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 electrodes 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 an efficient method is continuing. 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. However, the ideal binder material has yet to be identified. The current binder system burns out at temperatures above the melting point of the electrolyte. 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. Past researchers have stated that this electrode exhibits a p-type conductance, with room resistivities on the order of 1.0-0.2Ω at room temperatures. A possible conduction mechanism of the electrodes will be discussed in this report. 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.

Electrode Analysis

Full-cell testing this quarter utilized the new electrode supplied by ERC. These electrodes were pre-lithiated and oxidized as described above. It has been surmised by past researchers that the doping of the NiO lattice with the Li⁺ ion results in a p-type semiconductor according to the Equation (1), which utilizes Kröger-Vink notation.

The equation shows that the proposed Li doped NiO lattice would conduct via holes, making it a p-type semi-conductor. This semiconductor should have the property of increasing conductivity with increasing temperature. It has been suggested, however, that the actual mechanism of conduction in the material is polaron conduction. This proposed type of conduction occurs when ions of the same type, but with valences differing by one, occupy adjacent lattice sites. The application of energy allows the change in valence of these adjacent states. In this case, the Ni ion may would be present, after doping, in the Ni^{+2} and Ni^{+3} state within the lattice. The Ni^{+3} would exist to offset the charge imbalance imposed by the doping of the lattice with the Li^{+1} ion. Thermal excitation would allow the transfer of electrons from the Ni^{+2} ions to the Ni^{+3} ions. The concentration of carriers is dependant only upon the dopant level in the NiO, but the mobility of the electrons is dependant on the temperature and activation energy. A polaron-conducting material will thus show a similar dependance to temperature as a p-type or n-type semiconductor. In addition, the doping level for polarons will tend to be on the order of percent levels, whereas the doping level for a semiconductor can be on the order of parts per million. The formula for the doping of NiO with Li would be $Li_xNi_{1-x}O$.

This type of doping mechanism may be supported by Baumgartner and Zarnoch¹, who studied the effect of in-situ doping of the NiO electrodes in Molten Carbonate Fuel Cells (MCFC). They found that efficiency of the electrodes used increased over time as they were exposed, in situ, to $(Li,K)CO_3$. In addition, when the electrodes were doped

ex-situ prior to use, they still exhibited an increase in efficiency when exposed to the carbonate melt, but did reach a peak efficiency at a much faster rate than the in-situ doped electrodes. Polaron conduction may be the mechanism, as the doping level may have increased over time, increasing the number of available conducting sites, and increasing the efficiency of the electrodes. Further, the rate of doping may be exaggerated due to the possible electrochemical reactions of Li^+ with NiO as suggested by Passerini and Scrosati² seen in the below equations:

Full Cell Testing

A full cell test of the SO_2 removal system was run this quarter. The test utilized a tape cast membrane of Si_3N_4 of $d_p=0.5\mu\text{m}$, in the polyvinyl binder system. The resulting tape was 0.497mm thick, with 48 vol% voids. The electrodes were pre-lithiated and pre-oxidized as described above. The anode housing used was plated with pure nickel utilizing an electrochemical NiCl bath. The housing was then oxidized and lithiated at a temperature of 600°C for 12 hours prior to use. This was done in response to the high anodic potentials present in past runs, being due possibly to the pitting and corrosion of the anode.

Potentials/Overpotential

Run 19 9/9/93

Figure 1

The system exhibited large potentials with very low applied currents as seen in Figure 1. Poor removal was also exhibited. A contact problem was evident, as the potential of the cell was seen to oscillate when the system was touched. The system was shut down for analysis.

Upon cooling, it was found that the membrane had wetted well. This had been surmised due to an excellent external wet seal, and fairly strong initial internal cross-cell seal. Over time, however, the cross-cell seal had degraded. The electrodes, too, were wetted. It was noted, however, that the electrodes and the membrane were not connected at all upon cooling.

This lack of intimate contact suggests that the electrodes were not closely contacting the membrane. If this were the case, although the membrane and electrodes would wet, there would be gaps in between them, which would have to be filled by

electrolyte. Capillary action would also tend to pull the molten salt electrolyte from this gap into either the electrode pores or the membrane pores. This gap would also be initially free of SO_3 and SO_2 . The chemical equilibrium of the pyrosulfate and sulfate with SO_3 in Equation (4) and with SO_2 and O_2 in Equation (5) still would need to be achieved when in contact with these gaps. The pyrosulfate would decompose to the sulfate species in these gaps. Sulfate has a limited solubility in pyrosulfate of 4 wt%.

