodes did not work as well as expected, although they were observed to stick to the membrane upon breakdown.

A corresponding technique has also been to place gold wire upon the current collectors, and place the electrode on top of the gold wire. This scheme has been successful in the past, but is undesired due to the incorporation of the cost-prohibitive gold.

A second technique, which has also been successful is allowing the warping of the electrode in the flow channel. The electrode is a nickel powder tape-cast in a similar way to the above described matrix. Upon burnout, if the electrode is not uniformly supported, diffusional and thermal gradients will develop, inducing warping in the electrode. If the organic in the electrode is allowed to burn out while the electrode is in a full scale housing, the electrode will tend to warp and form to the housing, warping as greatly as it can in the given environment. Free electrode material has been observed to curl drastically. While this method has met with reasonable success, it is also not a

desired method. The warping of the electrode, while it will allow contact between the electrode and the cell housing, and the electrode and the matrix, will reduce both overall contact areas. This reduction of contact area and area for migrational transfer of SO_4^{2-} from the electrode to the matrix can become limiting.

The last area of concentration has been the anode housing. Figure 1 shows the large anodic potential resulting from the application of relatively small amounts of current. Contact between the electrode and matrix was found to be excellent, and the electrode touched the current carriers at various points. The housings have become suspect.

Figure 1: Potential with applied current. Note the large anodic potential.

Analysis revealed that resistances of 3-100 Ω were present on the anode side.

Currently, the anode housing is being electroplated with high purity Ni. When a layer is built, the Ni will be lithiated and oxidized in a manner consistent with the electrodes themselves. Increased conductivity should develop. Results will be reported at a later date.

Electrolyte

Recent studies have shown the existence of vanadium in the III, IV, and V oxidation states in similar melts.² This existence may help to validate the assumption that the production of SO₂ at the cathode may be due to an inability of the O₂ to re-oxidate the vanadium compounds present to the V state. Further research will be done into this work as well as others to determine the applicability to this system.

Conclusion

The experiments performed this quarter provided a great deal of information, and look promising for experiments in the future. Care needs to be taken with the development of this cell so as to not neglect any of the factors mentioned previously in this report. Free electrolyte experiments are currently being planned as a supplement to the above work in determining the mechanisms and effects of insufficient O₂ present in the melt.

Endnotes

1. D. M. McHenry, *Development of an Electrochemical Membrane Process for the Removal of SO_x/NO_x from Flue Gas*, Ph.D. Thesis, Georgia Institute of Technology (1992).
2. Karydis, D. A., Eriksen, K. M., Fehrmann, R., and Boghosian, S., *Extended Abstracts*, (Electrochemical Society, Pennington, N.J.) 92-1, Abstract 1421 (1993).

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 performed this quarter concentrated on incorporating rigidized zirconia membranes produced in our laboratory. Other concerns, sealants, electrode materials, and cell housing longevity, were also investigated, evolving feasible solutions.

Membrane

The self produced membranes consist of two thin-weaved zirconia mats (3" x 3" x .03"), containing an 85% void fraction. Effective utilization requires a 65% porosity, obtained by hardening

(rigidizing) the membrane in an aqueous suspension of zirconia particles. Cost comparison to similar conventional membranes (3" x 3" x .036"), \$150.00/tile to \$10.00/tile, extenuates the fabrication efforts. Problems can arise (e.g. micro-cracks or >65% voids), during the rigidizing process. However, past experimentation validated the effectiveness of the self-produced membranes if the 65% porosity was achieved.

Run #11

Focus of this experiment was on removal efficiency of H_2S , due to past deficiencies when using stainless steel housings. Initial set-up involved painting aluminum onto cell housing surfaces and heating to 600 °C, upon which aluminum was converted to alumina. This alumina covered surface in theory reacts with Li_2CO_3 in the eutectic $\text{Li}(0.62)\text{K}(0.38)\text{CO}_3$ to form lithium aluminate which creates an effective sealant for retaining process gases. Excessive reaction of the aforementioned system with applied current completely depleted H_2S removal. Ni converted in-situ to NiO provided sites for the electronation of H_2S . A conventional zirconia membrane, 65% porous, was used.

H_2S was never introduced to the cell after attempts to transport carbonate failed. Aside from problems with parasitic reactions, clogged flow tubes and loss of electrical contact ultimately terminated the cell after 60 hours of operation.

Run #12

Housing materials for this experiment consisted of machineable ceramic(MACOR). A 66% porous zirconia membrane, purchased from Zircar, supported the eutectic $\text{Li}(0.62)\text{K}(0.38)\text{CO}_3$ electrolyte. Ni electrodes converted in-situ to NiO provided reaction sites. Once again attempts were made to seal the cell housings with aluminum paint.

100% carbonate transport provided evidence of adequate cell performance, prompting addition of H_2S to the cell. Equilibrium gas compositions comprised (8.51% CO_2 , 23.49% CO , 9.49% H_2O , 58.51% H_2 , and 115 ppm H_2S). Application of stoichiometric(4 mA) current failed to remove any H_2S . Administering several current steps showed removal but at high currents(500 mA). The logical explanation involves the parasitic nature of the aluminum paint system. Due to past problems aluminum paint application as a sealant were terminated. The cell was operable for 128 hours.

Run #13

Reversion to aluminum foil gaskets, successful in past experiments(Run #4 & Run #5), sealed the MACOR housings. Ni electrodes were allowed to go to NiO in-situ. A 68% porous self-produced membrane provided stability against hydrogen cross-over and a low resistance path for ion diffusion and migration.

Strong seals immediately developed, containing process gases the duration of the experiment. 100% carbonate transport was observed inciting H_2S addition. Equilibrium gas compositions consisted of (8.51% CO_2 , 23.49% CO , 9.49% H_2O , 58.51% H_2 , and 219

ppm H₂S). A laboratory power failure caused the cell temperature to drop below the electrolyte melting temperature, ensued by membrane thermal shock. The cracks created by thermal shock allowed extensive amounts of hydrogen cross-over. Attempts to restart the cell failed, resulting in shut down after 99 hours.

Run #14

Similar run conditions to run #13 existed using a self-produced zirconia membrane, 65% porosity. 100% CO₂ reduction occurred on the cathode side of the cell, followed by addition of H₂S. The cell reached equilibrium gas compositions of (8.51% CO₂, 9.49% H₂O, 23.49% CO, 58.51% H₂, and 156 ppm H₂S). Application of current ineffectively removed H₂S. The assumption of electrode degradation on the cathode side fouled attempts to transport carbonate. The compositions upon application of 100 ppm gas creates a molten electrode, Ni_{2-x}O, causing loss of electronation sites. Due to this degradation shut-down occurred after 98 hours.

Summary

Application of a self-produced zirconia membrane sufficiently provided stability in the cell environ. The aluminum foil gaskets proved a process friendly sealant containing process gas throughout the experiments. The current effects of the aluminum foil gaskets have yet to be determined, however past experimentation resulted in favorable H₂S removal.

Planned Work for Next Quarter

Work will continue with the self-produced membranes and aluminum foil gaskets. The main focus will be on providing adequate cathode materials due to Ni degradation. Cobalt seems the obvious choice from past experimentation and lack of a molten state in the system of equilibrium gases.

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