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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 for 12-24 hours 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.

Materials

Work this quarter has concentrated upon the identification and verification of the applicability and stability of new matrices. Two new materials have been used: the first is Si₃N₄ courtesy Oak Ridge National Laboratories, and the second is a new Al₂O₃ matrix

courtesy Professor R. Gerhardt, School of Material Engineering, Georgia Institute of Technology.

Matrix Processing

The Si_3N_4 used ('F') had a $d_p = 0.5 \mu\text{m}$ ($d_{90} = 1.10 \mu\text{m}$; $d_{10} = 0.23 \mu\text{m}$), with a surface area of $10.9 \text{ m}^2/\text{g}$. This is in contrast to the previously used Si_3N_4 (SN-R) from Phillips Petroleum (see previous reports) which had a surface area of $90 \text{ m}^2/\text{g}$, and a $d_p = 0.2 \mu\text{m}$. The SN-R had been unusable due to the inability of process the ceramic and achieve a thin, uniform membrane. Techniques such as slurry processing and tape casting had little success in achieving a membrane which was self-supporting, due primarily to the high surface area.

The F Si_3N_4 however, has a significantly lower surface area, allowing the relatively easy casting of the material in thin tapes. As previously mentioned, Metoramic Sciences provided the binder system, a polyvinyl, used in creating the tapes, which were then cut and burned out to deliver a usable matrix.

Scanning Electron Microscopy (SEM) was used to determine the homogeneity and porousness of the resulting casts. As discussed in previous reports, Si_3N_4 sintered on alumina in air had yielded a highly densified new phase, seen in Figure 1. Such a phase is not desired. Although it may be inert to the system, the ceramic will not allow impregnation by the electrolyte to any appreciable extent. Interconnecting microchannels are necessary for migration of sulfate from cathode to anode where it can be oxidized.

Intimate connection through the matrix is desired.

Tape cast F, however, has shown excellent results to date. Figure 2 shows the results of loading levels of 50 vol%, after the binder is burned out. It can easily be seen that there exist interconnecting channels into which electrolyte can be impregnated. The picture does exhibit surface roughness, a sign that the particles are not as structured as might be desired.

Figure 1: Si_3N_4 sintered on alumina in air environment.

This may lead to lower capillary force at the surface, and possible loss of electrolyte from the matrix, neither of which is desired.

To correct this problem, the tape is pressed prior to use in full cell testing. This pressing will tend to remove any trapped gases, and order the particles, especially at the surface. The results of such pressing can be seen in Figure 3. The surface of the membrane is much more uniform than the unpressed membrane. In addition, average pore size was qualitatively reduced, leaving smaller pores. Testing showed this matrix would saturate with molten electrolyte, though not as quickly as matrices with larger

pores. This is to be expected. The use of this matrix material in full cell testing has just begun, with results to be published in the next quarterly report.

The second material tested as a matrix material is Al_2O_3 , pressed by a new leach technique developed by Professor Gerhardt. The chemical stability of this material needed to be tested, as well as the ability of the electrolyte to saturate the matrix. To this end, two samples of different

Figure 2: Tape cast F, unpresse, after binder burnout. 50 vol% loading.

manufacture were tested with electrolyte for 48 hrs at 400° C and air. The results were then analyzed using SEM and X-ray diffraction.

The first sample (10-90) surface was non-discernable (see Figure 5). The counterpart to this sample, which was tested as described above, wet throughout with electrolyte. The SEM analysis, however, only picked up what may be frozen electrolyte on the surface, as seen in Figure 4. X-ray analysis of the sample showed the presence of the potassium pyrosulfate, but whether or not there exists a new phase is still under discussion.

The second sample analyzed (3070) was of greater porosity, and apparently greater pore size than the first. The most striking feature of the surface is the rod-like formations. This matrix material easily saturated with electrolyte at a much greater speed than the 10-90 sample. The resulting SEM of the saturated material is shown below.

FUTURE EXPERIMENTS

Figure 3: Pressed, tape cast F, showing an ordering of the surface over the unpressed tape.

Future testing of the new matrix material will be performed. Analysis of new phase formation due to reaction is required, however, before the new Al_2O_3 matrix material can be used. In addition, chemical inertness will not insure electrochemical inertness. Unknown electrochemical reactions may take place, and must be considered. Full-scale processing will also be a challenge associated with the new material if it proves inert. Matrix diameters of 3" are required, and present processing of the leached material has reached diameters of only 1".

However, the use of the F
 Si_3N_4 material seems promising,
and full scale testing will be
reported in the next quarter.

Figure 4: Tested 10-90 SEM.

Figure 5: Sample 10-90 SEM. Surface structure unresolvable.

Figure 6: 3070 SEM prior to electrolyte impregnation.

Figure 7: 3070 SEM after electrolyte testing.

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

Developing a cathode material capable of structural stability was the focus of experiments this quarter. The necessity to replicate a morphologically consistent cathode is critical to experimentation with 100ppmv inlet H₂S. Previous use of nickel electrodes in 100ppmv system resulted in unfavorable cathode phase degradation upon system equilibrium.

An alternative material forming a stabilized conductive cathode under 100ppmv H₂S conditions is possible with Co. Development of

a Co cathode identical in porosity and pore size to aforementioned nickel cathodes was attempted this quarter.

Experiments

Experiments to generate a viable cathode from Co powder were investigated in several steps. Initial tests were performed with 2 micron cobalt powder singularly and with a mix of 25 wt% methocel, followed by 149 micron cobalt powder singularly and with mixtures of methocel and naphthalene. Two batch experiments followed incorporating a variety of binding materials at varying weight percentages.

Sintering pressed disk occurred at high temperatures, $>800^{\circ}\text{C}$, in a nitrogen atmosphere. Nitrogen used to avoid oxidation of Co to non conductive CoO. Best results required temperatures of $\sim 1200^{\circ}\text{C}$, in close proximity to the melting point of Co(1492°C)

Initial tests

Sintering pressed disk of pure cobalt powder, 2 and 149 micron particles, resulted in electrodes that were conductive but structurally insufficient due to high densities($\sim 50\%$). A binder additive, methocel, mixed with the cobalt powder in an attempt to increase porosity provided better void fraction. The amount inserted in initial tests(25 wt%) gave porosities around 55%.

Next, an assembly of cobalt-binder disk were sintered at 1195°C in a nitrogen atmosphere. Binders used included methocel and naphthalene. The best electrode used a combination of 56 wt% methocel, balance 2 micron powder producing a highly conductive

electrode with 80% void fraction. Scanning Electron Microscopy(SEM) confirmed proper pore diameter and in lab bubble tests proved interconnecting channels existed for electronation of H₂S.

Follow-up batch tests incorporating similar binder content and sintered in an identical manner, again provided an acceptable electrode. Pore size and interconnecting channels availed with a high porosity(80%) and conductivity.

Summary

Successful fabrication of Co electrodes, similar in morphology to previous nickel electrodes, were produced using a mixture of 60 wt% methocel, balance 2 micron cobalt powder. A fabricated membrane 69% porosity was also produced for use in run #15.

Planned Work for Next Quarter

Work will continue with the self-produced membranes and aluminum foil gaskets. The main focus will be on effectiveness of cobalt as a cathode material.

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