Once this limit has been exceeded locally, the sulfate would begin to precipitate out of the melt, inhibiting the current pathway, and increasing the potential required to drive current across the cell.

The average ERC electrode thickness used to date is 0.960 ± 0.251 mm (a 26% variation). The depth of the electrode well in the 316L SS housings is 1.19 mm, a 20% difference. This difference in the well depth and the electrode thickness may be leading to the before-mentioned gap between the electrode and the membrane, increasing the resistance to current transfer from the cathode to the anode, and decreasing the removal ability of the cell.

To correct this problem, two steps are being explored: first, the layering of the electrodes. While simply using two electrodes in the place of one seems reasonable, the additional electrode on each side may increase the diffusion distance for the sulfate ion transport from the cathode to the anode. In addition, greater amounts of electrolyte will be needed to fill the additional pore area. To counteract these two occurrences, it may be possible to add additional thickness, in the form of electrode material, only at the points where the housing normally would contact the electrode.

The second possible step is to reduce the well depth, through the machining of new or existing electrodes. Such a step would not be subject to the previously mentioned concerns. In addition, the use of new housings may be appropriate as the 316L SS has been cycled numerous times in the corrosive environment.

Other Work

The effect of the partial pressure of oxygen is under examination. SO_2 generation

at the cathode has been cited as a problem in the past³. It was suggested that the limiting step may be the re-oxidation of the SO_2 generated in the electrochemical step (Equation (6)) through the vanadium catalyzed reaction of SO_2 with O_2 to form SO_3 . If the oxygen is not reaching the vanadium to regenerate the V(V) state from the V(IV) state, the oxidation of SO_2 will be retarded.

Utilizing cyclic voltammetry, Franke⁴ found that a reversible vanadium couple existed in a potassium pyrosulfate/vanadium pentoxide melt at 400° C. The testing atmosphere was 3000 ppm SO_2 /3% O_2 /bulk N_2 . If in-situ vanadium will be affected by the partial pressure of oxygen, the results might be seen in cyclic voltammetry experiments at different O_2 partial pressures, as the re-oxidation process may show up as a reduced V(IV) presence after reduction of the V(V). This study will also utilize a lithiated nickel oxide electrode. Franke used only gold foil electrodes.

A cyclic voltammetry experiment has been set up. To first accurately determine the area of the lithiated nickel oxide electrode, the system is being tested in a (62mol% Li/38 mol% K) $_2\text{CO}_3$ at conditions identical to those used by Uchida, *et. al.*⁵. They found that the current exchange density for oxygen reduction on a 0.4 cm² NiO surface in the (Li/K) $_2\text{CO}_3$ melt was 10 to 20 mA/cm². This data was confirmed by ac impedance and

coulostatic relaxation methods. By direct comparison to Uchida's data and calculations, an accurate estimation of the LiNiO area will be determined.

The cell is set up as seen in Figure 2. The housing is made of pyrex glass, with the two individual parts connected by 1/16" holes. Each electrode is encased in a pyrex tube of 1/8" diameter, which is crimped and gas tight at the bottom, leaving only the extended area exposed for reaction. The reference electrode is composed of a gold wire in a 1/4" pyrex tube. Gas flows through the tube and bubbles into the melt, and the gold wire is in contact with the gas and the carbonate melt at all times. Some residual noise is seen due to the bubbling disturbance of the melt around the gold wire. The thermocouple is a K-type thermocouple contained in an alumina tube, sealed at the end in the melt. On the working side of the cell, the gas inlet is a pyrex tube whose height can be manipulated to bubble gas into the melt or flow gas over the surface of the melt.

Results of the experiment will be contained in future reports as the experiment is currently ongoing.

Future Work

The characterization of the O_2 partial pressure is the current focus of the work. In addition, electrodes must be developed which will eliminate the possible gap between the membrane and electrodes, bring the system parts into intimate contact. The results of the cyclic voltammetry experiments will be contained in future reports. The cyclic voltammetry, after characterization of the system, will be extended to the $\text{K}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5$ system at 400° C, to determine possible V_2O_5 dependency on O_2 for regeneration after catalytic reduction.

Figure 2: Cell design for cyclic voltammetry.

Endnotes

1. Baumgartner, C. E.; Zarnoch, K. P., *American Ceramic Society*, **64**[4] (1985), 593-597.
2. Passerini, S.; Scrosati, B., *Solid State Ionics*, **53-56** (1992), 520-524.
3. McHenry, D. M., Development of an Electrochemical Membrane Process for Removal of SO_x/NO_x from Flue Gas, PhD. Thesis, Georgia Institute of Technology, 1992.
4. Franke, M. D., Electrochemical Flue Gas Clean-Up, Ph.D. Thesis, Georgia Institute of Technology, 1988.
5. Uchida, I.; Mugikura, Y.; Nishina, T.; Itaya, K., *J. Electroanal. Chem.*, **206** (1986), 241-252.

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, previously discovered in MCFC testing.

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 successfully fabricated this quarter.

Manufactured zirconia membranes are still being investigated, with bulk process gases unable to penetrate the membrane. However, hydrogen cross-over is expected due to inadequate removal of H₂S during this quarters experiments.

Experiments

A full cell experiment conducted this quarter incorporated a fabricated Co cathode (80% porous), yttria-stabilized zirconia membrane for electrolyte support and a barrier to process gases, and an anode material of lithiated NiO (85% porous), discussed earlier in the SO₂ description. Aluminum foil gaskets served as the radial process gas sealant.

Stoichiometric removal of CO₂ at the cathode, addition at the anode were observed before addition of H₂S to the cell. Inlet H₂S equilibrated to 120 ppmv after the water gas shift reactor. Upon open-circuit equilibrium (H₂S inlet = H₂S outlet on cathode side), stoichiometric current applied corresponded to a flow rate of 150 cc/min. Negligible removal (>10 ppmv) incited current steps from the stoichiometric value (3 mA) to 200 mA. Incongruent H₂S removal with applied current, along with stoichiometric CO₂

removal was continuously observed along with a high internal resistance (~ 6 Ohms). Shut down occurred after 312 hours of operation for investigative purposes.

Zirconia membrane

A preprocessed zirconia membrane purchased from Zircar served as the encasement for the electrolyte, the amount (6.3 grams) corresponding to membrane porosity(66%). The membrane also creates a barrier to process gas cross-over from cathode to anode allowing preference to favored reactions.

Capillary forces in membrane pores inhibit the release of electrolyte unless the electrode pores are smaller in diameter. Assuming the later, pore flooding would occur creating greater mass transfer limitations of reactive species. Evaluation of Figure 1 along with stoichiometric CO₂ transport, refutes pore flooding as the cause of poor H₂S removal.

Post-mortem examination of the electrolyte-infiltrated zirconia membrane revealed micro-cracks, Figure 2. Although real-time examination of process-gas cross-over was negative, hydrogen cross-over is expected due to the minuscule size of the diatomic molecule. Parasitic reactions would proceed at the anode in the form of :

Figure 1. Cobalt cathode post-mortem

Figure 2. Zirconia membrane post-mortem

or

gas chromatography showed no evidence of reaction (A).

Reaction (B) should produce water that was not evident due to lack of condensate. However, low current levels (5mA) produces only 0.05% water in a flow of sweep gas, 70 cc/min.

Reaction (B) , utilizing carbonate from the electrolyte, induces the favorability of carbonate oxidation at the cathode over H_2S reduction due to higher CO_2 and H_2O pressure at the cathode (order of 10^5 higher than H_2S).

Summary

Co electrodes, similar in morphology to previous nickel electrodes, were successfully utilized in Run #15, evidenced by stoichiometric transport of CO_2 applied current. H_2S removal was inhibited by hydrogen cross-over from process-gases creating unfavorable alternative reactions. Back-pressure from the anode side (sweep side) should correct the problem.

Planned Work for Next Quarter

Work will continue with the cobalt cathodes, zirconia membranes and aluminum foil gaskets. The main focus will be on the effectiveness of cobalt as a cathode material and hydrogen permeability of the zirconia membrane.

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